From 2D to 3D Characterization of Materials Subjected to Extreme Pressure and Temperature Conditions

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I thought for seventy-two years, day and night It was revealed to me that I know nothing

> — Omar Khayyam (1048-1131) Mathematician, Astronomer, and Poet

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Abstract

Planetesimal were the first planetary objects to form in the solar system, which later grew to make the proto-planets. Most of these bodies were differentiated as a result of internal heating. Several differentiated bodies have then been accreted following the giant impacts to create the terrestrial planets. As a result of these impacts, the newly formed Earth was molten and completely differentiated. Subsequent crystallization has given rise to Earth's current structure. In order to bring new constraints on the differentiation and melting relationship in the planets we have studied natural and synthetic samples corresponding to different stages of planetary evolution through state of the art electron microscopy techniques.

We have first looked at carbonaceous materials in a ureilite meteorite (Almahata Sitta MS-170). Thin sections from ureilite diamonds, which were prepared by the focused ion beam (FIB), are observed with transmission electron microscopy (TEM) and spectroscopy. The morphology of graphite bands in diamonds indicated that they result from the diamond to graphite transformation during a shock event. Moreover, the diamonds in this meteorite with crystallite sizes as large as $\sim 20 \ \mu m$ can only form under static high-pressure condition of planetary interiors. We have also found three types of diamond inclusions in our samples. The majority of these inclusions are euhedral Fe-S inclusions. However, each of these inclusions has three phases, namely: kamacite (Fe, Ni), troilite (FeS), and schreibersite ((Fe, Ni)₃ P). The chemical analysis of the intact inclusions shows them to be a stoichiometric phase, (Fe, Ni)₃(S, P), that can only form above 21 GPa. The ureilite parent body (UPB) should have had the size about that of Mars to exert necessary pressure to grow the diamond inclusions in the core-mantle boundary. The other two types of inclusions are the Al- and Mg- free chromite, Cr₂FeO₄, and Ca-Fe phosphates that were previously observed only in iron meteorites. Our results suggest that the diamonds and their inclusions were formed from an S-rich metallic liquid.

In the second part of the thesis, we have studied melting and fractional crystallization of the lower mantle using a laser-heated diamond anvil cell (LH-DAC). San Carlos olivine is used as a proxy to the mantle composition. The recovered samples are first analyzed with the 3D chemical tomography using a dual beam FIB instrument. The molten region in all the samples at pressure range from 30 to 71 GPa have at least three distinct zones: a ferropericlase shell (Fp), an intermediate bridgmanite (Brg) region and the Fe-rich melt core. Thin sections from the center of the same samples are analyzed with TEM and energy-dispersive x-ray (EDX) spectroscopy. The results from the samples heated at 45 GPa for 1, 3, and 6 minutes demonstrated that the temperature gradient in the heated zone shrinks through the time and,

Abstract

thus, the crystallization continues toward the center of the heating. Consequently, the melt becomes richer in iron. The melt core also gets more iron-rich with increasing pressure. In fact, in \sim 70 GPa we observe an Fe-O core with small Si and Mg concentration. This implies that the melt at the bottom of the mantle could become denser than the solid phases and sink down. The presence of the iron-rich melt or the oxides crystallizing from such a melt can explain the ultra-low velocity zones (ULVZs) found in the seismic surveys of the core-mantle boundary.

Key words: 3D characterization, energy-dispersive x-ray (EDX) spectroscopy, focused ion beam (FIB), Transmission electron microscopy (TEM), Diamond anvil cell (DAC), differentiation, ureilite, diamond inclusion, deep mantle

Zusammenfassung

Planetesimale waren die ersten planetarischen Objekte, die im Solarsystem entstanden sind und welche später zu Protoplaneten herangewachsen sind. Die meisten dieser Körper wurden als Resultat internen Aufheizens entmischt. Durch gewaltige Einschläge haben sich verschiedene entmischte Körper vergrößert und erdähnlichen Planeten wurden geschaffen. Als Folge dieser Einschläge, wurde die neuentstandene Erde geschmolzen und komplett entmischt. Anschließende Kristallisation führte zu der aktuellen Erdstruktur. Um neue Belege in Bezug auf den Zusammenhang bezüglich Entmischung und Schmelze in den Planeten zu bringen, haben wir natürliche und künstliche Proben mit Hilfe hochmoderner Elektronenmikroskopie-Techniken studiert, die verschiedenen Stadien der Planetenevolution entsprechen.

Als Erstes haben wir kohlenstoffhaltiges Materialien eines Ureilit Meteoriten (Almahata Sitta MS-170) untersucht. Dünne Querschnitte von Ureilit-Diamanten wurden mit dem fokussierten Ionenstrahl Mikroskop (focused ion beam, FIB) präpariert und mit Transmissionselektronenmikroskopie (TEM) und Elektronenspektroskopie untersucht. Die Morphologie von graphitischen Bändern in Diamanten weißte darauf hin, dass sie durch die Transformation von Diamant zu Graphit während eines Schockereignisses entstanden sind. Zudem können sich die Diamanten in diesem Meteoriten, welche eine Kristallitgröße um die ~20 m aufweisen, nur unter stationärem Hochdruck geformt werden, wie er im Planenteninneren auftritt. Des Weiteren haben wir drei Arten von Diamanteinschlüssen in unseren Proben gefunden. Die Mehrheit dieser Einschlüsse sind idiomorphe Fe-S Einschlüsse. Dennoch weist jede dieser Einschlüsse drei Phasen, namens Kamacit (Fe, Ni), Troilit (FeS) und Schreibersit ((Fe, Ni)₃P), auf. Die chemische Analyse der intakten Einschlüsse zeigt auf, dass es sich dabei um eine stöchiometrische Phase (Fe, Ni)₃(S, P) handelt, die sich nur oberhalb von 21 GPa ausbilden kann. Der Ureilit Parent Body (UPB) müsste in der Größenordnung des Planeten Mars gewesen sein, um den nötigen Druck aufzubringen, um Diamanteinschlüsse in der Kernmantelgrenze auszubilden. Die anderen beiden Arten von Einschlüssen sind Al- und Mg-freie Chromite, Cr₂FeO₄ und Ca-Fe Phosphate, die bisher nur in Eisenmeteoriten beobachtet werden konnten. Unsere Ergebnisse legen nahe, dass die Diamanten und deren Einschlüsse aus einer S-reichen, metallischen Flüssigkeit entstanden sind.

Im zweiten Teil dieser Arbeit haben wir das Schmelzen und die teilweise Kristallisation des unteren Erdmantels mit Hilfe einer Laser-geheizten Diamantstempelzelle (laser-heated diamond anvil cell, LH-DAC) untersucht. San Carlos Olivin wird als Analogum für die Mantelzusammensetzung verwendet. Die erzeugten Proben werden zunächst mittels chemischer Tomographie in einem sogenannten "Dual Beam" Elektronenmikroskops (mit zusätzlichem Ionenstrahl) untersucht. Der geschmolzene Bereich in allen Proben, die bei Drücken zwischen 30 und 71 GPa hergestellt wurden, weisten mindestens drei individuelle Bereiche auf: einen Ferroperiklas-Mantel (Fp), eine Zwischenbereich aus Bridgmanit (Brg) und einen Eisen-haltigen Schmelzkern. Dünne Querschnitte des Probenkerns werden mit TEM und energiedispersiven Röntgenspektroskopie (energy dispersive X-ray spectroscopy, EDX) analysiert. Die Ergebnisse der Proben die bei einem Druck von 45 GPa 1, 3 und 6 Minuten geheizt wurden zeigten, dass der Temperaturgradient in der geheizten Zone mit der Zeit kleiner wird und daher die Kristallisation in Richtung des Hitze-Zentrums fortschreitet. Folglich wir die Schmelze Eisen-haltiger. Tatsächlich beobachten wir bei ~70 GPa einen Fe-O Kern mit geringer Si- und Mg-Konzentration. Das bedeutet, dass die Schmelze am Grund des Mantels dichter als die festen Phasen werden könnte und sinken würde. Die Anwesenheit der Eisen-reichen Schmelze oder der Oxide, die aus so einer Schmelze kristallisieren, können die ultra-low velocity zones (ULVZ), die in den seismischen Untersuchungen der Kernmantelgrenze gefunden wurden, erklären.

Contents

Ac	Acknowledgements			i
Ab	Abstract (English/Deutsch) i			iii
Li	List of figures x			
Li	stof	tables		xv
In	trodu	uction		1
1	For	mation	and evolution of planets	5
	1.1	Plane	t formation	5
		1.1.1	Star Formation and Accretion Disk	5
		1.1.2	Planetesimal formation in Solar System	6
		1.1.3	Planetesimal formation mechanisms	7
		1.1.4	Runaway growth of planetary embryos	9
		1.1.5	Formation of gas-giant planets	11
		1.1.6	Giant impacts	12
		1.1.7	Grand tack scenario	14
	1.2	Differ	entiation and Meteorite groups	16
		1.2.1	Chondrites	17
		1.2.2	Differentiation of planetesimals and achondrites	19
		1.2.3	Ureilites	21
	1.3	The E	arth	24
		1.3.1	Bulk composition of Earth	24
		1.3.2	Accretion of the earth and moon formation	24
		1.3.3	Core and its formation	25
		1.3.4	Mantle	28
2	Exp	erimer	ntal methods	37
	2.1	High-	pressure high-temperature experiments	37
		2.1.1	Diamond anvil cell	37
		2.1.2	Laser heating	40
		2.1.3	Temperature, pressure and compositional gradient in LH-DAC	42
	2.2	Electr	on microscopy	44

		2.2.1	Electron-matter interactions	44
		2.2.2	Electron beam generation	46
		2.2.3	Scanning electron microscope	47
		2.2.4	SEM EDX	48
		2.2.5	Focused ion beam	49
		2.2.6	Transmission electron microscopy	52
		2.2.7	Scanning transmission electron microscopy	54
		2.2.8	TEM EDX	56
		2.2.9	Electron energy-loss spectroscopy	56
3	Dia	monds	and their inclusions from a Mars-sized planet	59
	3.1	Intro	luction	59
	3.2	Methe	ods	60
		3.2.1	Focused ion beam (FIB) sample preparation	60
		3.2.2	Electron energy-loss spectroscopy (EELS)	61
		3.2.3	Weak-beam imaging and electron diffraction	62
		3.2.4	STEM imaging and energy dispersive x-ray spectroscopy (EDX) \ldots .	62
		3.2.5	Electron tomography	63
	3.3	Resul	ts and discussion	63
		3.3.1	Graphitization of diamond	63
		3.3.2	Comparison with shock-induced diamond formation $\ldots \ldots \ldots$	67
		3.3.3	Diamond inclusions	69
		3.3.4	Formation of diamonds in UPB	76
		3.3.5	Implication for the size and formation of the UPB	78
	3.4	Concl	usion	78
4	3D a	analyti	cal investigation of melting in lower mantle conditions	81
	4.1	Intro	luction	81
	4.2	Methe	ods	83
		4.2.1	High pressure and high temperature experiments	83
		4.2.2	3D EDX acquisition and analysis	84
		4.2.3	TEM section preparation	86
		4.2.4	STEM EDX	87
		4.2.5	EELS	87
	4.3	Resul	ts and discussion	88
		4.3.1	Single-sided laser heating	88
		4.3.2	Evolution of melt with time at 45 GPa	88
		4.3.3	Pressure effect on the melting	102
		4.3.4	Thermo-chemical diffusion	107
	4.4	Concl	lusions	109

5	Spir	n and valence dependence of iron partitioning in Earth's deep mantle	113
	5.1	Article	113
		5.1.1 Introduction	113
		5.1.2 Materials and methods	114
		5.1.3 Results and discussion	115
	5.2	Supplementary information	118
		5.2.1 Experimental and analytical procedure	118
		5.2.2 Results	121
6	Con	nposition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lowe	er
	Mar	ntle Heterogeneities	129
	6.1	Introduction	129
	6.2	Methods	131
	6.3	Results	134
		6.3.1 Phase identification	134
		6.3.2 Compositions of coexisting phases and partitioning	135
	6.4	Discussion	139
		6.4.1 Multivariable effects on partitioning	139
		6.4.2 Mantle partitioning model	143
	6.5	Summary	147
7	Car	bonate stability in the reduced lower mantle	151
	7.1	Introduction	151
	7.2	Methods	153
	7.3	Results	155
	7.4	Discussion	156
	7.5	Conclusions	160
8	Con	clusions and perspectives	163
	8.1	Diamonds and their inclusions from a Mars-sized planet	163
	8.2	3D analytical investigation of melting in lower mantle conditions	164
Bi	Bibliography 2		
Curriculum Vitae			211

List of Figures

1	Schematic view of the layered structure of the Earth	2
1.1	Protoplanetary Disk	6
1.2	Hit-and-run collisions	14
1.3	Migration of gas-giants	15
1.4	Planet formation in grand tack scenario	16
1.5	Solar and chondritic abundance of elements	18
1.6	Oxygen three isotopic plot	19
1.7	Stable isotopic dichotomy of Solar System materials	23
1.8	Abundance of elements in bulk silicate Earth	26
1.9	Metal-silicate separation in magma ocean	27
1.10	Preliminary reference Earth model	30
1.11	Mantle transition zone	31
1.12	Spin transition of iron ions	32
1.13	Crystalline structure of bridgmanite and post-perovskite	33
1.14	Heterogeneities in the mantle	34
0.1		00
2.1		39
2.2		41
2.3	Temperature gradient in LH-DAC	42
2.4	Electron-matter interaction	45
2.5	Energy-loss of electron and x-ray generation	46
2.6	EDX spectrum	48
2.7	TEM specimen preparation with FIB	50
2.8	3D FIB-SEM	51
2.9	Electron diffraction and image generation in TEM	54
2.10	Detectors in STEM	55
2.11	EELS spectra of carbon K edge	58
3.1	Graphite-Diamond map from EELS	62
3.2	Deformation defects in diamond crystal	64
3.3	Graphitization of deformation twins	65
3.4	Graphitization around an inclusion cut by twins	66
3.5	Graphitization band cutting through the inclusion veins	67

List of Figures

3.6	Diamond and graphite boundaries	68
3.7	Shock-induced diamonds from Popigai crater	69
3.8	(Fe,Ni) ₃ (S, P) inclusions in the diamond matrix	70
3.9	(EDX analysis of Fe-S type inclusion	71
3.10	Electron diffraction from diamond inclusion	71
3.11	Formation pressure of $Fe_3(S, P)$ versus P/(S+P) molar ratio	72
3.12	Morphological difference between graphite and diamond inclusion	73
3.13	inclusions in graphitized region	74
3.14	Chromite and phosphate inclusions in diamond	75
3.15	Fe-C and Fe-S binary phase diagrams	76
3.16	An inclusion vein in the diamond	77
3.17	Summary of diamond and inclusion formation	79
4.1	Schematic view of the Earth in the basal magma ocean model	82
4.2	Crystallization of melt during the laser heating	84
4.3	Volume rendering the elemental intensity maps	85
4.4	Segmentation and 3D reconstruction of phases	86
4.5	Schematic temperature gradients in single-sided laser heating	89
4.6	3D models and chemical map for the sample melted at 45 GPa	90
4.7	Evolution of the core composition with time	92
4.8	HAADF and EDX map of 45 GPa sample heated for 1 minute	93
4.9	HAADF and EDX map of the core in 45 GPa sample heated for 1 minute	94
4.10	Iron distribution in ferropericlase phase	96
4.11	Melt core boundary in 45 GPa sample heated for 6 minutes	97
4.12	Core grain in 45 GPa sample heated for 6 minutes	98
4.13	EDX map, BF, HAADF and DF images from a core grain in 45 GPa sample heated	
	for 6 minutes	99
4.14	HAADF image and Fe^{3+} distribution in a core grain in 45 GPa sample heated for	
	6 minutes	99
4.15	Iron L-edge EELS spectrum from the phases in the melt core of in 45 GPa sample	
	heated for 6 minutes	100
4.16	Ternary phase diagram at 45 GPa and it relations with the experiments	102
4.17	Predicted and measured phase composition at 45 GPa	103
4.18	3D models and chemical map for the sample heated for 3 minutes at 30, 45, and	
	71 GPa	104
4.19	Evolution of the core composition with pressure	105
4.20	HAADF image and EDX maps of 30 GPa sample	106
4.21	HAADF image and EDX maps of 71 GPa sample	107
4.22	HAADF and EDX map of the solidus region	108
4.23	Schematic demonstration of the melting in the LH-DAC and it evolution by time	111
5.1	BF and EDX map from Fp and Brg grains	115
5.2	Iron partitioning data for olivine and pyrolite system	117

List of Figures

5.3	TEM specimen preparation with FIB from a DAC sample	120
5.4	EDX spectrum of Fp and Brg phases	121
5.5	EELS for iron valence state measurements	122
5.6	Fe^{3+} and Al^{3+} incorporation mechanisms in Brg	125
5.7	Radial viscosity profile of Earth mantle	127
6.1	SEM micrograph of hot spot for sample at 40 GPa	132
6.2	SEM micrograph of hot spot for sample at 52 GPa	133
6.3	Diffraction patterns from the phases in Fa72 samples	135
6.4	[Diffraction patterns from the phases in Fa45 samples	136
6.5	EDX maps and spectra	137
6.6	HAADF and EDX maps of Fa72 sample at 82 GPa	138
6.7	HAADF and EDX maps of Fa72 sample at 52 GPa	138
6.8	STEM BF and HAADF images of Fa45 sample at 40 GPa	139
6.9	Fa# in bridgmanite and ferropericlase phases	140
6.10	Lattice parameter and Fa# for bridgmanite versus pressure	141
6.11	Exchange coefficient of iron between bridgmanite and ferropericlase	142
6.12	Unit cell volume of oxide phase	143
6.13	Densities of bridgmanite and ferropericlase versus composition	144
6.14	Density of lower mantle versus birdgmanite content	145
6.15	Density of lower mantle for varied Fe content	146
7.1	SEM micrograph of the thin section from sample heated at 66 GPa	153
7.2	EDX maps from the sample at 51 GPa and 113 GPa	156
7.3	EDX map and spectrum from the phases at 113 GPa	157
7.4	EDX map of the sample heated at 66 GPa	158
7.5	In-situ X-ray diffraction patterns	159
7.6	Ternary phase diagrams of Mg-Fe-Ca	160
7.7	Volume change of (Mg, Fe)O with the pressure	161

List of Tables

3.1	Composition of phases in diamond inclusions	72
4.1	Phase composition for samples melted at 45 GPa	91
4.2	Phase composition for samples melted at 30 GPa and 71 GPa	107
5.1	Synthesis conditions of phase assemblages and corresponding chemical analysis	s126
6.1	Starting material composition	131
6.2	Compositions obtained from XRD and EDX	148
6.3	Compositions and partitioning coefficient data from EDX	149
7.1	X-ray diffraction peaks of starting material	154
7.2	Starting material composition from x-ray fluorescence	154
7.3	Pressure and temperature condition of sample synthesis in LH-DAC	155

Introduction

Earth is the only known planet that has life. It has been appropriately referred to as mother Earth which emphasizes on the fact that all the living beings are depended on the characteristic of this planet that gave birth to them. Thus, human beings have always been trying to investigate and understand their home planet. However, the Earth, with ~6730 km radius, is a large dynamical system, whereas the deepest hole that humans drilled into it so far is only ~12 km deep. Although there are diamond and xenolith samples from the deep Earth that have been brought to the the surface by dynamical activities such as volcanoes, we still have very limited access or no access at all to the rest of Earth's interior. Therefore, indirect measurements and experimental methods have been developed to study the deep Earth. One such a method takes advantage of earthquakes waves that travel at depth before reaching the surface of the planet. Seismologists measure the velocity of compressional (P-wave) and transverse (S-wave) waves inside the Earth by recording their arrival time in several stations. This provide us with the information on the density and state of matter throughout the Earth. These results demonstrate that Earth has a layered structure (figure 1), and the mineralogy of these layers is known through the high-pressure and high-temperature experiments on the Earth compositions. It starts with the crust at its surface, followed by the upper mantle down to ~410 km depth (figure 1). Then, there is a transition zone where the olivine, (Mg, Fe)₂SiO₄, as the major mineral in upper mantle goes through a chain of phase transformations until it breaks down to the ferropericlase, (Mg, Fe)O, and bridgmanite (or perovskite), (Mg, Fe)SiO₃, at the regions deeper than 660 km. This is the starting point of the lower mantle that continues down to ~2900 km inside the Earth (figure 1). The rest is the metallic core that itself consists of the liquid outer core and the solid inner core. Seismic surveys indicate that the last hundreds of kilometers at the bottom of mantle is heterogeneous (figure 1), and there are large low shear velocity provinces (LLSVPs) and ultra-low velocity zones (ULVZs) in this region that can sometimes be correlated to the features on the Earth surface such as hot spots and subduction zones. This gives a simple picture of the current Earth. Nevertheless, like most answers, it brings up many new questions, for instance: How has the Earth formed? Why it has layered structure? And what is the origin of the heterogenities in its structure? The answers to these questions are progressively becoming clearer. But there are still a pending quest to obtain a comprehensive model describing the Earth's differentiation and the resulting structure.

The history of Earth and the Solar System begins with the formation of the Sun through



Figure 1: Schematic view of the layers in the Earth's structure. Starting from the surface towards the center there are crust, upper mantle, transition zone, lower mantle (D'' layer at the bottom of lower mantle), liquid outer core, and solid inner core. After [1]

gravitational collapse of the molecules and dust of the nebula gas. The conservation of angular momentum creates a disk of gas and dust around the forming proto-star that represents the starting materials for the formation of all the planetary object in the Solar System. The first large objects forming from the particles in the disk are the planetesimals. Then, some of the planetesimals grow to Moon- to Mars- sized protoplanets in the inner Solar System. The Earth and other terrestrial planets have formed from these proto-planets. The proto-Earth materials have been mixed with the materials accreted from other sources and the direct study of them is not possible. However, the Solar System still hosts numerous asteroids and comets that are remnant of the initial stages of the planet formation. Many of these asteroids hit the Earth throughout its history and the remaining materials from them are recovered as meteorites. Meteorites are the invaluable samples that help us to understand the Solar System and the formation of the planets. They can be classified into two main groups, namely: chondrites and achondrites. Chondrites are the materials from the planetesimals that were not substantially altered after their formation. Thus, their composition (except for highly volatile materials) is

similar to the initial gas that formed the Sun and all the other planetary bodies. Hence, they provide an estimate for the total composition of the Earth. They also contain the first solid particles that formed in the Solar System about ~4.5 billions of years ago. On the other hand, achondrites are originating from the planetesimals and proto-planets that have formed early in the Solar System, and altered through heating by the decay of short-lived isotopes. The first material to melt during the heating is the S-rich iron alloy that sinks to form the initial core due to its high density. The melting, then, continues for silicates. The initial silicate melt, enriched in incompatible elements like Al, erupts to the surface and makes up the crust. The rest of the silicates form the mantle, while most of the iron separates to the core. This process is called differentiation, and achondritic meteorites sample different layers and regions of the differentiated bodies. It is noteworthy that the meteorites have went through one or several stage of shock-metamorphism during the ejection from their parent body or the impact with the Earth. Therefore, the information we can obtain from these materials depends on the extent that we are able to characterize them and distinguish shock-induced features from the pristine ones.

The Earth itself has formed from the accretion of several proto-planets following their impacts. Indeed, the Moon is believed to be the result of the last giant impact between the Earth and a Mars-sized body. These impacts transferred the energy to the Earth that completely (or extensively) melted the planet, and induced its efficient differentiation. The layers and structure of the Earth as we know it today has shaped through the crystallization of this melt. Thus, to understand the evolution of our home planet, we need to look into the melting and subsequent solidification relationships relevant to the Earth's composition and thermodynamical conditions.

This thesis starts with a literature review in **chapter 1**. This chapter is divided to three main sections. The first one discusses the current theories for the formation of planetesimals and their evolution into planets. The second section looks into the meteorites and their classification. The models for the differentiation of planetesimals and protoplanets are explained in this section. Extra weight has been given to the ureilite due to its relevance to the later chapters. In the last section, we have explored the Earth and its structure with details.

Chapter 2 is dedicated to establish a background on the experimental instruments and techniques used in the thesis. First, the laser-heated diamond anvil cell (LH-DAC) is introduced as the unique tool to experimentally reach the static high-pressure and high-temperature conditions of the Earth's interior. Then, the scanning and transmission electron microscopy (SEM and TEM) is explained. The data, acquired from the synthetic or natural samples, is limited by the characterization methods. Different techniques can give information about different aspects of the materials. Our objective in this thesis was to push the limits of these methods and, also, take advantage of the cutting edge development in the characterization techniques to fully characterize and understand the samples related to Earth sciences at a nanometer scales.

List of Tables

We have studied the carbonaceous materials in ureilite meteorites. The ureilites form a unique meteorite group that are samples of the mantle from a partially differentiated parent body. Thus, they capture an intermediate stage between undifferentiated and differentiated planetesimals or proto-planets. This group of meteorites are exceptionally carbon rich, and the carbonaceous materials are mainly found as graphite and diamond between the silicate grains. The formation mechanisms of these diamonds are still controversial. In this study, we have looked at the diamonds in a ureilite sample (Almahata Sitta MS-170), and for the for the first time we have observed and analyzed the inclusions in the ureilite diamonds. These inclusions help to estimate the pressure and temperature conditions inside the ureilite parent body (UPB). Moreover, they contain materials that can be linked to the segregated liquid at the beginning of differentiation in this body. This project is presented in **chapter 3**.

In **chapter 4**, we explain the results from the melting experiments at 30-71 GPa corresponding to lower mantle conditions. The experiment are performed with the LH-DAC using San Carlos olivine as the starting material. Olivine has been selected for two main reasons. First, it has close composition to the mantle and it transforms to the bridgmanite and ferropericlase at high pressures (>~23 GPa) similar to the lower mantle. Moreover, many LH-DAC experiments have been carried out on the olivine to understand the high-pressure and high-temperature phase relations as well as melting and crystallization processes, which provides a rich source to make comparison with our experiments. However, due to the small sample size and non-homogenous heating, the are many issues remaining for interpretation of the obtained results. Thus, the recovered samples in our studies are fully characterized with 3D chemical tomography and, then, with TEM and related spectroscopy techniques. The variation in temperature gradient during the melting can be qualitatively inferred from the chemical gradients in the samples. This study represents the conditions during the crystallization of the molten mantle after the giant impacts and discusses its relationship to the current structure of the Earth.

The author of this thesis has contributed to several works through the electron microscopy and spectroscopy studies. The manuscripts (submitted or published) of these projects are presented in **chapters 5, 6, and 7**. The **chapters 5 and 6** focus on iron partitioning between ferropericlase and bridgmanite phases in the lower mantle. This has major effect on the density of the respective phases and the mantle rheology because of the higher mass of iron atoms compared to other major elements (Mg, Si, O). In the **chapter 7**, we have looked at the interaction of carbides with metallic iron at pressures up to the core-mantle boundary, which has implications for the carbon storage and cycle in the deep Earth. Finally, **chapter 8** concludes the main results of **chapter 3 and 4** and discusses the future perspective of these works.

1 Formation and evolution of planets

1.1 Planet formation

1.1.1 Star Formation and Accretion Disk

Protostellar cores are formed from molecular clouds collapsing under self-gravity [2, 3]. These cores are rotating. Therefore, a disk of gas and dust supported by centrifugal force forms around the collapsing core as a result conservation of angular momentum (figure 1.1)[3]. These disks are smaller than 1000 AU with a peak of ~200 AU for the measured outer radius size distribution [3, 4]. Multiwavelength submillimeter observation of young stars in Taurus-Auriga star formation regions indicates a disk mass in the range of $10^{-4}M_{\odot}$ to $10^{-1}M_{\odot}$ (with M_{\odot} being the solar mass) [5]. And rews and Williams (2005) found a median mass of ~0.5% M_{\odot} for 153 young stellar object [5]. Minimum mass solar nebula (MMSN), $10^{-2}M_{\odot}$, is minimum mass required to build the current planets and objects in the solar system (with the largest planet being Jupiter) [6, 7]. This mass is close to the median measured mass of accretion disks. However, these measurements can systematically underestimate the disk mass by large extent. Particles larger than millimeter size would have weak submillimeter emission [7]. Thus, if significant fraction of disk mass is stored as large particles or planetesimals, we should expect much greater mass than the measured values [3, 4, 7]. Moreover, there is a significant number of discovered exoplanets larger than Jupiter (some with few times of Jupiter's mass), which would probably need initial disk mass considerably larger than MMSN to form [7]. In MMSN the gas density decreases radially by a power low ($\rho \propto R^{-11/4}$), while the submillimeter measurements shows shallower slope for density decrease [6, 7].

Protostars accrete the mass from the surrounding disk by magnetic, hydrodynamic or selfgravitating mechanisms [3]. Although the accretion rate, \dot{M} , can vary for the stars with the same mass depending on their age and magnetic activity of their disk, the rough relationship of $\dot{M} \propto M^{2.1}$ (M being the star mass) has been found for the stars in the range of 0.02-3 M_{\odot} [7, 8]. For a star with the mass close to our sun, this rate would be about $10^{-8}M_{\odot}$ to $10^{-7}M_{\odot}$. Due to this accretion, the gas and small particles coupled with gas (up to few micrometers) move inward with the speed of few centimeters per second [9]. This speed decreases with time

5



Figure 1.1: Interferometry image taken by Atacama Large Millimeter/submillimeter Array (ALMA) from the protoplanetary disk around the HL Tau a Sun-like star located 450 light years away from us in Taurus constellation. This star is estimated to be about 1 Myr old and the gaps in the disk are though to be generated by forming planetary object (however, the exact nature of the gaps is still under debate). The visible disk is ~160-200 AU in diameter.

and with the distance from central object.

The initial temperature in the disk is typically above 2000 K close to the protostar and as a result most of the materials are in gas state [10]. However, by increasing distance from the center of the disk or by passing time, the temperature decreases, which allows the condensation of gas into dust particles . These particles are thought to have size distribution with a peak around 100-300 nm [11, 12].

1.1.2 Planetesimal formation in Solar System

The accretion disk around the forming star provides the starting material for planetesimal and protoplanet formation (figure 1.1). Thus, it has also been called protoplanetary disk (PPD). The age of Solar System is determined by radionuclide dating of the first condensed solids. The main constraints on planetesimal formation has been derived from evidences in the Solar System. The oldest found solids in Solar system are millimeter to centimeter sized calcium-aluminum-rich inclusions (CAI), which are condensed from gas during a very short span (less

than 50,000 years) after formation of the Solar system [13, 14, 15]. One of the most common systematics used for dating CAIs is 207 Pb- 206 Pb chronometer [13, 14, 15]. This is based on 238 U and 235 U isotopes which decay in chain into 206 Pb and 207 Pb isotopes respectively. The half-life for 238 U- 206 Pb is ~4.47 Gyr and for 235 U- 207 Pb is ~704 Myr. Therefore, the 207 Pb/ 206 Pb isotopic ratio changes over time after the system is closed [13, 14, 15]. Connely et al. (2013) determined the CAI formation age and, consequently, Solar System age of 4567.30 ± 0.16 Myr [15]. The chondrules, primitive ferromagnesian silicates, are formed starting at the same time of CAI and up to ~3 Myr after CAI [15].

Recently, dating of iron meteorites with short-lived, and now extinct, 182 Hf- 182 W chronometer (half-life of ~8.9 Myr) indicates that the differentiation of their parent bodies and core formation occurred in the range of ~0.7 Myr to ~2.9 Myr after CAI [16]. Since the planetesimals should be larger than about 30 km in radius to retain their heat [17], such large planetesimals should have accreted in the Solar System as early as ~0.1 Myr to as ~0.3 Myr [16].

In 2006, the Stardust space craft returned the collected materials form comet Wild 2 [18, 19, 20]. This comet has formed in Kuiper belt (beyond Neptune) and has been recently placed in its current orbit which reaches the inner Solar System [18]. Therefore, it accreted some primitive nebular dust as well as remnants of other disrupted bodies along with ice in early Solar System [18]. The analysis of collected particles showed a large portion of nanometer- to submicrometer- sized particles as well as occasional large particles (>1 μ m) [18, 19]. However, the most intriguing discovery was the presence of refractory particles (some similar to CAIs) which should have formed in inner Solar System [18, 19, 20]. Matzel et al. (2010) investigated a ~5 μ m refractory particle from stardust mission with ²⁶Al-²⁶Mg chronometer, and showed that it formed at least 1.7 Myr after CIA in the inner Solar System and it requires few million years to be transported to the outer Solar System (\geq 30 AU), and to be accreted by cometary bodies [21]. Moreover, based on their numerical simulation results and the composition of objects scattered in the solar system, Bottke et al. (2006) suggested that differentiated planetesimals formed in terrestrial planet region and, then, scattered into the main asteroid belt by interaction with the large planet embryos [22]. This implies that the planetesimal formation started close to the sun and continued outward to the outer Solar System [22, 23].

1.1.3 Planetesimal formation mechanisms

Despite many experimental and simulation studies, planetesimal formation remains as the most controversial and mysterious step in the planet formation and evolution of planetary systems. Any comprehensive model for planetesimal formation should start with the sticking of initial dust particles.

The experimental study on collision and sticking behaviour of particles have been usually performed using silica particles of $\sim 1 \ \mu m$ in size [23]. The mineralogy of silica is different from silicates, which are the main group of minerals among nebular particles. However, using silica, diamond, enstatie and silicon carbide, Poppe et al. (2000) showed that the sticking

behavior mainly depends on the grain size and the morphology of particles rather than their compositions [24]. In such a small grain sizes, the gravitational force between particles cannot lead to sticking. Moreover, aggregates in protoplanetary disks are not expected to be magnetic or charged in general [23]. Therefore, the only attractive force between the particles is electrostatic force generated by dipole-dipole interaction of molecules [23]. Two particles can stick together upon collision, if their velocity is under the threshold velocity, v_{th} [23, 24]. This threshold velocity decreases with increase in the size of particles. The collision velocities of particles for minimum mass solar nebula [25], surpasses the threshold velocity once they grow beyond few centimeters [23]. Therefore, planetesimals can not form through direct collisional sticking. There are several special conditions that have been suggested to assist the sticking mechanism of particles [23]. The organic material layer on the particles [26], sticking in the presence of water frost [27] and magnetic particles [28] are examples of these conditions. However, they are yet to be able to fully explain the formation of large objects.

Decreasing gas density and temperature by increasing distance from the central object in the protoplanetary disk, generates an outward acceleration for gas molecules opposing the gravitational acceleration toward the center [29, 30]. Therefore, the gas rotates more slowly than the local keplerian velocity. However, the solid particles are only affected by gravitational force of the star [29, 30]. Thus, they feel a headwind from slowly rotating gas and lose their velocity. Rotating below the Keplerian velocity causes them to drift inward [29, 30]. Due to this inward drift, the life time of a meter-sized body would be ~100 years. Hence, independently of their mechanisms, all planetesimal formation model should account for fast formation of kilometer-sized bodies to overcome the meter-size barrier [23].

Other models have a top down view for planetesimal formation. Early models discuss the formation of planetesimals by gravitational instabilities in the midplane of the disk, where the density of solid material is high due to their sedimentation [31, 32]. This models can work in laminar protoplanetary disk. However, the increased relative velocity of particles in turbulent gas disk would inhibit gravitational instabilities [30, 33]. The sedimentation of particles into the midplane will result in a particle-rich layer that orbits with local Keplerian velocity, while the gas-rich regions above and below the midplane will orbit the central star with sub-Keplerian velocity [30, 33]. This is one of the many sources of turbulence which prevents gravitational instabilities.

More recent models have addressed turbulence issues in the protoplanetary disks. One of these models was introduced by Johansen et al. (2007) [34]. In their model, centimeter- to meter- sized particles concentrate in gas pressure and density maxima which was produced by gas density fluctuations due to turbulence [34, 35]. High concentration of particles in these regions and coupling of gas with particles decrease their inward drift rate. Thus, particles from outer parts of the disk (which are still experiencing faster inward drift) concentrate in this region and further increase the particle density [34, 36]. This so called "streaming instability" generates swarms of particle which eventually can form planetesimals of about 100-1000 km in size by gravitational collapse [34, 35, 36]. Another model, proposed by Cuzzi et al. (2008),

shows that millimeter-sized particles (comparable to the size of chondrules) concentrate in low velocity regions between the turbulent eddies which is called "turbulent concentration" [37, 38]. These small particles can not undergo a gravitational collapse due to a strong coupling with the gas. However, they can survive long enough thanks to the gravitational bounds and gradually concentrate to make planetesimals with the sizes of 10-100 km [37, 39].

The most interesting result of these recent models is the direct formation of large planetesimals without going through the km-sized planetesimal phase. This is consistent with the simulations that show the initial size distribution of 100-1000 km size planetesimals is required to produce post-accretion size distribution of asteroids in the main asteroid belt [40]. Although both of these mechanisms are sporadic, sufficient concentration of particles to form large planetesimals occurs in the regions with high solid to gas ratios. This condition might be achieved earlier in inner regions of the Solar System, thus, leading to earlier formation of differentiated planetesimals [22, 41].

1.1.4 Runaway growth of planetary embryos

Once a large number of planetesimals is formed in protoplanetary disk they start to interact with each other. In this stage the planetesimals are large. Therefore, gravitational attraction is the main form of interaction between them, which causes planetesimals to accrete upon collision with one another [41]. The probability of such collisions depends on the geometrical collisional cross-section which is the projected surface area (= πR^2) of a given planetesimal. However, once the gravitational force become large and important, we also need to consider the enhancement of collisional cross-section by the so called gravitational focusing factor F_g , which is given by equation (1.1) [41, 42]:

$$F_g = 1 + \frac{V_{esc}^2}{V_{rel}^2}$$
(1.1)

Where V_{esc} and V_{rel} are the escape velocity of the planetesimal and the relative velocity of other planetesimals in its environment, respectively. Then, the accretion rate of a body would be proportional to its collisional cross-section [41, 42, 43]:

$$\frac{dM}{dt} \propto A * F_g = \pi R^2 * (1 + V_{esc}^2 / V_{rel}^2)$$
(1.2)

Where A and R are the projected surface area and radius of the planetesimal, respectively (the shape is assumed to be spherical). As we can see from equation (1.2), the accretion rate strongly depends on V_{esc}/V_{rel} ratio. The escape velocity, is the velocity required by a second body to escape the gravitational attraction of planetesimal, with the mass M and radius R, and it is given by:

$$V_{esc} = \sqrt{\frac{2GM}{R}} \tag{1.3}$$

Greenberg et al. (1978) showed that the large escape velocities of large bodies compared to the relative velocity results in their runaway growth, in a way that the large planetesimals grow faster than the small ones [44]. This was later shown in Wetherill and Stewart (1989) model with physical accuracy by considering equipartition of energy between the bodies of different sizes [42, 43]. In their model the dynamical frictions and gravitational perturbations between the planetesimals leads a body with the mass of m_1 and the velocity of v_1 to change its velocity due to another body with the mass of m_2 and velocity of v_2 in the following form [42, 43]:

$$\frac{dv_1}{dt} \propto m_2 v_2^2 - m_1 v_1^2 \tag{1.4}$$

Due to the conservation of energy, v_2 would also change similar to v_1 with the opposite sign in equation (1.4). In a given size distribution of planetesimals, this will increase the velocity of smaller bodies and decrease the velocity of large bodies [42, 43]. After planetesimal formation, the largest bodies would make up only a small fraction of the total mass. Therefore, the relative velocity of planetesimals would be determined by smaller planetesimals [41]. In this condition the average relative velocity will be close to the escape velocity of small bodies, $V_{rel} \approx V_{esc(s)}$. We can rewrite the equations by replacing R as a function of M as below where the ρ is the planetesimal density [41]:

$$M = \rho * \frac{4}{3}\pi R^3 \Rightarrow R = \left(\frac{3M}{4\rho\pi}\right)^{\frac{1}{3}}$$
(1.5)

Then, for small planetesimals, where $V_{rel} \approx V_{esc(s)}$, the relative growth rate from equation (1.2) and (1.5) would be [41]:

$$\frac{1}{M}\frac{dM}{dt} \propto M^{-\frac{1}{3}} \tag{1.6}$$

At the same time, however, the escape velocity of large planetesimals is much larger than the escape velocity of small planetesimals and the relative velocity ($V_{esc(l)} >> V_{rel} \approx V_{esc(s)}$. Therefore, the relative growth rate of large bodies using the same (1.2) relationship and replacing $V_{esc(l)}$ from equation (1.4) will be [41]:

$$\frac{1}{M}\frac{dM}{dt} \propto M^{\frac{1}{3}} V_{rel}^{-2} \tag{1.7}$$

Thus, the relative growth rate for the large bodies is increasing by increasing the size and the mass of planetesimals and this results in runaway growth. Moreover, when the velocities of small bodies increase due to gravitational perturbations, which decreases the gravitational focusing of large bodies, they start to collide with one another. Then, their high relative velocities leads to collisional fragmentation into even smaller bodies with lower relative velocities, easy to capture by large bodies [45].

When the substantial fraction of the total planetesimal mass is stored in large bodies, the $V_{esc(l)} >> V_{rel}$ would no longer hold. In this stage the large bodies would dictate the dynamics

and the relative velocity will be close to the escape velocity of large bodies, $V_{esc(l)} \approx V_{rel}$. Therefore, the gravitational focusing factor, F_g , will decrease to be of the order of unity and the relative growth rate of large bodies will follow the (1.6) relation [41]. Ida and Makino (1993) found the condition for this regime change to be [46]:

$$n_M M^2 > n_m m^2 \tag{1.8}$$

where n_M is the number of large bodies (protoplanets) with mass M and n_m is the number of small bodies (planetesimals) with mass m. In this stage the growth rate of protoplanets has inverse relationship with their mass (eq. (1.6)). This means that the large protoplanets will grow slower than the smaller protoplanets. Hence, their mass ratio will get closer to unity [47]. However, we should note that the planetesimals will still grow slower than the the protoplanets. This is because of the large relative velocity of planetesimals [47, 48]. The relative growth rate is determined by (1.7) relationship. If we replace m in (1.7) for the mass of planetesimals and $V_{esc(l)} \approx V_{rel}$, then, we obtain the relative growth rate for planetesimals. The growth rate of protoplanets (with the mass M) in this stage would be $(\frac{M}{m})^{\frac{1}{3}}$ time higher than the planetesimals (with the mass m). This phase of the planetary formation is called oligarchic growth, at the end of which we will have bimodal protoplanet-planetesimal system [47, 48].

The mentioned mechanisms will result in the formation of Moon- to Mars-sized protoplanets, which are often called planetary embryos. At 1 AU, these embryos form in about $10^5 \cdot 10^6$ years [41, 42, 43, 48]. The distance among these embryos with one another is in the order of 10^{-2} to 10^{-1} AU [41]. The formation time of planetary embryos is much shorter than the formation time of the Earth, which is estimated to be about 30-100 Myr after CAI [49, 50]. Moreover, there were tens of these planetary embryos in the inner Solar System and their sizes were one to two orders of magnitude smaller than that of the Earth. This indicates that the formation of terrestrial planets happened later.

1.1.5 Formation of gas-giant planets

The life-time of protoplanetary disk is estimated to be about 1-10 Myr [51]. Thus, unlike the terrestrial planets, gas-giant planets should have been formed early in the solar system before the protoplanetary disk runs out of gas. These planets form beyond the snow line, where the temperature of gas in the disk is below 145 K to prevent the sublimation of ice [52]. This is located at ~2.7 AU in our solar system (though it can change during the evolution of Solar System)[53]. Condensation of ice in this regions increases the solid surface density and allows the formation planetary embryos with the mass equal or larger than Earth [54, 55]. However, the critical mass for the solid core of gas-giant to be able to accrete substantial gas envelope is about ten times of Earth mass [56]. In order to form such a large cores in the life time of the gas disk, the initial disk should be at least ten times as massive as MMSN [57].

Recent models addressed this problem with a different approach. Lambrechts and Johanson (2012) showed that a solid core ~1000 km or larger in radius can rapidly accrete centimeter-

sized particles (pebbles), which are moving with sub-Keplerian velocities due to gas drag [58]. For the efficiency of this mechanism, a significant fraction of solid in the disk should be in the form of pebbles. The accretion rate depends on the pebble size and their total available mass. The pebble accretion model can potentially decrease the accretion time for critical core mass by two to four orders of magnitude beyond 5 AU [58]. Morbidelli and Nesvorny (2012) showed that the doubling time for an Earth size core in the presence of MMSN stored in 20 cm pebbles would be 5500 years [59]. However, this model still cannot explain the formation of only few gas- and ice- giant planets [59]. Simulations show that if pebble are formed together with planetesimals, ~100 Earth mass objects will form [60]. These protoplanets will be excited to high eccentricities and inclinations due to mutual perturbations. As a result, they will have minimal crossing with the midplane (where pebbles sediment) and the growth rate will significantly decrease. On the other hand, according to Levison et al. (2015) simulations if the pebbles form slowly due to the viscous stirring caused by planetesimals, only a few large objects can grow to the earth mass and, subsequently, become gas giants [60]. The early formation of these giants has a crucial influence on the formation of terrestrial planets which will be discussed in the following sections.

1.1.6 Giant impacts

The third major stage in the formation of planets starts when the protoplanetary disk runs out of gas. At this point, the inner solar system consists of planetesimals and planet embryos, while giant planets have already formed in outer solar system [41]. In the previous phases of planet formation, drag from slow rotating gas could damp the motion of large bodies and force them into circular orbit. However, in the last stage of the planet formation, the absence of gas drag would allow planetary embryos to increase the eccentricities of their orbits due to the gravitation perturbation among each other which leads to their collision [61]. Therefore, embryo-embryo and embryo-planetesimal collisions are frequent and these bodies can merge and accrete each other by such collisions.

Numerical N-body integrations show that at the aftermath of giant collisions, typically, one to four planets are formed in the terrestrial region [41, 61, 62, 63, 64]. Several parameters can be used to constrain and evaluate these simulations. Raymond et al. (2009) used five such constraints which are discussed below [63]. The first constraint is the mass distribution of terrestrial planets, especially, the small size of Mercury and Mars. In fact, small Mars is the most challenging constraint to reproduce in classical planet formation models [65]. Few models could achieve small Mars size by changing the orbit and increasing the eccentricity of Jupiter and Saturn [63, 66]. However, this was mainly inconsistent with the other constraint and also with the present architecture of the gas giants. The second constraint is the eccentricity and inclinations for the planets incompatible with the present orbits [61, 62]. This was first corrected by O'Brien et al. (2006) by using bimodal population of planetary embryos and planetesimals [67]. Dynamical frictions between large embryos and small planetesimals

lowers the final eccentricity and inclination of produced planets to the values comparable to the terrestrial planets [67, 68]. The third constraint is the formation time of the planets. The time scale for accretion of planets in simulations are generally in the order of $\sim 10^8$ years which is in agreement with the formation time of Earth discussed above.

The next constraint is the structure of the asteroid belt. The asteroid belt currently contains equal to ~0.05% of Earth masses [69], but it is believed to have lost more than 99.9% of its mass [70]. The asteroid belt is relatively close to the Jupiter. Therefore, unlike the terrestrial planet regions it is crossed by multiple strong resonances with Jupiter [70]. Large planetary embryos in this region perturb each other to high eccentricity until they fall into resonance with Jupiter where their eccentricity rapidly increases. Consequently, embryos and most of the planetesimals obtain eccentricities so high that they get absorbed by Sun or ejected from the Solar System [41, 70]. Two main taxonomic types of asteroids in the main belt namely: S-type and C-type are linked to ordinary chondrites and carbonaceous chondrites respectively [71, 72]. S-type asteroids are mainly located in the inner belt (2.1-2.8 AU) whereas the C-types are mostly in the outer belt (beyond 2.8 AU). However, there is an overlap and mixing among several types of asteroids in the main belt [73]. Since the planetesimals form from the materials in their formation location, the mixing in the taxonomical types of asteroids is thought to be the result of scattering by perturbation among the early embryos and planetesimals.

The fifth constraint is the water content of the Earth. The Earth is in the habitable zone of the Solar System where it can sustain liquid water. However, ironically, this same region is not suitable for the condensation of water in the early Solar System. Although there are no samples of the primitive materials that formed the earth, the inner Solar System chondrites (mainly enstatite and ordinary chondrites) are devoid of sufficient water to explain the water content of Earth. This means that the Earth was formed dry and then the water was delivered to it [74]. This water could be delivered by comets or C-type asteroids. Since the D/H ratio of the water on earth is in agreement with the carbonaceous chondrites and substantially different from comets, the accretion of carbonaceous chondritic materials by Earth is considered to be the main source of water delivery [74]. However, we should note that there are other mechanisms like oxidation of H-rich atmosphere to explain the water content of the Earth [75]. It has been shown that the eccentric Jupiter results in drier planets in the simulations, whereas Jupiter with low eccentricity can result in the high water delivery to the terrestrial planets [63, 76] .

In planet formation models, the collision between two embryos are often treated as a perfect merger. However, the outcome of the impact between two bodies depends not only on their sizes, but also on the impact velocity and impact angle [77]. Smoothed particle hydrodynamic (SPH) simulations show that low velocity and more direct impacts favor the accretion of two bodies with only a small fraction of the mass ejected as fragments [77]. On the other hand, very high velocity impacts will result in disruption of the target and the mass loss [77]. In the intermediate velocities and impact angles, the collision could result in hit-and-run impacts where some of the total mass will be ejected as fragments and the two colliding bodies will bounce inelastically and escape (figure 1.2) [77]. In realistic conditions relevant



Figure 1.2: The image shows the SPH simulation results of Asphaug et al. (2006) where a target body with the mass of M equal to 0.1 Earth mass is hit by the impactors of M/2 and M/10 mass in a and b respectively. The red parts and blue parts indicate core and mantle materials respectively. No net accretion is happening in these collisions and we can see lost fragments mainly from mantle materials in a and, also, metal-rich bodies in b. After [79].

to the planet formation in the Solar system, only about a half of the collisions will result in accretion. Integration of this factor into the N-body simulation (considering the other half of the collisions result in simple bouncing) shows that it has a negligible effect on the outcome of the simulation or the formation time of the planets. This is due to the fact that two colliders stay in the system after the bouncing, and they merge when they next encounter [78]. However, these collisions are important in terms of the chemistry and taxonomy of asteroids and planets. Since the colliding bodies are often differentiated, the eroded materials are iron-poor and silicon-rich compared to the composition of the whole body. This could change the overall composition of the planets during their formation time. Moreover, the separated fragments can stay in the Solar System as asteroids which explains the present time compositional diversity among the asteroids (figure 1.2) [79].

1.1.7 Grand tack scenario

As mentioned above, forming small Mercury and Mars in classical planet formation models has proved to be challenging. To address this problem, Hansen (2009) adopted a new approach where he assumed the material in the terrestrial planetary region to be confined in the narrow annulus between 0.7 AU an 1 AU in the form of small planetary embryos [80]. In their model, they showed that small Mercury and Mars analogs would form in their respective distance from Sun (~0.4 AU for Mercury and ~1.5 AU for Mars) due to accretion of materials scattered by forming Earth and Mars analogs. The formed planets, also, have eccentricity and inclinations



Figure 1.3: The plot from Walsh et al. (2011) shows the evolution of the mass and semimajor axis for gas- and ice- giants. Jupiter is fully grown at the starting time of the plot and located at \sim 3.5 AU and it migrates inwards until \sim 1.5 AU, while the Saturn is still growing at \sim 4.5 AU. Once the Saturn is almost fully grown it migrates inwards until and catches the Jupiter at 2:3 resonance and then they both migrate outward. After [81].

comparable to the present day planets. Although there are suggested mechanisms to alter the mass distribution in the protoplanetary disks, the assumption in Hansen (2009) study is not supported by physical theories. Rather, this study shows a possibility to change the initial conditions to establish new models [80].

The idea introduced in Hansen (2009) study was later used by Walsh et al. (2011) to develop the so-called "grand tack" model where the planetary embryos and planetesimals in terrestrial planetary region are confined by the migration of giant planets [81]. This is the result of two stage inward and outward migration of these planets as illustrated in figure 1.3. In this model first Jupiter forms and reaches to its final mass before the Saturn [81]. The isolated Jupiter then migrates inward due to the interaction with the gas disk. Saturn grows approximately to its final size later, but migrates inward faster until it catches up with Jupiter in 2:3 mean motion resonance (where the orbital period ratio of Jupiter to Saturn is 2/3), and, then, they both migrate outwards [81, 82].

If the Jupiter tacked at ~1.5 AU, the narrow and confined annulus of planetesimals and embryos forming the terrestrial planets necessary for small Mars formation will be naturally obtained (figure 1.4) [81]. Although there are still uncertainties about the formation history and condition of giant planets, grand tack scenario is widely accepted due to its ability to reproduce the constraints observed in the present day Solar System. In this model the asteroid belt, initially populated with volatile-poor bodies (S-type), gets cleaned out by the inward migration of Jupiter. Most of these materials are scattered inward, but some of the S-type planetesimals end up in the distances beyond 3 AU. On the other hand, some of the volatile-



Figure 1.4: The image from Walsh et al. (2011) shows the evolution of inner Solar System by time. The filled black planets are gas-giants (and ice-giants) which migrate inward and then outward. S-type planetesimals are indicated as red dots. C-types planetesimals are indicated as light and dark blue dots between the giant planets and beyond them respectively. The illustration shows the scattering of planetesimal by migration of Jupiter and final four planets (indicated by empty circles) in the inner Solar System as well as mixture of planetesimals in the asteroid belt. After [81].

rich (C-type) planetesimals from beyond the Jupiter, are excited to high eccentricities and placed in the terrestrial planetary region which could be the source of volatile materials and water on the terrestrial planets [83]. Later, during the outward migration of giant planets, Jupiter encounters the out-ward scattered S-type materials again and some portion of them are scattered inward to occupy the asteroid belt. As a result, the asteroid belt gets populated by the mixture of S-type and C-type materials similar to the observations as shown in the figure 1.4[84, 85].

1.2 Differentiation and Meteorite groups

Meteorites are samples of the material accreted in different regions of the Earth. Analysis of these materials not only gives us a better view of the Solar System in general, but also provides crucial information regarding the formation, composition and evolution of the Earth. Meteorites can be grouped as iron, stony, or stony iron meteorites upon collection. Although this classification is practical for initial descriptions, it does not hold any scientific importance. The most common classification of meteorite, divides them to chondrites and achondrites (or non-chondrites) [86, 87]. Chondrites are materials with a Solar-like composition, the parent body of which did not experience differentiation. On the other hand, achondrite meteorites have been derived from differentiated asteroids or planets. Non-chondritic meteorites can
also be divided to achondrites and primitive achondrites [86]. Primitive achondrites are the material with achondrite texture (igneous) which show chemical similarities to their chondritic precursor. In this section, first, chondritic materials will be discussed. Then, the discussion will expand to differentiation and formation of achondritic materials. Extra focus will be regarded to the ureilite meteorite group due to its relevance to the later chapters.

1.2.1 Chondrites

Chondrites often consist of chondrules with 0.01 mm to 10 mm in size [88]. Chondrules are igneous particles which were completely or partially molten in nebula and, subsequently, crystallized in minutes to hours at varied temperatures between 1300 K to 1800 K [89, 88]. These particles are mainly composed of olivine, $(Mg_xFe1-x)_2SiO_4$, and low calcium pyroxene, $(Mg_xFe_{1-x})SiO_3$, and commonly contain Fe,Ni metal [89, 88]. These chondrules (and other constituents) are imbedded in the matrix material which is, also, mainly composed of the mentioned silicate minerals [89]. The other two constituents of chondrites are refractory inclusions, silicates and oxides rich in Ca, Al and Ti (like CAIs), and Fe,Ni metallic particles [88]. These five components are found with varied proportions in different chondrites. The chemical composition of chondrules and overall chondritic materials depend on the location where they have condensed and accreted in protoplanetary disk. Nowadays chondrites are not considered to be condensed directly from the solar nebula and, therefore, not as pristine as it was thought before [88]. The exact location and mechanism of chondrule formation is still controversial. They could have formed by melting of the dust from solar nebula [90] or as a result of impact between molten bodies [91]. In any case, isotopical studies show that chondrules have formed in the span of several million years [15], which may suggest that the oldest and youngest chondrules have been formed with different mechanisms.

Chondrites are divided to 15 groups (the number could be different based on the classification) based on their composition (ratios of refractory or moderately volatiles elements), mineralogy and oxygen isotopic concentration [86]. These groups are themselves divided between three main classes, namely: carbonaceous (C) chondrites including 8 groups (CI, CM, CO, CV, CK, CR, CH, and CB), ordinary (O) chondrites including 3 groups (H, L, and LL), and enstatite (E) chondrites including 2 groups (EH, and EL) [86]. The naming of these classes does not bear any significance. For instance ordinary chondrites are named so because they are the most common meteorites. Some of the carbonaceous chondrites are rich in carbon (like CI and CM with 1-6% carbon), but others are not (like CO and CV) [88]. Two other groups (R and K) are not classified as any of the three main classes. There are also many ungrouped chondritic meteorites which could be the first samples of their own group. Each of the mentioned chondritic groups are considered to have their individual parent bodies. Among all groups CI chondrites show the closest similarity to Solar photosphere in terms of elemental abundances except for highly volatile elements (H, He, C, O, N) and noble gases (figure 1.5) [93]. Hence, it is usually used as a reference to compare the chemical composition of chondrites and other Solar System materials. Warren (2011) used the ratio of ϵ^{54} Cr versus ϵ^{50} Ti stable isotopes plot from



Figure 1.5: The plot shows the abundance of elements in the Solar photosphere versus the CI carbonaceous chondrites in logarithmic scale. As we can see, except for highly volatile elements (H, C, O, N) and noble gases, there is a very good match between the two compositions [92].

various chondritic and achondritic materials to show a dichotomy among the Solar system materials which is shown in figure 1.7 [94]. Indeed, the studied materials are plotted in two distinct clusters for carbonaceous chondrites and non-carbonaceous chondrites (as well as the achondrites derived from them) with orthogonal trends with respect to each other (figure 1.7), which shows their origin from two distinct reservoirs. The same thing was confirmed by ϵ^{92} Mo and ϵ^{100} Ru isotopic measurements [95]. Based on this, Warren (2011) suggested to classify the Solar System materials based on their origin in the inner Solar System (sun-ward of the snowline) for non-carbonaceous ones and outer Solar System (out-ward of snowline) for carbonaceous ones [94]. This notion is also compatible with the recent planetary formation theories (grand tack scenario) [81].

Oxygen with its three important stable isotopes (¹⁶O, ¹⁷O, ¹⁸O) plays an important role in the cosmological and geological studies, especially because it is abundant in the Solar System and can be found in gas (H₂O and CO) and solid (silicates, oxides, and ice) forms [96, 89]. This is shown by $\delta^{17}O = {}^{17}O/{}^{16}O$ versus $\delta^{18}O = {}^{18}O/{}^{16}O$ plots (figure 1.6) with the unit of deviation in parts per thousand from standard mean ocean water (SMOW) [96, 97]. Most chemical reactions (like equilibration) cause mass-dependent fractionation of oxygen isotopes which follows a line with slope of 0.52 [97]. Thus, the oxygen isotopic plot of almost all differentiated bodies (like Earth/Moon, Mars, and Vesta) plot in a parallel line with the same slope (figure 1.6b). The vertical deviation of these lines from the terrestrial fractionation line is shown as $\Delta^{17}O = \delta^{17}O - 0.52*\delta^{18}O$, and it is unique for most of the differentiated bodies. However,



Figure 1.6: $\delta^{17}O$ versus $\delta^{18}O$ plot for a) chondritic materials and b) achondritic meteorites and planetary bodies. TFL is the terrestrial fractionation lines and the fractionation line of differentiated bodies are parallel to it, except for ureilites which have similar O fractionation line as CV chondrites. After [97].

refractory inclusions and chondrules plot along a line with the slope of ~ 1 (CAIs are closest to 1) which indicates mass-independent fractionation of oxygen (figure 1.6) [98, 97]. These chemical reactions occur among the gaseous molecule in the nebula and gas disk [99] and, therefore, are preserved in the solid formed from that specific oxygen reservoirs [88]. The slopes of oxygen isotope plots for chondrites of different groups lie between 0.5 and 1 (figure 1.6a) which shows the effects of both mass-independent fractionation and mass-dependent fractionation in their parent body (like aqueous or thermal alterations) [97].

1.2.2 Differentiation of planetesimals and achondrites

The other group of meteorites sample the differentiated bodies in the Solar System. Wide variety of such meteorites exist. Iron meteorites which can be divided to several groups (IIAB, IIIAB, IVA, IVB, ID, etc.) are the samples of the the metallic cores of differentiated bodies [100]. Then, there are pallasites (also known as a member of stony iron meteorites) which are the assemblage of silicate (olivine) and metal, and they are thought to be originating from core-mantle boundary of their parent body (or bodies) [101]. Others, like ureilites, are believed to be mantle rocks [86]. Howardites-Eucrites-Diogenites (HEDs) have basaltic composition originating from crust of a differentiated body and they are linked to Vesta by spectroscopic observations [102].

Differentiation requires melting or partial melting of the initially accreted materials on the parent body. The most important heat sources for this process for the planetesimals and planetary objects are the decay of short-lived radioactive (SLR) isotopes, particularly ${}^{26}Al$

(which decays to ${}^{26}Mg$ with the half-life of 0.74 Myr) and ${}^{60}Fe$ (which decays to ${}^{60}Ni$ with the half-life of ~ 1.5 Myr) [103], and the gravitational energy released by collisions among these bodies [104]. For the smaller bodies (R < 1000 km) the gravity is weak and therefore the contribution of impact energies is insignificant [104, 105]. A planetesimal should accrete early enough in the history of Solar System to have sufficient amount of SLRs to provide energy for differentiation. Most studies show that differentiated bodies should have formed in the first 2-3 million years after CAI [105, 106, 107], which is also in agreement with the core formation datings [16, 108]. Moreover, heat conduction can remove the energy from interior of a body, therefore, there is a minimum size for planetesimals to retain the heat necessary for differentiations. This size is estimated to be about 20-30 km in diameter [17, 105]. However, it has been shown that the differentiation for planetary embryos, also, depends on the initial size of the planetesimals as well as the rate and duration of growth [104]. For example, a planetesimals could be too small to retain the heat, but then it grows to be large enough to cover the interior parts and prevent the energy from escaping. For a body with a given final size and duration of accretion, the growth rate determines the time that the planetesimal was too small to retain the heat [104]. In additions, large embryos (R > 1000 km) would also have the contribution of collisional heating which can produce a shallow magma ocean on their surface [104]. Thus, these objects could have layered structure of differentiated and undifferentiated parts [104]. This argument is in favor of a theory which suggests that the different families of chondrites and achondrites originate from single partially differentiated parent body [109].

¹⁸²Hf-¹⁸²W chronometer provides an important tool to study differentiation and core formation. 182 Hf is a lithophile element that decays with half-life of ~9 Myr to 182 W which is a siderophile element [110]. Therefore, if differentiation happens when the ¹⁸²Hf is alive, it would stay in silicate and later decay to ¹⁸²W to introduce positive ¹⁸²W anomalies and the metallic part will show negative anomalies [110]. Using this chronometer, Kruijer et al. (2014) showed that the core formation occurred in the range of ~ 0.7 to ~ 2.9 Myr for 5 studied iron meteorite groups [16]. Surprisingly, the formation time has direct correlation with volatile and S depletion in most of the samples which suggest a two stage core formation in planetesimals by melting Fe-S eutectic composition and, then, Fe itself [16]. When the temperature in the body increases, first, the Fe-S eutectic composition with the lowest melting temperature (~1250 K at ambient pressure) starts to melt [111]. It has been shown that only 5 vol% of this melt in solid silicate is enough to percolate and form the early core [17]. The next thing to melt is the silicates with ambient pressure solidus at ~1400 K (and liquidus at 1900 K) [112]. The early silicate partial melt could migrate to surface to form basaltic crust [113]. In case of bodies smaller than ~ 100 km, the basaltic melt could erupt due to exsolution of gas (H₂O and CO) with enough velocity to escape the body [114]. In this stage ²⁶Al preferentially partitions to the silicate melt and get removed from the interior to the surface of the body which can alter thermal evolution of the planetesimal [105]. In the next step, the iron melts at 1800 K (in the ambient pressure) [115]. Because of the inefficient wetting and the high dihedral angle between molten iron and solid silicate (90-100 degrees), high volume of partial melting is

needed for segregation of the iron [17, 116]. If the temperature increases above the liquidus of both silicate and iron, then everything would be molten in that region which would be a magma ocean. The segregation of iron core in the magma ocean is very efficient and fast. The basaltic crust can, also, form from the fractional crystallization of magma ocean. Greenwood et al. (2005) showed that most of the meteoritic parent bodies with uniform Δ^{17} O are required to be globally molten (>50%) in order to explain homogenous oxygen isotopic concentration in them [117].

1.2.3 Ureilites

Ureilites are often considered as complicated meteorites due to the possession of both primitive and achondritic characteristics. They are ultramafic rocks mainly consisting of olivine and pyroxene with carbonaceous veins between the silicate grains [118, 119]. Olivine grains in the olivine, often, have iron-depleted rim of up to $10 \,\mu\text{m}$ which are induced by reduction of oxides with smelting reaction (FeO_(*silicate*) + C \rightarrow Fe + CO_(*gas*)) [118]. Metallic iron in the grain boundary supports this idea, and considered as a sign of sudden pressure drop at high temperature accompanied by rapid cooling (2-6 °C per hour) from ~1050-1100 °C [120]. Except these rims, the olivine and pyroxene composition is homogenous in each monomict ureilite and they show equilibration temperature of 1200-1300 °C. However, Fo or #Mg (=MgO/(MgO + FeO) atomic%) of silicates varies substantially among different ureilite samples [118, 121]. This variation of Fo is in the rang of \sim 74-95, with approximately 58% of all ureilites falling in the Fo range of 76-81. Goodrich et al. (2004, 2007, 2013) explained this variation by pressure controlled smelting reduction (same type of reaction as the iron depleted rims) of silicates depending on the original depth of the samples in the ureilite parent body (UPB) [122, 123, 124]. However, Warren et al. (2006) argued against that by considering the abundance of siderophile elements in ureilite [125]. If substantial amount of iron was reduced from the silicate grain and drained to the core, the signature would have been preserved as siderophile depletion. In addition, Warren (2012) argued that the pronounced peak in the Fo of ureilites samples would mean very selective sampling from a narrow range of depth from the parent body which is implausible [126]. Therefore, he estimated minimum size of 690 km for the UPB to prevent smelting. In this model, the variation of Fo is attributed to the primary compositional differences in the materials accreted to form the UPB [126].

Very low degree of extremely siderophile elements against depletion of chalcophile and weakly siderophile elements, lead Warren et al. (2006) to conclude that differentiation in ureilites started with separation of S-rich metal and did not continue until the efficient separation of the iron itself [125]. Barrat et al. (2015) confirmed this model by measuring Fe isotopic composition, and showed that the S-rich metallic melt efficiently separated in ureilite near Fe-FeS eutectic before the melting of silicates [127]. Thus, an S-rich core formed in the UPB, samples of which are yet to be found. The other missing part of ureilites is their basaltic (basalt and feldspar) part, which make them extremely Al-depleted. This was interpreted as UPB lacking a crust, due to explosive removal of the silicate partial melt rich in CO and CO₂ gases

with such a high velocities that it escaped the parent body [128]. Another model, based on the thermal history of UPB, suggests that ~15% of the melt was trapped in sill-like intrusions ~7 km below the surface [129]. The rare basaltic component found in polymict ureilites show fine grained or glassy structures which is an indication of a rapid temperature drop [130]. Composition of ureilites and variation in their Δ^{17} O value unlike other differentiated bodies, sets the melting degree in the UPB to only 20-30% of silicates [117, 118]. This also removes the possibility of ureilites being cumulates as opposed to restites.

One of the most distinct characteristics of ureilites is their high carbon content in the range of 1-7 wt% (with average of 3.2 wt%) [118]. Although the carbonaceous part used to be considered as a late addition to the ureilites, the observation of euhedral graphite grains intergrown with metallic phase along silicate grain boundaries as well as carbides in metallic spherules imbedded in silicate grain pointed to their nature as indigenous [131, 132, 122]. Such a high carbon content have been only seen among the CI and CM chondrites with up to ~6 wt% carbon. The carbon isotopic composition (δ^{13} C) of ureilites is, also, similar to CI and CM which suggest possible link between the source of carbon in these materials [118]. The other similarity between ureilites and carbonaceous chondrites is their oxygen isotopic composition. Ureilite samples are along a line with the slope of ~1 in δ^{17} O versus δ^{18} O plot which is parallel to the line generated by CAIs and chondrules of CV chondrites with slight shift to left (figure 1.6) [133, 134, 135]. Previous studies considered primary oxygen isotopic composition of Solar System to be a line with the slope of 1 to the left of CV chondrites line with the water ice and solid silicates as the ¹⁶O-poor and ¹⁶O-rich endmembers respectively. Therefore, they attributed the location of CV chondrite line to the aqueous alteration on the parent body [136, 137]. By analogy, Goodrich et al. (2015) concluded that the UPB should have experienced the similar water-rock interactions which implies that high water content accreted on UPB [118]. This sets origin of UPB beyond the snow line and outer in the Solar System.

On the other hand, the lithophile composition of the ureilites (in particular Si/Mg and Mg/Mn ratios) is compatible with the ordinary and R-chondrites which are believed to be originating from the inner Solar System [118]. More importantly, ϵ^{54} Cr and ϵ^{50} Ti isotopic compositions indicated a pronounced dichotomy between the carbonaceous and non-carbonaceous chondrites, where ureilites lie in the same cluster as non-carbonaceous cluster ruling out the carbonaceous chondrites as UPB's building blocks (figure 1.7)[138]. However, considering the theory about the late injection of neutron-rich isotopes by a super nova explosion [139, 140], Goodrich et al. (2015) argued that the ureilite could have formed in the same location as carbonaceous chondrites before the injection of heavy isotopes and separation of two reservoirs [118]. Thermal models obtain the accretion age of ~0.5-0.7 Myr after CAI for ureilites [118, 129]. Although isotopic dating results show a large range for ureilite samples [141, 142], most recent study by van Kooten et al. (2017) using ⁵³Mn-⁵³Cr and ²⁶Al-²⁶Mg systems showed that there is a dichotomy in the melting and differentiation time of ureilite sample [143]. Early differentiation which formed most ureilite restites happened ~0.7 Myr after CAI, while a second melting event occurred at ~3.8 Myr after CAI which is possibly the result of heating by



Figure 1.7: $\epsilon^{50}Ti$ versus $\epsilon^{54}Cr$ is plotted for carbonaceous and non-carbonaceous chondrites as well as several planetary bodies and meteorite groups. The plot shows pronounced dichotomy between the materials with carbonaceous chondritic origin and non-carbonaceous chondritic origin. Ureilites plot in the same cluster as non-carbonaceous chondritic materials. After [94].

impacts [143].

Carbonaceous materials in the ureilites are mainly in the form of graphite and diamond. These diamonds are, generally, considered to be formed by the shock-induced transformation of graphite to diamond [144]. The correlation between diamond content and the shock-degree has been shown in ureilites [145]. Another theory, suggests the CVD condensation of these diamonds from the gas in the nebula [146]. However, in a recent study, Miyahara et al. (2016) demonstrated that the diamonds in MS-170 Almahata Sitta ureilite are formed in static high pressure conditions of the interior of their parent body as evidenced by their large crystallite size and the sector zoning of nitrogen isotopes [147]. This would require a parent body with at least 1000 km in diameter. This and the challenges in understanding the properties of ureilite meteorites motivated us to look in more details into the carbonaceous phases of ureilites, which will be discussed in chapter 3 of this thesis.

1.3 The Earth

1.3.1 Bulk composition of Earth

In Geochemical studies, the composition of bulk earth is, often, considered to be the same as the starting materials which formed the Sun except for volatile elements. Therefore, due to the compositional similarity between CI chondrites and the Sun's photosphere (figure 1.5), the Earth has been considered to be chondritic [148, 149]. However, this assumption has many flaws. For instance, the oxygen composition of the Earth cannot be derived from that of carbonaceous chondrites [150]. Also, the composition of $\epsilon^{54}Cr$ and $\epsilon^{50}Ti$ stable isotopes in Earth falls in the same cluster as ordinary and enstatite chondrites as opposed to carbonaceous chondrites (figure 1.7)[94].

These discrepancies lead to other model considering the Earth to be formed from enstatite chondrites which have similar compositions to Earth for many isotopes [150]. In particular, the oxygen isotopic composition of Earth can be derived from enstatite chondrites by mass-dependent fractionation. However, more recent studies excluded the enstatite chondritic model as well by measuring the $\epsilon^{30}Si$ isotopic compositions and proposed a combination of different chondritic groups as primitive materials that formed the Earth [151]. Looking at the Si isotopic composition, shows that the Earth composition is indeed an end-member that can not be produced by combination of chondritic materials if there is no hidden reservoir inside the Earth that can change the Si isotopic ratio of the bulk Earth [152]. Therefore, the building blocks of Earth were different than any known chondritic meteorite, but they probably were similar in their formation process and, consequently, in their chemical properties like relative abundance of refractory elements [153].

1.3.2 Accretion of the earth and moon formation

As it was discussed in section 1.1, terrestrial planets formed in the aftermath of the giant impacts. The earth has a particular souvenir remaining from that stage of the planet formation. A widely accepted theory explains that the Moon has formed by accretion of disk of debris formed as a result of an off-center collision between proto-earth and a Mars size planetary body often referred to as Theia [154, 155, 156]. This theory is supported by the similar composition of Moon and Earth'mantle. Also, the Moon forming from the Earth mantle would have iron-depletion and, therefore, Moon has a very small core which makes less than ~3% of its mass.

The Moon-Earth similarities goes beyond the chemical compositions. In fact, these two bodies have identical isotopic compositions for many measured systems like titanium, tungsten, and oxygen [157, 50]. Particularly, the same $\Delta^{17}O$ has not been observed between different differentiated bodies. This contradiction becomes more important when considering the collision simulations, most of which show that the moon is mainly formed from the impactor rather than the proto-Earth [156, 158]. This was first explained by the formation of the Theia in about the same heliocentric distance as earth [157]. However, the identical oxygen isotopic

composition of two different planetary body is still unlikely when considering for example Mars, located at ~1.4 AU, has $\Delta^{17}O = 0.32\%$ [159]. Moreover, the same heliocentric distance cannot account for the same tungsten isotopic ratio [50]. Therefore, the turbulent mixing between the silicate vapor from Earth and the Moon forming magma has been invoked to explain the isotopic and compositional equilibration between the mantle and the moon [160, 50]. Another study explained this similarity by considering approximately equal mass for the impactor and target in the Moon forming giant impact [161]. In this case, the Moon and the Earth will inherit almost the same ratio from each body, but, in general, the probability of the impact involving two such a large body (each with about the half of earth mass) is low. In the most recent development, Lock et al. (2016) suggested that a high energy and high angular momentum impact pushes the earth beyond the so called corotation limit where earth formed an extended structure with the core connected to the outer disk and they called this structure "synestia"[162, 163]. This corotation limit depends on the mass, thermal state and angular momentum of the planet. In the outer region of the synestia, the condensed silicate vapor can form the moon in tens of years, while in the inner side the condensed silicate droplets will melt again [162, 163]. The synestia mixes very rapidly in the time scale of weeks which explains the homogeneity between moon and the Earth. In this model, the angular momentum of Earth-Moon system later decreases to its present value due to resonance with the Sun [164]. It is important to note that based on the theories for Earth-Moon homogeneity, the mantle (or part of the mantle) melts during the giant impact to form a magma ocean. This magma ocean and its solidification plays a major role in producing the current structure and chemical distribution in the Earth and will be discussed in later sections as well as chapter 4 of this thesis.

Although there were later addition of material to the Earth (late veneer), Moon forming giant impact is considered as the last major event in the formation of Earth with significant effects. Therefore, the formation age of the Earth is usually inferred from the formation age of the Moon. Touboul et al. (2007) calculated this age with ¹⁸²Hf-¹⁸²W and ¹⁴⁶Sm-¹⁴²Nd chronometry to be 60^{+90}_{-10} Myr after the CAI [50]. Other recent studies, also, put the Moon forming event in a timescale of 70-130 Myr after CAI [165, 166].

1.3.3 Core and its formation

Most pronounced boundary in the Earth's interior is located at the depth of ~2900 km which separates the mantle from the core. The differentiation and core formation process has been discussed for planetesimals. However, the core formation process in Earth is different from planetesimals, due to the fact that the Earth has been formed by accretion of planetesimals, most of which were already differentiated. The shortest timescale estimated for the core formation of Earth by 182 Hf- 182 W system is ~30 Myr after CAI [49], in contrast with the planetesimal core formation at the first ~3 Myr after CAI [16].

Better understanding of core formation can be achieved by comparing the core and mantle



Figure 1.8: The figure shows the ratio of elemental abundances between Earth and CI chondrites normalized with respect to Mg ratio versus the temperature of 50% condensation. After [110].

differentiation with experimental data on metal-silicate partitioning of elements. The composition of core cannot be derived by the direct methods. However, the composition of bulk silicate earth (BSE) or primitive mantle has been estimated by studying mantle materials (peridotite) and using chemical constraints [167]. Figure 1.8 shows the abundance of elements in BSE versus their 50% condensation temperature [110]. The concentration of elements are divided by those of CI chondrites as an estimate for bulk Earth composition [110]. Elements with lower condensation temperature are naturally more volatile. There are several notable inconsistencies between the experimental partitioning data and the estimated mantle composition. One of them is the abundance of siderophile elements like Ni and Co which is called "excess siderophile problem" [168, 169]. This was later explained by obtaining Ni and Co partitioning data for metal-silicate at high pressures thanks to the invention and development of new high pressure apparatuses, especially diamond anvil cell [170, 171]. These experiments showed that Ni and Co become less siderophile by increasing the pressure. This lead to the models of core formation at high pressures. In this model the metallic iron droplets separated from silicates or originating from the core of accreted planetesimals will sink to the bottom of the magma ocean and they equilibrate with silicate melt during the fall (figure 1.9)[172]. Then they get stored in the metal ponds on top of the solid silicate layer below the magma ocean before they sink to the core as large metal diapirs (figure 1.9) [172]. Therefore, the metal has been equilibrated with the deep magma ocean as indicated by Ni and Co abundances in the mantle. Moreover, the mantle is rich in highly siderophile elements (like Pt group elements), which has been often explained by late addition of chondritic materials to the Earth during the "late veneer" [173, 174].



Figure 1.9: The cartoon illustrate the separation of metallic droplets from liquid silicate in magma ocean. These droplets then fall to the metal layer ponded at the bottom of magma ocean and on top of the solid mantle before descending to the core through the mantle. After [172].

The other anomaly in the mantle is the depletion in slightly siderophile elemetns (SSE) like Cr and V compared to partitioning data [171, 175]. The partitioning of these elements could be explained by equilibration in temperatures well above the mantle liquidus which is unlikely due to the presence of solid mantle under the magma ocean in the core formation models and fast solidification of fully molten magma ocean in the bottom [176]. The models proposed to explain Cr and V concentration assume a step like growth of Earth starting from a highly reduced materials which enhance the siderophile behaviour of SSE elements [177, 178, 179]. In these models, the FeO content of mantle later increases to its current value (8% wt) by reactions such as oxidation of iron by reduction of silica, or disproportionation of Fe²⁺ to Fe and Fe³⁺ accompanied by subsequent separation of metallic iron into the core. These reactions depend on the size and pressure of the Earth [177, 178, 179]. On the other hand, recent high-pressure and high-temperature experiments show that the siderophility of Cr and

V increases by the solution of oxygen in iron melt [180]. In this model, differentiation starts in a relatively oxidized condition and the FeO reaches to its current value by removing oxygen from mantle into the core [180, 176].

In the present Earth, seismic surveys shows a pronounced boundary ~2900 km deep inside the Earth which is attributed to the core-mantle boundary and corresponds to the pressure of ~135 GPa. From this boundary down to ~5100 km (~330 GPa) is where the S-wave does not propagate (figure 1.10), and this has been considered as an evidence for the liquid state of this region called the outer core [181]. The wave velocity measurements and density calculations indicated that the density of outer core is too low to be pure iron. This density deficit is explained by the presence of nickel and light elements [181]. However, there is no consensus on the exact type and concentration of these light elemetrs in the core. For instance, the initially reduced Earth would incorporate large amounts of Si into the core, while the initially oxidized Earth implies the presence of both Si and O as dominant light elements in the core [176, 182]. S is another candidate due to low Fe-S eutectic temperature [183]. H and C are other candidates due to their cosmochemical abundances [184, 185]. Beyond the ~5100 depth, there is a solid metallic region which is called the inner core. The crystalline structure of iron in the inner core is considered to be hexagonally close packed (hcp) based on the structure of the iron at the same pressures [186]. On the other hand, based on the presence of light elements in the composition and the high temperature range (up to 6000 K), other studies suggest a body centered cubic (bcc) structure for the inner core [187].

1.3.4 Mantle

The mantle makes up to \sim 82% of Earth's volume and \sim 65% of its mass [188]. In this section we will discuss the mantle by starting from its composition and then going down in depth through the mantle. The upper mantle and transition zone will be discussed briefly, and, then, we will focus on the lower mantle and its mineralogy which is the most relevant background for the chapter 4, 5, 6, and 7 of this thesis.

Bulk silicate composition

Other than the primitive meteorite samples (chondrites) and the Sun photosphere composition leading to chondritic model for the bulk earth, there are two main constraints and source of information about the composition of Earth. One of them is the samples originated from the Earth interiors which helps to estimate the composition of bulk silicate Earth (BSE) including crust and mainly the mantle. The most well-known of these models is pyrolite mantle model developed by Ringwood [167, 189]. In this model, Ringwood used different groups of peridotites as residual samples of mantle after partial melting as well as basaltic rocks as a melt extracted from the mantle by up to 20-30% of the silicate melting. For instance, the first pyrolite composition proposed by Green and Ringwood (1963) was a combination of primitive basalt and refractory dunite in proportions of 1 to 3 [190, 191]. Later experiments on melting relations in pyrolite composition lead to the refinement of it by choosing more appropriate peridotite and basaltic components. The framework established by these studies has been used extensively by other researchers to estimate the BSE composition [191]. These studies agree very well among each other, especially for major elements. They found the composition of BSE to be mainly 45.0-46.2% SiO₂, 36.3-38.3% MgO, 7.5-8.4% FeO, 3.3-4.8% Al₂O₃, and 3.1-4.4% CaO [191, 192]. The fact that several studies estimated similar compositions for BSE while using different types and samples of peridotites and basalts indicates the credibility of this method [192].

The other constraint on Earth composition comes from the seismological studies. Preliminary reference Earth model, is the one dimensional model developed by Dziwonski and Anderson (1981) using large seismologic data set to obtain the elastic properties and density of Earth interior down to the inner core illustrated in figure 1.10 [193]. Naturally, any model describing Earth's composition should be compatible with PREM. One argument about the pyrolitic model is that it is based on the mantle materials which are originating from the upper mantle and, thus, it cannot be representative of the lower mantle. This has been put to test by studying the pyrolitic composition at high-pressure and high-temperature conditions of lower mantle and comparing it with PREM. Several studies experimentally measured density [194, 195] and sound velocity [196], or computationally obtained the elastic properties of main minerals (ferropericlase and bridgmanite) [197] in the lower mantle. However, there are two groups of results among these studies. While some studies show a pyrolitic composition for lower mantle [195, 197], others agree with more Si-rich lower mantle compared to upper mantle or pyrolitic composition [194, 196].

Upper mantle and transition zone

The upper mantle starts under gliding plate tectonics followed by asthenosphere and it reaches to the transition zone between 410 km to 660 km. The composition of upper mantle is estimated by pyrolitic model as described above. This model estimates the upper mantle volume to be composed of \sim 56% olivine (Mg,Fe)₂SiO₄ [198]. The rest of the mantle is composed of garnet (Mg, Fe,Ca)₃Al₂Si₃O₁₂ and pyroxenes, namely: orthopyroxene (Mg, Fe)SiO₃ and clinopyroxene (Mg, Ca)SiO₃ [198]. There are two major seismic discontinuity in the mantle at 410 km and 660 km (figure 1.10) [193]. These discontinuities were first attributed to the phase change rather than the compositional change by Bernal (1936), who proposed that olivine transforms to a denser spinel phase at high-pressure based on the previous experiments on analogous materials [199]. Few decades later, experiments confirmed that at ~14 GPa corresponding to 410 km depth (α -)olivine with orthorhombic structure and space group of Pnma transforms to denser orthorhombic structure with the Imma space group which is called wadsleyite or β -phase or sometimes modified spinel [200]. By increasing pressure this phase itself transforms to a spinel phase (space group of Fd-3m) at ~17.5 GPa corresponding to the depth of 520 km which is called γ -phase or ringwoodite [200]. Then, at ~24 GPa (660 km) the ringwoodite phase breaks down to magnesium silicate perovskite (Mg, Fe)SiO₃ and



Figure 1.10: The plot shows the variation of S-wave and P-wave velocities (indicated as V_S and V_P respectively) and density (ρ) by depth based on seismic data. the absence of S-wave propagation between ~2900 km depth and ~5100 km depth is the indication of molten outer core. After [193].

ferropericlase (Mg, Fe)O phases which is marked as the starting point of the lower mantle [201, 202]. The phase transformations of olivine is shown in figure 1.11. The olivine to wads-leyite and ringwoodite breakdown are sharp and occur in the interval of \sim 7 km and \sim 4 km respectively [198]. On the other hand, wadsleyite transforms to ringwoodite in an interval of \sim 25 km [198]. Also, we should note that the mantle condition like temperature drop around the subducted lithospheric slabs can locally shift the phase transformation depth and, thus, seismic discontinuities (figure 1.11) [188].

Phase transition in other components of upper mantle occurs more gradually. First, the pyroxene components start to dissolve into garnet in the depth range of 350-500 km by substitution of Al in the octahedral sites with Mg and Si [198, 203]. Then, at the pressures above 18 GPa (~580 km), calcium silicate perovskite CaSiO₃ starts to dissociate from garnet [198]. After the 660 km depth the garnet breaks down to high-Al perovskite (Mg, Fe, Al)(Si, Al)O₃ and calcium silicate perovskite [204]. This transformation takes place upon the pressure range of 2-3 GPa and, therefore, the Al concentration in magnesium silicate perovskite increases in the first 50-100 km of the lower mantle [198].

Lower mantle and the role of iron

As we discussed, the main minerals of the lower mantle are ferropericlase and magnesium silicate perovskite along with minor amount of calcium silicate perovskite. In 2014 magnesium silicate perovskite has been found in a shocked chondritic meteorite and since then it has been



Figure 1.11: The schematic plot shows the phase transitions in the mantle transition zone for olivine compositions in pressure of 10-25 GPa and temperatures of 1000-2600 K. We can see the thickness of transition zone and phase transformation ranges changes for subduction zones due to the lower temperature. After [188].

called bridgmanite (Brg) [205]. Bridgmanite has an orthorhombic structure with space group of Pbnm in lower mantle condition with the octahedral and dodecahedral sites occupied by Si⁴⁺ and Mg²⁺ (or Fe²⁺) respectively (figure 1.13). Ferropericlase has the NaCl structure with space group of Fm-3m, where both O^{2-} and Mg^{2+} (or Fe^{2+}) are in the octahedral sites. MgO and FeO has both the same structure and they make a wide compositional range of solid solutions. However, a phase change to rhombohedral has been seen for the iron-rich end-member at ~20 GPa [206]. Also, dissociation of ferropericlase into iron-rich rhombohedral and Mg-rich cubic structures has been reported at ~86 GPa [207]. The Mg-rich and Fe-rich end-members of (Mg, Fe)O are called periclase and wüstite respectively. Therefore, any composition lying in between are called ferropericlase (Fp) for Mg-rich ones and magnesiowüstite (Mw) for iron-rich ones. Iron is the heaviest element among the major elements of the Earth interior and it can be incorporated both in perovskite and ferropericlase. Therefore, the distribution of iron profoundly affects the total and relative density of the minerals, which, in turn, dictates the physical and dynamical properties of the lower mantle. However, the transition metal characteristics of iron makes it complicated to determine its partitioning behavior between the mantle minerals. Iron in the lower mantle can exist in its neutral metallic form Fe with the electronic structure of $[Ar]3d^{6}4S^{2}$ or in its two oxidized states, namely: Fe^{2+} with $[Ar]3d^{6}$ and Fe³⁺ with [Ar]3d⁵ electronic structure. Fe²⁺ is the dominant iron type in most of the lower mantle and it preferentially partitions to ferropericlase. On the other hand, Fe³⁺ can only substitute Mg²⁺ by creating cation vacancies or in presence of monovalent cation impurities due to the charge difference which is energetically unfavorable and Fe³⁺ concentration in ferropericlase is insignificant [208]. It has been discussed that the Brg in lower mantle incorporates Al³⁺ in its structure. Al³⁺ replaces Si⁴⁺ in octahedral sites, but due to the charge difference it has to create oxygen vacancies which is not energetically favorable in the lower

Chapter 1. Formation and evolution of planets



Figure 1.12: The figure shows spin transition for Fe^{2+} and Fe^{3+} in octahedral sites as well as for Fe^{2+} in dodecahedral sites. In octahedral sites there are low-spin (LS) and high-spin(HS) state. However, in dodecahedral sites iron first transitions to intermediate spin (IS) state before going to low-spin state. After [216].

mantle conditions [209]. Instead, Al^{3+} and Fe^{3+} are incorporated in Brg structure together in the octahedral and dodecahedral sites [209, 210]. In fact, the crystallization of Brg would trigger disproportionation of the iron ($3Fe^{2+} \rightarrow Fe + 2Fe^{3+}$) which will introduce both Fe and Fe^{3+} in the lower mantle [211, 212]. The presence of Fe^{3+} in pyrolitic lower mantle Brg has been shown computationally and experimentally to match the seismic models [197, 213]. The concentration of Fe^{3+} in Brg can change by the pressure and temperature conditions [214].

Another intriguing aspect of iron as a transition metal is the spin transition of its electrons. As a result of the influence from negative charge of non-bonding electrons of ligands for a positively charged cation, five d orbitals split into two series including two (e_g) and three (t_{2g}) orbitals with the energy difference of Δc (figure 1.12)[215, 216]. This splitting strongly depends on the geometry and structure of the bonds, and, thus, on the crystallographic site occupied by the cation [215, 216]. For instance, t_{2g} has a lower energy than e_g for Fe²⁺ in the octahedral sites of ferropericlase while it is the opposite for the same cation in dodecahedral sites of bridgmanite (figure 1.12)[216]. By increasing the pressure and decreasing the volume, the energy cost for high energy orbitals, e_g in case of ferropericlase, increases. Therefore, while in the ambient condition there are 1 full orbital and two half-filled orbitals in t_{2g} and two half-filled orbitals in e_g (high-spin state), at high enough pressures, electrons empty the e_g level and there would be three full t_{2g} orbitals (low-spin state) [216].



Figure 1.13: The figure shows the crystalline structure of bridgmanite (perovskite) and postperovskite. SiO_6 octahedrals are shown in gray and magnesium ions in red. After [230].

Badro et al. (2003) showed the spin transition for Fe^{2+} in ferropericlase between 60-70 GPa [217]. This spin transition depends on the composition and for high iron concentration (above ~20% Fe) it increases by increasing the iron content [218]. Increase in the temperature can also widen the transition interval [219]. High-spin to low-spin transition decreases the ionic radius. Fe^{2+} radius decreases from 0.78 Å to 0.61 Å during the spin transition which correspond to \sim 52% volume change and it affects the iron partitioning between Fp and Brg [216, 220]. Several studies observed the change in partitioning coefficient above 70 GPa towards the more iron-rich ferropericlase as a result of spin transition [221, 222]. The spin transition has also been reported for Brg starting at ~70 GPa and ending at ~120 GPa [223]. Later studies also showed spin transition of Fe²⁺ from high-spin to intermediate-spin in Brg above 30 GPa and, then, into the low-spin state [224, 225]. Fe³⁺ spin transition in Brg is more complicated and since it can occupy both dodecahedral and octahedral site, the spin transition pressure could vary substantially [226, 227]. The change in iron partitioning to incorporate more iron in Brg has been shown above ~90-100 GPa and it was attributed to the spin change of iron in Brg [228, 229]. Iron partitioning and spin transition will be the main focus of chapters 5 and 6 and it will be also discussed in relation to the experiments in chapter 4.

Core-mantle boundary and post-perovskite phase

The bottom few hundred kilometers of the lower mantle, known as D'', has been shown to have low radial seismic velocity gradient (figure 1.10) which was attributed to the heat flow in core-mantle boundary (CMB) [193]. Later studies also indicated discontinuous shear velocity increase and large lateral heterogeneities in this region (figure 1.14)[231, 232]. Some of these characteristics was linked to the phase transition in the mantle minerals. Murakami et al. (2004) observed that bridgmanite transforms to a CaIrO₃-type orthorhombic structure with Cmcm space group above 125 GPa (figure 1.13) [233]. In this structure the SiO₆ octahedrals are stacked in sheet-like structure and density increases by 1% during the phase transition



Figure 1.14: The figure shows tomographical S-wave velocity variations in the mantle in equatorial cross-section on the right and the magnified panel on the left. Low (LLSVP) and high V_S are indicated by red and blue coloring respectively. The illustrated ULVZ has a yellow color on the edge of LLSVP directly on top of the core. Pv, pPv and STZ are referring to bridgmanite (perovskite), post-perovskite and spin transition zone respectively. After [232].

(figure 1.13). Ab initio calculations could explain several observed seismic properties of $D^{''}$ layer such as its anisotropy to the newly found post-perovskite phase [234]. Moreover, the pair of discontinuity observed in some regions for $D^{''}$ layer has been explained by transformation of bridgmanite to post-perovskite and, then, back transformation to bridgmanite due to the increase in temperature beyond the post-perovskite stability field [235, 236]. In any case, $D^{''}$ is a general depth shell and not all the characteristics of this layer is due to the phase transition as other anomalies has been known to take place in this region (figure 1.14) [232].

Heterogeneities in deep mantle

About 30-50% of the core-mantle boundary is covered by region with lower than average velocities called large low-shear-velocity provinces (LLSVP) (figure 1.14)[232, 237]. Two regions of LLSVP, each ~1500 km across, are observed beneath Pacific and Africa with (at least) about 500 km and 1000 km of height respectively and thought to be hotter and denser than the surrounding mantle [232, 238, 239]. The sharp edge and large seismic velocity anomalies in LLSVPs could not be easily explained by only thermal convection [240, 241]. Therefore, thermo-chemical convection is suggested as a mechanism to form and preserve these plumes [240, 241]. The location of LLSVPs are also shown to be correlated with hotspot volcanoes on the Earth [242, 243]. Moreover, Zhang et al. (2014) find the dissociation of bridgmanite phase into iron-free bridgmanite and an iron rich hexagonal phase (H-phase) which could be linked to the heterogeneities in $D^{"}$ layer and possibly LLSVPs [244].

On the other hand, directly on top of the CMB there are regions denser than the surrounding mantle with a low seismic velocity and the thicknesses of about 5-50 km which are called

ultralow-velocity zones (ULVZ) (figure 1.14) [232, 245, 246]. The P-wave and S-wave velocities in these regions decreases up to 10% and 30% respectively [232, 245]. Presence of dense iron-rich phases, post-perovskite [247] or ferropericlase [248], and interaction with the outer core are suggested for possible mechanisms of ULVZ formation [232]. However, a higher decrease in S-wave velocity compared to P-wave velocity is taken as evidence for presence of partial melt in these region [232, 245]. Labrosse et al. (2007) suggested that a melt layer of about 1000 km existed at the base of the mantle and on top of the core [249]. In this model the patches of melt enriched in incompatible elements have formed by fractional crystallization of basal magma ocean and preserved in the deep mantle [249]. Fiquet et al. (2010) performed melting experiments up to CMB pressures and concluded that partial melting can occur in CMB which explains the formation of ULVZs [250]. On the other hand, Andrault et al. (2012) argued against the preservation of melt in deep mantle by measuring the iron partitioning between solid and liquid phases and considering the melt buoyancy [251]. In another study, Andrault et al. (2014) linked ULVZs to the partially molten subducted oceanic crust [252]. To understand the dynamics and heterogeneities in the lower mantle understanding of its melting relationships is crucial. This will be the primary focus of chapter 4 of this thesis and the melting and subsequent fractional crystallization in lower mantle conditions will be discussed in details.

2 Experimental methods

In this chapter, we will first review the laboratory techniques that have been used through this thesis to prepare samples at high pressure and high temperature. Then, a background will be given on the electron microscopy tools and methods for sample characterization. Detailed description of the procedures employed for each study are given in the relative chapter.

2.1 High-pressure high-temperature experiments

2.1.1 Diamond anvil cell

The advances in high pressure physics greatly depends on the available experimental equipments that allows the investigation of materials at extreme pressure conditions. This is especially important in Earth sciences due to the inaccessibility of the most of deep Earth. Therefore, our understanding of the Earth has been continuously evolved through the development of new apparatuses capable of reaching to higher pressures and temperatures. One of the pioneer in this field was P. W. Bridgman who invented the Bridgman anvil and piston-cylinder device for generating pressure up to 10 GPa [253]. These equipment not only opened new doors in high pressure experiments, but they were also the starting point of the later developments such as multi-anvil apparatus. A high pressure module is used in the multi-anvil system to convert the force from a hydraulic press into the motion of 8 anvils enclosing around the sample. This device allows the high pressure experiments up to ~25 GPa, touching the top of lower mantle (although the new designs based on multi-anvil press could reach up to ~100 GPa [254]). These devices are generally called large volume presses (LVP) based on the sample size which are of the order of millimeters or larger.

A major evolution in high pressure experiment had arisen from the invention of diamond anvil cell (DAC). Diamond, as the hardest known natural substance, was first used for generating high pressures in 1950 [255]. However, it was not until 1959 that first diamond anvil cells were invented independently in University of Chicago and National Bureau of Standards (NBS) [256, 257]. Since then there has been many developments in the design of the DAC

and many different types of it have been introduced which differ in the way of applying the force[253]. In our experiments, we use a symmetrical design with identical diamonds as piston and cylinder (figure 2.1). DAC diamonds are cut at their tip to create a flat surface called culet (figure 2.1). The size of the culet varies from tens of micrometer up to hundreds of micrometer depending on the targeted pressure. Naturally, the smaller culet sizes with lower surface ares are used to generates higher pressures. In the DACs used for our experiment, the force applied by tightening the four screws symmetrically placed to push two diamond anvils closer and increase the pressure (figure 2.1). Nowadays, the DACs are used to generates pressures from few GPa up to ~400 GPa exceeding the pressure at the center of the Earth [258, 186]. DAC still remain the unique equipment to reach the static pressures of the Earth interior. Moreover, using nano diamond on top of the diamond anvil culet, Dubrovinsky et al. (2012) could reach to 600 GPa [259]. Although such a high pressure is not relevant for the Earth, it is necessary to study the interior of large planets and exo-planets.

Using gaskets in DAC experiment was one of the important steps in advancement of this apparatus [260]. The gasket is crucial in the confinement of the sample and pressure transmitting mediums between the two anvils (figure 2.1). The initial gasket is often a foil with a thickness of about 200-250 μ m. This foil is then subjected to the pressure between two diamond to bring the thickness of the culet area down to few tens of micron depending on the intended pressure of the experiment and the culet size (figure 2.1). This procedure, called gasket indentation, creates a ridge around the indented area of the gasket in both sides that supports the diamonds during the experiment and prevents it from breaking (figure 2.1)[253, 261]. Moreover, the gasket strength increases by work hardening mechanism as a result of deformation. Afterward, a circular whole with a diameter of about 1/3 to 1/2 of the culet size is drilled in the center of the indented area as a sample chamber. A suitable gasket should be made of materials with high toughness to avoid any sudden crack during the experiments. Also, the strength should be high enough to tolerated the applied pressure and the material should not react with the sample. Thus, several metals and alloys are applicable for making the gaskets. The most affordable options are stainless steels which are mainly suitable for relatively low pressures and temperatures. Rhenium gaskets are frequently used for large range of pressures due to their high yield strength. Beryllium gaskets are used for x-ray spectroscopy because of their transparency to the x-ray, but brittle nature and high toxicity limits their application.

Other than their strength, the chief advantage of diamond anvils is their transparency to the wide range of electromagnetic waves. This allows the utilization of wide range of in-situ characterization methods such as x-ray diffraction and spectroscopy, Raman spectroscopy, infrared spectroscopy. which have been the most important tools to acquire information in high pressure physics. When the x-ray diffraction is used with the DAC, pressure can be measured given the equation of state of the materials inside the sample. However, the precise equation of state is not known for all the compounds and, in general, these measurements are not feasible with many of the other characterization techniques. Hence, optical methods have been developed to measure the pressure in DAC experiments. One of the most widely used methods is the measurement of the pressure-induced shift in the R-line fluorescence



Figure 2.1: a) shows the piston and cylinder of a DAC used in our studies. The same DAC is closed at panel b, and the screws are tightened to bring the diamonds closer and increase the pressure. c) is the schematic image of a DAC diamond with a cut tip. d) demonstrates the schematic view of diamond anvil cell with an indented gasket and sample chamber.

of ruby (Cr^{3+} doped Al_2O_3) proposed by Forman et al (1972) [262]. In this method, a small ruby chip or particle is placed on one of the culets before closing the cell (figure 2.1) and, then, it is excited with a laser (generally blue laser) to obtain the red R-lines. Early measurements indicated a linear shift in the wavelength with the increasing pressure up to ~30 GPa [263]. This was later corrected with experiments up to ~100 GPa and a positive deviation from linear model has been shown to become important at high pressures [264, 265, 266]. Later studies, also, demonstrated the temperature and compositional dependence of the wavelength for ruby R-lines [267]. Although this method is still efficient at relatively low pressures, it is not accurate for the high pressure (above ~100 GPa) due to the weakening of the fluorescence peak [268]. In addition, the position of ruby inside the sample chamber could lead to the reaction with the sample itself. An alternative pressure gauge is the Raman spectrum of diamonds. This technique does not require any additional pressure marker, and the Raman spectrum is directly measured on one of the culets. Hanfland et al. (1985) showed that the frequency of the first-order Raman mode in diamond varies linearly with the R-line wavelength shift of the ruby up to 40 GPa [269]. Akahama and Kawamura (2004) have studied the Raman shift of diamond for different pressure mediums, culet size and gasket materials, and concluded that it does not depend on the loading condition [268]. They have, also, proposed a function fitted to their data obtained up to 410 GPa to measure the pressure based on the frequency shift [270]. This method is still one of the most frequently used pressure gauges in DAC experiments.

2.1.2 Laser heating

Temperature is the other thermodynamic parameter necessary to simulate the Earth interior in the experimental environment. In the piston-cylinder device or multi-anvil press this is achieve through resistive heating with the electrical current. This method has also been applied for DAC experiments [271]. The heating wire could surround the sample or go through it. However, the achieved temperatures are limited to maximum of about ~2500 K. Thanks to the transparency of diamond, the laser heating method has been introduced for the DAC [272]. The most common type of lasers used for this purpose are the solid-state lasers, especially yttrium-aluminum garnet (YAG) lasers. Accordingly, we have used Nd doped YAG (Nd:YAG) laser in our experiments which emits light with the wavelength of ~1.06 μ m. It should be noted that the sample requires to have sufficient absorption for the laser wavelength to ensure efficient heating. If the absorption of the sample composition is not adequate, it can be mixed with high absorption materials such as Fe or Pt powders. Although the early laser heating diamond anvil cell (LH-DAC) studies were performed by heating the sample from a single side [272], nowadays, the samples are heated from both sides to achieve better symmetry in the temperature gradient during heating (figure 2.2). This procedure is done using one laser source and by splitting the beam by polarization which are controlled to heat each side independently (figure 2.2). Laser heating in DAC allows to reach temperatures up to ~7000 K [273], and therefore, LH-DAC permits to cover the conditions of the Earth's interior down to its center at ~365 GPa and ~6000 K.

In the LH-DAC experiments, temperature is measured by recording the spectrum emitted by the sample. This is often done at the center of the laser heated zone. The wavelength range of the measured spectrum depends on the detectors, but it usually includes a range of few hundred nanometers of the visible and infrared wavelength. The obtained spectrum is then fitted to the electromagnetic radiation of a black-body at temperature T described by Planck's function (eq. 2.1) [273, 274]:

$$I = \epsilon \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$
(2.1)

where ϵ , h, c, λ , and k are the emissivity, Plank's constant, light velocity, wavelength, and the Boltzmann's constant. However, since the fitting to this equation could give rise to inaccuracies,



Figure 2.2: Figure shows a DAC inside the laser heating system for double-sided heating.

the simple approximation, called Wien approximation, is commonly used. In this simpler model, the $e^{\frac{hc}{\lambda kT}}$ » 1 is assumed. Thus, equation 2.1 is reduced to 2.2 [273]:

$$I = \epsilon \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}}}$$
(2.2)

Then, using the equation 2.2 for I and by defining a normalized intensity, called Wien, as below we get to equation 2.3 [273, 274]:

$$Wien = \frac{k}{hc} ln(\frac{2\pi hc^2}{I\lambda^5}) = \frac{1}{T} \frac{1}{\lambda} - \frac{k}{hc} ln(\epsilon)$$
(2.3)

This equation give a linear relationship with the newly defined normalized intensity (Wien) and $\frac{1}{T}$, which is used to simply and accurately fit the data and obtain the temperature (T). The assumption of $e^{\frac{hc}{\lambda kT}} \gg 1$ works well for low temperatures, but it does not hold for the higher temperatures [273]. Therefore, the Wien approximation cannot be used to accurately measure the high temperatures. Nevertheless, it gives a good approximation that can be used as the starting point to fit the data to the Plank's distribution. This procedure of acquiring spectrum to measure the temperature is called spectroradiometry. The black body approximation does not hold for many materials studied in LH-DAC and the emissivity changes with temperature [273, 275]. This together with fluctuations in laser power leads to errors in the measured temperature of about 100-200 K. The LH-DAC and spectroradiometry techniques are used in



Figure 2.3: SEM micrograph of a quenched sample and the 2D radial temperature distribution for a Re sample melted at 50 GPa with a LH-DAC. After [279].

chapter 4 to 7 of this thesis.

2.1.3 Temperature, pressure and compositional gradient in LH-DAC

Meaningful measurements of equilibrium chemical interactions in the LH-DAC experiments depend on stable heating with minimal temperature gradients. However, small sample size, laser profile, thermally conductive diamonds, and uneven absorption and insulation in diamond anvil cell samples cause temperature gradients of ~100-1000 K over a few microns [276]. The direct way to quantify variations in temperature is to measure it during the experiment. Usually this measurement is done in the center of the heated zone. However, several studies have measured the radial temperature gradient across the heating zone [277]. Campbell (2008) developed a multi-wavelength radiometry imaging method that can be used to measure the 2D temperature distribution in the LH-DAC [278]. In this technique, only four narrow bands of wavelength is used instead of the whole spectrum to fit the Planck function [278]. This reduces the precision of fitting; however, since the precision of fitting is much higher than reliability of spectroradiometry, this sacrifice is acceptable [278]. Figure 2.3 shows an example of this method used to measure the 2D temperature distribution in melting experiment on Re, which was then compared with the SEM image of the recovered sample to obtain the melting temperature [279]. The radial temperature change in ~10 μ m reaches 2000-2500 K. Although this method is useful to measure the radial temperature gradient, it cannot provide information about the axial temperature gradient.

Due to the limitations of temperature gradient measurements, there have been several attempts to numerically simulate them and calculate the corresponding temperature gradient for varied conditions of sample and heating. These calculations show that heat flow is mainly controlled by the laser shape and dimension in radial direction and by heat loss of diamonds in axial direction. One important parameter governing the temperature gradient is the insulation around the heated sample. Analytical models for axial temperature distribution demonstrate that the axial temperature drop depends only on sample filling ratio (sample thickness/gasket thickness) and thermal conductivity ratio of the sample to the insulator [280]. By increasing the thermal conductivity ratio, the total temperature drop within the sample will decrease, but the filling ratio has an optimum value depending on the thermal conductivity of the sample and the insulator [280]. Rainey et al. (2013) developed a three-dimensional code, TempDAC, to model the steady state heat flow in LH-DAC and used it to study different loading geometries and laser heating [281]. For a single-sided laser heating, they showed that the temperature peak shifts toward the heating side with increasing the sample thickness or absorption coefficient [281]. Moreover, they observed that for a double-side heated foil insulated with MgO, the temperature is slightly lower in the center than at the surfaces [281]. Using a flat-top laser profile instead of the common Gaussian profile has been suggested to decrease the temperature gradient [282]. However, Rainey et al. (2013) demonstrated that even higher radial gradient created with flat-top profile [281]. All the mentioned studies only consider the conduction as the heat transfer mechanism. Therefore, they are mainly relevant for the solid state experiments. Recently, simulations indicated that although the conduction remains the main heat transfer mechanism in the molten samples, convection is efficient enough to induce material flow [283]. In additions, these models do not consider the possible changes in the structure and chemistry of the samples, which can affect the conductivity and the laser absorption.

Since the heated sample in the DAC is prevented from thermal expansion, thermal pressure will be created depending on the heating temperature and its gradient [284]. Dewaele et al. (1998) used finite element simulation to show generation of 2.7 GPa thermal pressure in a typical DAC sample heated to the peak temperature of 2900 K at 10 GPa [285]. The value of thermal pressure increases for higher pressures but its relative importance decreases [285]. Consequently, this effect is mainly important for relatively low pressure experiments.

In addition to the uncertainty in temperature measurements, temperature gradient can cause thermal diffusion of chemical elements which is often called Soret diffusion. In silicate melts, this diffusion is controlled by the Z/r ratio of cations (Z and r being cation charge and ionic radii)[286, 287]. Thus, this is particularly important for iron. It has been frequently reported that iron is depleted from the heated zone which in turn decreases the laser absorption in the target volume of the sample [288, 289, 290]. Sinmyo and Hirose (2010) studied the Soret diffusion in solid sample and showed that Mg and Fe segregate to the cold edges of the heating zone [287]. However, the segregation of Fe is much stronger than for Mg. To explain the observed segregation of elements, they concluded that in the solid state phase Soret diffusion is controlled by the volume of chemical species rather than by Z/r ratio of cations[287]. The thermo-chemical diffusion decreases with reducing the temperature gradient through incorporation of laser absorber materials in the sample. The Soret diffusion can change the elemental ratios through the sample and introduce significant uncertainties for elemental partitioning measurements.

In our studies, the temperature was only measured in the center of the heated zone, and the temperature gradient has not been quantitatively determined. Nevertheless, the possible variation of the temperature gradient and its outcome is discussed in chapter 4 for the molten samples based on the ex-situ chemical analysis. Despite the problems in the LH-DAC experiments, it remains the unique tool to achieve the static pressure and temperature conditions of the deep Earth and planetary interiors.

2.2 Electron microscopy

Light microscopes have been used for centuries to observe small features beyond the limit of our eyes. However, the visible light has its own limits related to its wavelength. After Louis de Brougli theorized the wave behavior of electrons and won a Nobel prize for that in 1929, the ideas of using electron for microscopy emerged because of the shorter wavelength of electron at high energies [291]. Moreover, electron beam can be focused and shaped using magnetic or electrostatic lenses. The important benefit of lenses in electron microscopy is the possibility to change their power by changing the electrical current. Nowadays, two main class of electron microscopes are commonly used, namely: scanning electron microscope (SEM) and transmission electron microscope (TEM). Although the first motivation for developing electron microscopes was mainly to overcome the resolution limit of light microscopes, the advancement in the techniques introduced many other advantages that makes electron microscopes indispensable equipments for the researchers in a wide variety of fields ranging from biology to material sciences and geology.

2.2.1 Electron-matter interactions

Several types of signals are generated from the interaction of electrons with materials, most of which are typically used for characterizing and measuring different properties of the materials (figure 2.4) [291]. For the purpose of general discussion, we assume a thin sample transparent to electron. When an electron beam strikes such a specimen, most of the electron will go through the empty interatomic and intra-atomic space without any interactions. These electrons are called directly transmitted beam (or direct beam) (figure 2.4). However, a portion of electrons, depending on the thickness and the density of the sample, are scattered by the electrons and nucleus of the sample atoms. Assuming a coherent incident beam with an energy of E_0 , the scattered electron can be divided into elastically scattered ($E_{el} = E_0$) and inelastically scattered electrons ($E_{el} < E_0$). Each of these groups can be further classified into coherent and incoherent electron. Coherent electrons are the ones that keep their phase relationship after the scattering, while incoherent ones have no phase relationship. Most of these scattering events occur through the interaction of electrons with the electron cloud of atoms and they have low scattering angle. Therefore, for thick samples, all the transmitted electron shown in figure 2.4 will be trapped and absorbed in the sample. On the other hand, incoherent elastic scattering occurs mainly through the deflection of electrons by the nucleus



Figure 2.4: Different types of scattering events as well as the generated signal from the interaction of electrons with the material atoms. Transmitted electrons (blue) will only appear for thin samples (<300 nm).

of the atoms, also called Rutherford scattering, which has large angle. The probability of this event is related to Z^2 (Z being the atomic number of the atom) and increases with the density of the sample material. Backscattered electrons are the electron from the incident beam that went through the Rutherford scattering with an angle larger than 90 degree (figure 2.4).

The energy loss of an incident electron can arise from the interaction with the nucleus or the electron cloud. During the interaction with the nucleus, the incident electron will be deflected an decelerated by the positive charge of the nucleus and the lost energy will be released as a photon. This photons form a continuous spectrum of energy, generally in the x-ray range, and it is called Bremsstrahlung (braking radiation) (figure 2.4). Bremsstrahlung can also be generated through electron-electron interaction, but it is less probable and, therefore, it is negligible compared to Bremsstrahlung from electron-nucleus interactions. Another possibility is the ejection of an electron from the sample atoms by an incident electron (figure 2.5). The electrons ejected from the sample are called secondary electrons (SE). In this case, the incident electron (depending on its energy level). If an electron with low energy level is removed from the atom, the hole that is left behind will be filled with an electron from higher energy levels in order to minimize the total energy of the atom (figure 2.5). The energy





Figure 2.5: The schematic figure shows that an incident beam electron (purple) ejects and electron from K shell of atom. This electron loses energy equivalent to the energy difference between unoccupied sites and the K shell. On the other hand, the empty hole generated in K shell is filled with an electron from M shell and the energy difference is emitted as an x-ray photon.

difference between these two energy levels will be emitted as a photon. Therefore, the emitted photon has a characteristic energy specific to that atom and can be used for spectroscopy and chemical analysis (figure 2.5). Each atoms can emit several photons with several characteristic wavelengths that are divided into K, L, M, etc. groups based on the electron shell of the ejected electron (figure 2.5). The emitted photons for the electrons knocked out of the inner shells are always in the x-ray range, but for outer shells they could fall in the visible-light range. The same energy of the characteristic x-ray can also be transferred to an electron which is called Auger electron. The ratio of x-ray emission to the total of x-ray and Auger electron emissions is called the x-ray yield. The x-ray emission for light atoms and it increases with increasing atomic number. Thus, the x-ray emission for light atoms is not efficient enough for accurate spectroscopy.

2.2.2 Electron beam generation

First thing required for electron microscopy is the electron source, also called electron gun. The conventional sources were thermionic guns. They consist of a tip (usually bent tungsten wire or LaB₆) used as cathode, which was heated by passing an electrical current through it. This decreases the work function and electron can then be extracted and accelerated using an anode with a positive potential. The other source type is the field emission gun (FEG). Here the gun is a sharp tip (usually single crystalline tungsten tip) and the electrons are extracted through tunneling mechanism by applying strong electrical field around the tip. In both systems, the emitted electron beam goes through condenser lens and aperture, which are adjusted to obtain the desired beam current and shape. Although the thermionic guns are simpler and require lower vacuum, the field emission guns have the advantage of higher brightness as well as better and longer stability. Moreover, the energy spread is lower for FEGs (monochromacy). Therefore, modern microscopes (and all the microscopes used in

our studies) are equipped with field emission sources. The beam energy used for SEM and TEM is very different, but the general mechanisms of producing initial electron beams are similar in these microscopes.

2.2.3 Scanning electron microscope

In the scanning electron microscopes (SEM), the electron beam passes through the objective lens and aperture. Objective lens power is modified to focus the electron beam to a spot on the sample. Then, using a set of deflector coils, the beam can be moved to raster the sample pixel by pixel. The signals collected on each pixel are recorded to digitally create the image. The resolution of the image depends on the pixel size. However, selecting a pixel size smaller than the spot size in meaningless. Therefore, the most important parameter controlling the resolving power is the spot size. The spot size is controlled by the diffraction limit and lens aberration. The diffraction limit decreases with decreasing the wavelength (increasing high tension) or increasing the aperture size. The lenses suffer from several type of aberrations. Common low order aberration is astigmatism which the unsymmetrical focus power in the lens and changes the spot shape from a circle to an oval. This can be easily corrected with two quadrupoles. Chromatic aberration is the difference of the focus power for different wavelengths. Low energy spread in the FEG and the use of additional monochromator helps to avoid chromatic aberration. The most restricting aberration is the spherical aberration that is the result of variation of the focus power in the radial direction of the lenses. Thus, to decrease its effect on the spot size, the aperture size should be decreased. Other than the spot size, the interaction volume of the beam with the sample should be considered in the SEMs which increases with increasing the high tension or decreasing the density of the sample. Modern SEMs can reach a resolving power of about ~1 nm.

Backscattered and secondary electrons are the most important signals in the SEM imaging. Backscattered electrons (BSE) are sensitive to the atomic number and the density of the sample, and therefore, they produce a chemical contrast in the image. The BSEs have an energy similar to the incident beam and they are recorded by a detector under the pole piece. Secondary electrons (SE) are mostly the electrons ejected from the valence and conductive bands of the atoms and have an energy below ~50 eV. When there is an edge or a tip in the sample, the larger empty space around it allows more SEs to escape and generates brighter contrast in the image. This together with the large depth of field in SEMs, makes SE signal suitable to obtain topographic information from a sample. The SEs are generally detected with a positive collector attached to a photomultiplier in Everhart-Thornley detector. The in-lens detectors are also developed both for BSE and SE. In this case, the electrons are attracted to the column and separated by their energy before detection. It should be noted that a high quality SEM study requires a conductive sample are coated with metals (e.g. Au, Os) or an amorphous carbon layer before the microscopy.



Figure 2.6: The figure shows an EDX spectrum acquired with SEM working at 5 keV from an olivine sample melted in LH-DAC.

2.2.4 SEM EDX

The x-ray photons can be detected with a detector consisting of n-type and p-type doped semiconductors (usually Si). Therefore, the incident photon creates electron-hole pairs which can be measured as a current to obtain the energy of each photon. This technique is called energy dispersive x-ray (EDX) spectroscopy. The EDX spectrum gives the intensity of the recorded photons for the range of x-ray energies (figure 2.6). The count rate of the x-rays can be increased with increasing the beam current and the acquisition time. The beam current must be adjusted in a way to avoid the saturation of the detector and obtain a balance between the recording time and the processing time of the detector (dead time). To excite an x-ray peak with a certain energy (E_c), the beam energy should be slightly higher than E_c . However, to efficiently excite the E_c peak, the beam energy has to be at least ~2-3 times the E_c (overvoltage). The over-voltage affects the relative intensities of the x-ray peaks. On the other hand, increasing the high tension increases the interaction volume and generates x-rays from outside of the measured pixel and , consequently, limits the spatial resolution.

Several peaks can be related to artifacts. One such peak belongs to the excited x-rays from the detector (Si) by high energy x-rays emitted from sample. This is called internal fluorescence peak. As a result, the these sample photons will lose some of their energy and form another peaks at lower energy that is called escape peak. Also, the detector might confuse two photons and measure the sum energy as one photon which results in sum peaks. In addition, the electrons could excite x-rays from the microscope parts. These artifacts have to be considered for analyzing the spectrum.

The characteristic x-ray peaks are superimposed on the continuous Bremsstrahlung x-rays, and the background should be subtracted for quantification. The intensity of the x-ray peaks corresponding to each element in the sample is directly related to its concentration. Therefore, the simple quantification for element i can be obtained with the k_i ratio from standards with the following equation [292]:

$$\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i \tag{2.4}$$

where the c_i and c_i^{std} are the concentration of element i in the studied and standard samples, respectively. I_i and I_i^{std} shows the intensities of the x-ray peak measured for the sample and the standard. This method assumes the intensity of x-ray peak for element i to be independent of the other elements and the sample condition. Hence, the k_i ratio should be corrected with the so called ZAF matrix. This correction takes into account the penetration of the electrons into the sample depending on the materials (Z), the absorption of the emitted x-rays inside the sample (A), and the secondary fluorescence generating x-ray photons by higher energy x-ray photons emitted in the sample (F). Practical quantification methods use correction matrix based on ZAF. The I_i^{std} can be measured from the standards or calculated for standard-less quantification. The accuracy of quantification in SEM EDX is about ~0.5 atomic%. In our studies SEM EDX acquisition and quantification is performed with the INCA software from Oxford Instrument.

2.2.5 Focused ion beam

Similarly to electron, ions can also be used for microscopy. In this case, the ions from a wide variety of metals or metalloids (e.g. Au, Ga, As) are heated to the liquid state for the liquid metal ion source (LMIS) and then ionized by applying a strong electrical field. The field evaporated ions are controlled by a set of lenses and apertures to generate an ion beam. The beam formation and focusing are similar to the electron beam in an SEM. Ions have higher mass than electron. Thus, for a given energy, they have lower speed, but higher momentum. Upon striking the sample, they generated secondary electron and ions and, also, they remove atoms from the sample. The penetration of ions into the sample and the amount of generated secondary electron depends not only on the beam energy and the sample material but, also, on the crystallographic orientation of the sample material. However, in general, the ions have lower penetration depth than the electron because of their large size, and they produce higher amounts of SEs. Therefore, the ion beam itself can be used for microscopy. Nevertheless, the most important application of ion beam is for milling samples down to nanometric precisions. The common focused ion beam (FIB) instrument consists of an ion column and an electron column with an angle of about 50-54 degrees. The ion beam and electron beam cross each other in the preset working distance depending on the geometrical position of the beams, and



Figure 2.7: a) Carbon deposition on the target region for sample TEM specimen preparation in FIB. b) Three sides of the carbon deposition is completely removed and the section is thinned down to $\sim 1 \ \mu m$. c) The thin section is attached to a needle with carbon deposition and removed from the bulk sample. d) the section is attached to a copper probe and thinned down to obtain electron transparency.

the sample placed in this specific distance can be studied and manipulated with both beams. Moreover, ion beam can be used for deposition of materials such as carbon or platinum. In this method, a molecular gas containing carbon, and possibility metallic atoms such as Pt, is released to the sample chamber through a nozzle. These molecules attach to the surface of the sample and break down when struck by the ions. The carbon and metallic part remain on the surface and the rest of the gas is drawn out of the system through the vacuum pumps. The current and the dwell time must be adjusted in the low current range for FIB induced deposition to efficiently deposit the material, but not remove atoms from the sample. Although electrons can also induce deposition of the material, their efficiency is low because of their lower momentum.

One of the applications of the FIB is the TEM sample preparation. In order to be electron transparent TEM samples are required to be thinner than at most ~200 nm (dependent on the composition). Several techniques exists for TEM sample preparation depending on the material and the characteristics that are going to be studied. The FIB lift-out technique is an expensive and complicated technique for TEM sample preparation. However, it offers unmatched precision for selecting the target region to prepare the sample and the final thickness of the sample. Therefore, many TEM studies nowadays are only possible due to the development of this technique. TEM sample preparation with FIB starts with selecting the



Figure 2.8: Schematic view of 3D FIB-SEM analysis. The ion is perpendicular to the sample surface and parallel to the front surface. After removing each slice, the electron beam scans the front surface to acquire images or EDX map.

region of interest and depositing few microns of carbon (or metal) layer on it for protection (figure 2.7). Then, two sides of the carbon layer parallel to its length are completely emptied by FIB milling (or three sides to facilitate later steps similar to figure 2.7). The milling begins with high currents (up to ~45 nA) and the current is gradually decreased when getting closer to the carbon layer. The high currents mill the sample with high rates. On the other hand, the milling position is less precise and can induce relatively thick layer of amorphization on the sample. Moreover, majority of the atoms that has been ejected from the sample are removed from the chamber through the vacuum system, but some of them are redeposited on the sample. When the milling rate is high, there is less time to remove the ejected atoms and, therefore, the redeposition rate is higher. After reaching a thickness of $1-2 \mu$ m, the TEM section is attached to the needle with carbon deposition and lifted out of the sample (figure 2.7). This section is then attached to a grid and thinned down to ~100 nm for TEM analysis (figure 2.7). All the samples studied in this thesis were made with the FIB lift-out technique.

A state of the art utilization of FIB-SEM dual system is the 3D tomography of the sample [293]. In this technique the interested area is protected with a carbon (or metal) deposition and the materials in the three sides of the volume of interest are milled away with FIB. The front surface is then positioned parallel to the ion beam (ion beam perpendicular to the sample surface) (figure 2.8). In each step, images with desired signals are acquired from the front surface using the electron beam (figure 2.8). Then, a slice with preset thickness is removed by ion beam milling. Afterward, the image acquisition continues for the new front surface and this process is repeated for the entire target volume. The 3D map of the phases and the sample features can be reconstructed through attaching and processing of the slices. The FIB tomography is, often, conducted with SE and BSE signal. The voxel sizes down to 5x5x5 nm³ are achieved with this method. Moreover, 3D EDX and electron backscattered diffraction (EBSD) are possible but require longer acquisition time than the SE or BSE. In chapter 4, we have used 3D FIB-EDX to analyze the sample recovered from DAC.

2.2.6 Transmission electron microscopy

The general principle of transmission electron microscopy (TEM) is based on the transmission optical microscopes [291]. The samples studied with TEM are thinner than 100-200 nm to ensure electron transparency. The inelastic scattering of electron decreases with reducing sample thickness. Thus, most of the transmitted electrons are unscattered electron or coherent elastically scattered electrons. The electrons in TEM are usually accelerated in the range of 80-300 kV and they have much shorter wavelength (~2.5 pm at 200 kV) than light. Therefore, the atomic distances in a crystal acts as grating and diffracts the electron. For this reason, in TEM, coherent and elastic scattering of electron is called diffraction. This is similar to the x-ray diffraction through crystalline planes. The conditions for diffraction in a crystal was first described by von Laue in 3D geometry and, then, simplified by Braggs (father and son) in 2D geometry by assuming the scattering of electron similar to the reflection from a mirror. Braggs' law is derived from figure 2.9 considering that AB+BC should be equal to an integer multiple of the wavelength (λ). This leads to:

$$n\lambda = 2d\sin\theta_B \tag{2.5}$$

where the d is the interplanar distance in the crystal and n is an integer. The wavelength is known for the electron beam and θ_B can be measured in TEM. Hence, we can obtain the *d* spacing from eq. 2.5 and characterize the crystal structure.

Conventional TEM is operated with a parallel (or approximately parallel) beam shaped through the condenser lenses. As demonstrated schematically in figure 2.9, the parallel beam entering the sample is mostly divided into a directly transmitted beam and series of diffracted beams. The electrons in each transmitted beam, considered in figure 2.9, are parallel and coherent.
Thus, each beam is focused to a spot in the back focal plane by the objective lens and they make the image of the object in the image plane (figure 2.9). There are other intermediate lenses that can be adjusted to bring the diffraction pattern (back focal plane) or the image (image plane) into the charge-couple device (CCD) camera or the fluorescent screen. Due to the small thickness of the samples the spots will be broadened in the electron diffraction. Electrons diffract more strongly than x-ray and they can go through multiple diffraction events. Therefore, the lattice parameter measurement and quantified diffraction analysis is less precise with electron diffraction when compared to x-ray diffraction (although more advanced convergent electron beam diffraction (CBED) can solve some of these problems). However, the ability to produce diffraction patterns from a selected region of the sample as well as simultaneous imaging and diffraction is unique to TEM. The selected area aperture in the image plane is used to select a region and mask the rest of the sample (figure 2.9). Therefore, only the diffraction spots from the selected region will appear on the screen. This method is called selected area electron diffraction (SAED).

In fact, the diffraction pattern is the planar projection of the reciprocal lattice (fourier transform of direct lattice). Consequently, each (hkl) planes are represented as one spot and the angle among them is preserved, while the distance between the spots and the direct beam is related to 1/d and equal to $2\theta_B$ (eq. 2.5). This is measured with nm⁻¹ or mrad units. In practice, the sample needs to be oriented in a way that the electron beam is parallel to a low index zone axis. In this condition, several sets of low index planes are parallel to the zone axis and the electron beam (figure 2.9). Low index planes have higher degree of symmetry. Moreover, the low index planes with large d spacing will have smaller θ_B and they will appear closer to the central spot (directly transmitted beam). This simplifies the identification of the crystal structure (figure 2.9). The planes in the zone axis are not in the Bragg condition. However, small deviation from the Bragg condition only changes the intensity of the spots and their positions in the reciprocal lattice and the diffraction pattern are not affected. The Bragg angles for the spots in the SAED patten in generally lower than the ~10 mrad.

In an ideal situation, where the only scattering event in the sample is diffraction and if there is no apertures or lens aberrations, all the electron will be back in their position in the image and there is no intensity contrast (phase contrast still exist). Although this is never the case in the TEM, the images made from all the spots of back focal plane have poor contrast. Therefore, objective aperture is always used to select one or few spots to form the image (figure 2.9). If only the directly transmitted beam is selected, the image is called bright field (BF). The diffracting region (as well as thick and high density regions) will appear darker in this image. On the other hand, we can use a diffracted spot to make an image. This image is called dark field (DF) and it shows the region where that specific plane is diffracting. To avoid high spherical aberration, the incident beam is tilted to have the diffracted beam parallel to the optical axis for DF imaging (tilt-corrected DF). Moreover, phase contrast images with atomic resolution can be acquired with the directly transmitted beam and, at least, few diffracted beam. The objective lens is the most important lens in the TEM. Since the wavelength is very small for an electron beam, the resolution of TEM is mainly limited by aberration, especially



Figure 2.9: a) shows simple geometry of electron diffraction in a crystal. The Braggs' law is obtained by putting AB+BC equal to $n\lambda$. b) is a typical SAED from [110] zone axis of ferropericlase. c) demonstrates the passage of incident beam through the sample. parallel direct beam and diffracted beam are focused through objective lens to points (diffraction pattern) in the back focal plane. The magnified image forms in the image plane.

spherical aberration. Nowadays, the spherical aberration can be corrected with hexapoles or octupole and quadrupole combinations. This improves the resolution in TEM down to \sim 70 pm.

2.2.7 Scanning transmission electron microscopy

In the scanning transmission electron microscopy (STEM), the beam is focused to a spot (probe) and the image is acquired through rastering the sample (figure 2.10). Since the beam is converged, in the STEM mode the diffraction spots will become disks with a diameter equal to the convergence angle (two time the convergence semi-angle) and the diffraction corresponding to an (hkl) plane in the Bragg condition will be a dark line, deficiency line, in the directly transmitted spot and a bright line, excess line, in the diffracted spot. The STEM



Figure 2.10: The figure indicate the schematic position of circular BF and annular ADF and HAADF detectors in the STEM. Corresponding to their position, BF, ADF, and HAADF will mainly record the electrons from direct beam, diffracted beams, and Rutherford scattering. However, this strongly depends on camera length.

image is formed through the recording of signals for each pixel. Bright field image is recorded through a circular detector in the center of the column (figure 2.10). If the camera length is high enough to have only direct beam on the BF detector, the image will be similar to the BF in TEM mode. However, since the positions of the detectors do not change, the BF detector will detect part of diffraction disks if the CL is decreased. The dark field images can be acquired with annular detectors collecting the electrons scattered in a specific angle range (depending on CL) and, hence, they are called annular dark field (ADF) (figure 2.10). One of the major advantages of the STEM is the high-angle annular dark field (HAADF) images. This is performed with an annular detector with a large inner diameter that can collect the electrons scattered in a large angle range (figure 2.10). Since the large angle scattering is mainly due to Rutherford scattering, it increases rapidly with increasing atomic number and density of the sample. Therefore, HAADF images show a contrast that is mostly arising from the density (chemistry) and the thickness of the sample. However, we should note that the HAADF has also contribution from diffraction contrast, that can be minimized by decreasing the CL.

The electron probe in the STEM is formed with condenser lenses. Therefore, the aberrations in the condenser lenses are the most important limits for the resolution. Similar to the TEM, the spherical aberration can be corrected for the condenser lens in STEM to obtain the resolution

of \sim 70 pm. Unlike phase contrast in TEM mode, the atomic contrast in high resolution STEM (HR-STEM) does not change with the defocus and the thickness. Therefore, it is easier for interpretation.

2.2.8 TEM EDX

The principle of the EDX in S/TEM is the same as SEM. Since the high tensions used in S/TEM are higher than SEM, the problems from over-voltage is avoided. The EDX can be measured for a selected spot in TEM. However, STEM makes it possible to acquire maps with spectrum for each pixel. We have, therefore, used STEM EDX in this study. Moreover, since the samples are thin in S/TEM studies, the interaction volume is limited and high spatial resolutions can be achieved.

Considering the thin samples in S/TEM, Cliff and Lorimer used equation 2.6 to rewrite it for the ration of element A and B as below [294, 291]:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \tag{2.6}$$

where the k_{AB} is called the Cliff-Lorimer factor. Since the absorption (A) and fluorescence (F) are negligible for thin samples, the Cliff-Lorimer factor depends only on the atomic number (Z). Therefore, these k factors can be measured for all elements relative to one element and then they can be obtained for the rest of elemental ratios. In this method the sum concentration for the measured elements are considered to be 100 %. Despite of its limit based on the thin-foil assumptions, the Cliff-Lorimer approximation is still the most common procedure for S/TEM EDX quantification. The S/TEM EDX maps in this study were all acquired with FEI Tecnai Osiris microscope equipped with 4 windowless EDX detectors from Bruker and operating at 200 kV. The EDX spectrum are quantified with the Cliff-Lorimer method using the Espirit 1.9 software from Bruker.

2.2.9 Electron energy-loss spectroscopy

As discussed before the incident electron can eject an electron from the electronic shells of the sample atoms and, thus, loose energy (figure 2.4). These electrons can be used for electron energy-loss spectroscopy (EELS) which is similar to x-ray absorption spectroscopy (XAS). To do this, the transmitted electrons in S/TEM are separated by energy with a magnetic prism. In TEM mode the spectrum can be obtained for a selected region. Moreover, the images can be acquired using only the electron that have lost specific amount of their energy. The combination of these images through the whole range of interested energy-loss give the complete spectrum for the entire image. This method is called energy filtered TEM (EFTEM). In the STEM mode, similarly to EDX, we can obtain a spectrum for each pixel in a map, also

called EELS mapping. The TEM spectroscopy is used in chapters 4 and 5, and the EELS mapping is used in chapter 3 and 4 of this thesis.

The EELS spectrum has a large peak at zero energy loss. The intensity ratio of the zero-loss peak to the entire spectrum, for a given the composition, is used to determine the thickness of the sample. The later core-loss peaks are related to the energy required to remove an electron from the electronic shell and place it in an unoccupied site. They are called K, L, M, etc. edges. Unlike for EDX peaks, after each EELS edge there is an exponential decay of intensity with increasing energy-loss until the next peak. The extrapolation of the pre-edge intensity is used to remove the background for each edge.

The exact energy and the shape of an EELS edge depends strongly on the coordination and electronic state of the material. Although EELS can be used to obtain elemental compositions, in this thesis, we have only used EELS to study the electronic state of materials. For instance, the peak energy of L_{2,3} edge has been shown to shift to higher energy-loss with increasing oxidation state for the transition metals in the fourth period [295]. This edge indicates the energy required for exciting an electron from the 2p subshell to the half-empty 3d subshell and consists of two peaks. The shift of the L2,3 peaks is called chemical shift and is related to the number of electron on the d band [295]. We have used chemical shifts to measure the Fe^{2+} and Fe^{3+} ratio in minerals in chapter 4 and 5. Another application of EELS is to study the electronic state of carbon atoms. Carbon element has a 1s²2s²2p² electronic structure. However, depending on the materials, the 2s and 2p orbitals of carbon hybridize to form new orbital in covalent bonding. This hybridization can take place through combination of 2s orbital with one of 2p orbitals (sp^1) , two of 2p orbitals (sp^2) , or all three 2p orbitals (sp^3) . In all forms the hybrid sp orbitals will form strong σ bonds and the remaining 2p orbital will form weak π bonds. For sp³ hybridization, like diamond, the first peak in the K edge of carbon is related to the energy required to transfer a 1s electron to the lowest unoccupied σ^* orbital (figure 2.11). On the other hand, for the sp^2 hybridization, like graphite, k edge has an additional peak at lower energy corresponding to the transfer of a 1s electron to π^* orbital (figure 2.11). EELS is used to study the graphite and diamond inter-growth in chapter 3.



Figure 2.11: EELS spectra of carbon K edge from diamond and graphite in ureilite meteorites after removing the background.

3 Diamonds and their inclusions from a Mars-sized planet

3.1 Introduction

Ureilites are one of the main families of stony achondritic meteorites along with HEDs (originating from Vesta) [102], martian, and lunar meteorites [87]. Unlike the other mentioned groups, the ureilite parent body (UPB) has not been identified. They are ultramafic rocks made of coarse grained olivine and pyroxene [118]. The variation of Mg in silicates and Δ^{17} O isotopic ratio among different ureilite samples indicates that although the UPB had been partially differentiated (20-30% of silicate melting), it never went through an extensive magma ocean period [117, 118]. This confirms that ureilites are mantle restites as opposed to cumulates. Thermal models and isotopic dating estimated the formation and differentiation of the UPB in the first 1 Myr and 2 Myr after the formation of Solar system (CAI), respectively [118, 129, 143].

In 2008, for the first time in history, an asteroid, called 2008 TC_3 , was discovered and its trajectory was precisely determined ~19 hours before it had hit the Earth [296]. This asteroid exploded ~37 km above the Nubian desert in Sudan [296]. Close to ~700 meteorite fragments were recovered after this explosion and they have been collectively called Almahata Sitta after a nearby train station. Most of these meteorites (~79 mass%) are characterized as ureilites and the rest as chondritic materials [297]. The majority of chondrites are enstatite chondrites (EC), but there are some ordinary chondrites (OC) and rare occurrence of carbonaceous (CC) and R-type chondrites [297]. Such a wide spectrum of meteorite groups originating from several parent bodies among Almahata Sitta samples is unique and surprising. This lead various studies to conclude that the UPB has been disrupted and its fragments reaccreted to form one or more daughter bodies [118, 298, 299]. This daughter body (or bodies) accreted materials from other parent bodies during their formation or later in their life [118, 298, 299]. Nevertheless, the original formation region of UPB in Solar System is still matter of debate. High carbon concentration and the oxygen isotopic composition of ureilites similar to carbonaceous chondrites suggest their genesis beyond the ice line and in the outer Solar System [118, 135, 133]. On the other hand, the Mg/Si ratio of silicate grains and the composition of heavy isotopes ($\epsilon^{54}Cr$ and $\epsilon^{50}Ti$) matching that of enstatite and ordinary chondrites support

a source in the inner Solar System [118, 138].

Ureilites are distinct from other achondrites by their high carbon contents (~3.2 wt% in average) that is only matched by CI chondrites among the meteoritic groups. Although carbides (e.g. cohenite) and amorphous carbon has been found in ureilites, carbonaceous materials are mainly in the graphite and diamond forms. These phases appear between the silicate grains. The origin of the diamond in these meteorites remains controversial and three different mechanisms have been suggested for it. The earliest studies suggested diamond formation in the high pressure environment of the planetary interior. Lipschutz (1964) noticed the texture and close orientation of diamond crystallite in x-ray diffraction studies which can only arise from anisotropic formation [144]. Therefore, he suggested the shock-induced transformation of graphite to diamond when the UPB has been disrupted [144]. Another view based on high noble gas concentration of ureilite diamonds, proposed their formation through chemical vapor deposition (CVD) directly from the solar nebula [146]. Later reports and observations such as presence of hexagonal diamond (lonsdaleite) or the correlation between the shock-degree and the diamond ratio in ureilites mainly support a shock event for the origin of diamonds [145, 300]. However, in a recent study, Miyahara et al. (2016) looked at the diamonds in the MS-170 fragment of Almahata Sitta meteorites and noted the large size of diamond crystallites (up to $\sim 20 \,\mu$ m) which are unlikely to form during a shock [147]. Moreover, they noted the sector zoning of nitrogen inside the diamond grains pointing to a sluggish growth mechanism [147]. They thus suggested the growth of large diamonds in high pressure conditions inside the UPB that have been later segmented through graphitization [147].

In order to understand the process of diamond generation and the relationship between diamond and graphite phases, we have looked at the carbonaceous materials in the MS-170 Almahata Sitta ureilite with transmission electron microscopy (TEM) and spectroscopy techniques. The advantage of our characterization method is the ability to investigate the materials with sub-nanometer resolution and, also, to identify the morphology, the structure, the chemical composition and the electronic state of materials simultaneously on the same sample. In addition, if the ureilite diamonds are pristine, they can provide invaluable information on the deep region of their parent body similar to the natural diamonds found in the Earth.

3.2 Methods

3.2.1 Focused ion beam (FIB) sample preparation

Five thin section for TEM analysis were prepared with the conventional in-situ FIB lift-out method using Zeiss NVision 40 dual beam instrument (see figure 2.7). The polished surface of Almahata Sitta MS-170 meteorite was coated with a ~15 nm carbon layer to ensure sufficient electrical conductivity during scanning electron microscopy (SEM) and ion milling process. Then, using secondary electron signal in SEM mode, the relatively large diamond grains are

targeted. In order to protect the interesting region throughout the sample preparation, a ~2 μ m thick amorphous carbon layer is deposited with ion-beam induced deposition (IBID) process. The materials in three sides of the carbon deposition layer were milled away with Ga⁺ ion beam accelerated at 30 kV starting with a beam current of 27 nA and decreasing it down to 1.5 nA when getting closer to the targeted area. Afterward, the TEM section, ~1 μ m thick at this stage, was attached to a Kleindiek needle with IBID and then transferred to a copper grid. This section is further milled with 700 pA down to 80 pA current to obtain a ~100 nm thick sample that is transparent to the electron beam. Finally, the samples are polished in two steps with FIB working at 5 kV and 2kV with a beam current of 20 pA and 25 pA in deposition mode, respectively.

3.2.2 Electron energy-loss spectroscopy (EELS)

EELS analysis was used to study the relation between carbon and diamond phases. Carbon K edge in diamond with sp 3 hybridization of carbon atoms shows only the σ^* peak, but the same edge in graphite with sp² hybridization of carbon atoms includes both σ^* and π^* peaks (figure 2.11). This is used to determine the diamond to graphite ratio in the samples. However, it should be noted that the carbon bonds in graphite are anisotropic with the planar position of σ orbitals and π orbital perpendicular to them. Therefore, the relative intensity ratio between σ^* and π^* in graphite and the K edge shape strongly depends on the sample orientation. Operation in the specific set of convergence and collection angels, called magic angle condition (MAC) can cancel the anisotropic effect [301, 302]. These conditions are calculated for different beam energies considering the relativistic behavior of the electrons [301, 302]. In our experiment, we used a FEI Titan Themis microscope operating at 80 kV with an entrance aperture of 2.5 mm and a camera length of 115 mm. This condition corresponds to a convergence angle and collection semi-angle of 3.78 mrad and 5.1, respectively, and satisfies the MAC for our beam energy. Moreover, the MAC is tested on a highly oriented pyrolitic graphite (HOPG) sample to ensure the orientation independency of the carbon K edge. The data are acquired in the scanning TEM (STEM) mode through EELS mapping with dual channels to simultaneously record the low-loss and core-loss spectrum using a 0.1 eV/channel dispersion.

The K edge was then corrected with respect to the zero-loss peak and its background was subtracted by fitting a power function to the pre-edge spectrum. The peaks were then normalized to their integral. The graphite (S_{Gra}) and diamond (S_{Gra}) spectra from the known regions were used as a standard to fit the spectrum of each pixel (S_{px}) of the map as below:

$$S_{px} = k_1 S_{Gra} + k_2 S_{Dia} \tag{3.1}$$

Thus, the graphite/(graphite+diamond) (r_{Gra}) and diamond/(graphite+diamond) (r_{Dia}) ratios

Chapter 3. Diamonds and their inclusions from a Mars-sized planet



Figure 3.1: STEM DF and graphite-diamond map from EELS. The map is and RGB image, with red, green, blue corresponding to graphite ratio, zero, diamond ratio.

are given by $r_{Gra} = k_1/(k_1+k_2)$ and $r_{Dia} = k_2/(k_1+k_2)$. This has been demonstrated through RGB images with the red, green, and blue being equal to r_{Gra} , zero, and r_{Dia} , respectively. Figure 3.1 is an example of graphite-diamond maps.

3.2.3 Weak-beam imaging and electron diffraction

The weak-beam dark-field (WBDF) imaging technique is used to observe dislocations and stacking faults with a high contrast in the diamond matrix. In this technique, the crystal is first tilted to a systematic row two-beam (g reflection and direct beam) condition where the g reflection (from hkl planes) is in Bragg condition and excited. Then, the beam is slightly tilted to excite 3g reflection (in Bragg condition). In this setting, the g reflection is very weak because the corresponding planes in the crystal are not diffracting. However, these planes are bent in a narrow region in the deformation fields around the dislocation cores and stacking faults in a way that they satisfy the Bragg condition. Thus, by selecting the g reflection with the objective aperture, we can get dark field image where the matrix has dark contrast and crystalline fault are observed with sharp bright contrasts. Moreover, selected area electron diffraction (SAED) is used to identify the crystal structure of the phases. When the grain of interest was too small to be selected with the aperture, the nano-diffraction technique was employed. To do this, the smallest condenser aperture and highest spot size (smallest beam spot diameter) are selected in the nano-beam mode. The resulting beam is not exactly parallel, but the diffraction spots are sufficiently sharp for indexing. WBDF, electron diffraction, and TEM imaging were conducted on an FEI Tecnai Osiris machine operating at 200 kV.

3.2.4 STEM imaging and energy dispersive x-ray spectroscopy (EDX)

STEM imaging and EDX analysis were performed with a FEI Tecnai Osiris microscope with a beam accelerated at 200 kV. This microscope is powerful for chemical analysis due to its four window-less silicon drift (SSD) EDX detectors made by Bruker. The combined large effective area of these detectors substantially increases the count rate of detected x-ray photons, and therefore, improves the statistics and contrast. However, this geometry also induces shadowing

effects that might undermine the accuracy of the quantification results. This is particularly important for the measurements of the ratio between two elements with significantly different atomic numbers. In fact, the shadowing effect is more severe for lighter element (with lower x-ray energy). The simplest method suggested to overcome this problem consists of tilting the sample to face two of the detectors and to switch off the other two detectors [303]. We have acquired our data for EDX quantification with 2 detectors for a sample titled at 20 degrees. To test the condition a troilite (FeS) crystal in equilibrium with kamacite (Fe, Ni) was used. The crystalline structure of this phase had been identified by electron diffraction. The error in the Fe/S ratio was measured to be 4% which is acceptable for our analysis. The quantification was done with the Cliff-Lorimer method integrated in the Esprirt 1.9 software from Bruker.

3.2.5 Electron tomography

Tilt series of high angle annular dark field (HAADF) images were acquired from the diamond matrix including the inclusions. The camera length is adjusted to 91 mm and 58 mm in order to have a collection angle of lager than 63.8 and 100.1 mrad for HAADF detector which adequately reduces the contribution from diffraction contrast. Moreover, the convergence angle of the incident electron beam is set to 10 mrad to have acceptable depth of focus.

All the tilt series were obtained with the FEI Titan Themis microscope operating at 300 kV using a dual-axis tomography sample holder (Fischione model 2040). First series were collected in large magnification through tilting the specimen from -72 to 72 degrees with 2 degree increments. It was thus possible to clearly observe the faceted shapes of crystallites. However, the main objective of the electron tomography was to identify the inclusions that are completely inside the diamond matrix and are not cut by at the surface of the thin section. These inclusions are used to determine the bulk composition. Therefore, additional tilt-series were acquired in lower magnification between -54 and 54 degrees with the step size of 2 degrees. The reconstruction of the data is done with the Inspect 3D software from FEI. Then, the reconstructed data is visualized with Chimera software package.

3.3 Results and discussion

3.3.1 Graphitization of diamond

TEM studies show that diamonds in all five samples are highly deformed. This is evidenced by the high density of dislocations, stacking faults and twins throughout the diamond crystals (figure 3.2). Electron diffraction indicate that the stacking faults and twins are formed parallel to {111} planes (figure 3.2). The {111} twinning is typical of the face-centered cubic structure of diamond, and it has been observed to form during the growth (CVD) or deformation of both natural and synthetic diamonds [304, 305]. However, the morphology of these twins are distinct. The growth or annealing twins start and end at the grain boundaries between crystallites or at the junction with other twins. On the other hand, the deformation twins can



Figure 3.2: a) TEM BF image of a diamond grain oriented in the [110] zone axis. Dashed lines show the trace of {111} planes parallel to the zone axis. b) WBDF image of dislocations and {111} stacking faults in diamond. c) TEM DF image using the $(1\overline{11})$ plane reflection of deformation twins (indicated with orange circle in d). d) SAED of the [110] zone axis in diamond with indexed diamond reflection, and including the mirror reflections from twins.

start or end inside a crystal. The morphology of twinnings in our sample, as demonstrated in figures 3.2 and 3.3, can only result from deformation. Diamond is brittle at room temperature, and with increasing temperature plastic deformation begins mainly through mechanical twinning and dislocation glide. In general, high stress rate and concentration favors twinning over dislocation slide. The deformation of diamond in our samples, with large number of twins, is likely to have occurred during the shock event.

We have found large amounts of inclusions in the diamonds, and they are occasionally interacting with the crystal defects. The EELS analysis of the {111} twins in our samples show carbon sp³ hybridization identical to the diamond matrix. However, in many cases, when the twins are intersecting inclusions they are graphitized as shown by sp² hybridization. Figure 3.3 shows two {111} deformation twins formed in the same diamond crystallite. These twins have quite similar thicknesses and they are separated by only ~0.5 μ m. The one (twin 1 in figure 3.3) that cuts inclusions is graphitized and the other one (twin 2 in figure 3.3) is purely diamond. The graphitized region is distinguishable by a very high contrast in the bright field (BF) image. The dark field imaging using the (111) reflection of the twin crystals indicates that the graphitization starts close to the inclusions, and the twin has usual propagation in the matrix before the intersection. Moreover, as we can see in the graphite-diamond map, the graphite keeps the morphology of the parent twin (figure 3.3). Because of the lower density of



Figure 3.3: a) TEM BF image of the diamond grain oriented in the [110] zone axis shows two twins indicated as "1" and "2". The orange arrows in all panels show the inclusions intersecting with twin 1. The graphitized region along this twin has very bright contrast in BF image. b) TEM DF image using the (111) plane reflection of twins. Twin 1 transformed to graphite. C) STEM HAADF image of twinning regions. Green dashed rectangle indicates the EELS mapping region for d. d) Graphite-diamond map from EELS.

graphite than that of diamond, graphitization is accompanied by a volume increase which generates substantial strain in the diamond crystal. For a graphitized layer in figure 3.3, with a thickness of ~100 nm, ~1 degree of misorientation is measured between two sides of the layer in the same diamond crystal.

Figure 3.4 shows an inclusion close to the diamond/graphite boundary. This inclusion has been sliced by {111} twins. The graphite-diamond map shows that diamond has been graphitized around the inclusion, whereas the region next to it is untransformed (figure 3.4). This clearly reveals that the diamond and its inclusion were present before deformation and graphitization.

Another affirmation for graphitization of diamond can be obtained from the distribution of the inclusions. Although there are isolated inclusions in the diamond matrix, most of them are arranged in tails (figure 3.5). This morphology has been observed in three samples. One of these samples consists of several diamond fragments with close crystalline orientation, separated by graphite bands (figure 3.4). In this sample the inclusion tails stretch in a diamond fragment until they reach the graphite band where they disappear. They appear again on the same course and direction in the next diamond fragment. This is also a strong evidence that

Chapter 3. Diamonds and their inclusions from a Mars-sized planet



Figure 3.4: An inclusion at a diamond/graphite boundary that has been cut in slices by twins. The direction of the cut is shown by a dashed line. The graphite-diamond map from EELS indicates graphitization around the inclusion.

a single large diamond crystallite with the inclusion tails existed before fragmentation and graphitization.

The diamond graphite boundaries in our samples show a kinked structure, in which the segments are parallel to the {111} planes. This can be seen in figure 3.4 and 3.6. Likewise, although the graphitized parts inside the diamond can have arbitrary shapes, they often keep the morphology of {111} twins. This suggests a similarity for the formation of large graphitic regions and the graphitization of the diamond. In figure 3.6 there is a small diamond grain that has been separated by a graphitic region and it has \sim 2.5 degrees of misorientation with respect to the large diamond grain. Thus, the small grain is likely a separated fragment of the large grain. Since this graphite band separating these two diamond is part of a larger graphitic region (figure 3.6), it seems that graphitization was strong enough to transform few micrometers of diamond.

There are two main mechanisms for graphitization of diamond. The first one is through temperature increase at ambient pressure (or low pressures). Graphite is the stable phase of carbon at ambient condition. However, diamond is metastable and will not transform at room temperature. By increasing the temperature graphitization starts around inclusions and on the diamond surface where nucleation requires less energy [306, 307]. The other mechanism is through high stress rate which induces the transformation of diamond into unoriented graphite [308, 309]. This transformation takes place due to shock-induced instabilities in the diamond lattice that breaks the sp³ bonds and it is highly anisotropic [308]. The required shear stress for this type of graphitization can, thus, vary greatly depending applied stress direction [308, 310]. Although the first principle calculations predict the necessary stress for



Figure 3.5: HAADF image of diamond grain broken to smaller fragments in the left. Yellow dashed line are the graphite and diamond boundary. HAADF image of inclusion veins (red dashed line) cut by graphite band from the region indicated with green dashed rectangle in the left images.

this transformation to be the ideal shear strength of the diamond, namely ~95 GPa [308], He et al. (2002) observed graphitization even at ~50 GPa which was the lowest pressure in their shock experiments [309]. Interestingly, for both mechanisms, graphitization preferentially begins at the {111} planes of diamond. The shock degree of the Almahata Sitta MS-170 meteorite is estimated to be S3 based on the morphology of olivine grains which corresponds to a pressure below 20 GPa. In our samples, there has been no sign of graphitization in the diamond matrix where there are no inclusions. In fact, all the graphitic material that is present in the samples are also full of the inclusions. This means that the shear stress of the shock event alone is not responsible for the graphitization. On the other hand, the observation of graphitization along the twins intersecting the inclusions indicates that the shear played and important role in the phase transformation. Therefore, we suggest that graphitization was the result of the stress concentration around the inclusions. This mechanism could have been assisted by elevated temperatures and by the phase transformation of the inclusions which will be discussed in the later sections of this chapter.

3.3.2 Comparison with shock-induced diamond formation

The grain size of diamonds were not statistically measured in our studies. However, the diameter of diamond segments used for sample preparation always exceeded 10 μ m. Moreover, Miyahara et al. (2016) using electron backscattered diffraction (EBSD) showed that the diamond segments (up to ~20 μ m in diameter) separated by graphite bands have close orientation and, together, they are making assemblages up to 100 μ m in diameter [147]. They have concluded that these large diamonds are broken into smaller fragments through graphitization. Our observations, as discussed in the previous section, confirms their conclusions.



Figure 3.6: TEM BF image of the diamond oriented in [110] zone axis indicates diamondgraphite grain boundary with a kinked step-like shape. The grain boundary stays parallel to 111 planes of diamond. Dashed lines indicate the trace of 111 planes parallel to the zone axis. We can also see a separated small diamond grain in the left which has ~40 mrad (~2.3 degree) misorientation with respect to the main grain.

In contrast, the diamond crystallites in ureilites reported in literature are up to a few tens of nanometer in size [144, 311]. Therefore, there are two distinct types of diamonds in ureilite meteorites that can be formed through different mechanisms.

The diamond grains reported in the original study by Lipschutz (1964) had an average size of 10-30 nm [144], and the reasoning for shock-induced transformation of graphite to diamond based on their texture does not hold for the large diamonds observed in our samples. On the other hand, the hexagonal diamond (lonsdaleite) has not been seen in our study. Also, the lonsdaleite has not been made separately from cubic diamond and its existence is still controversial. In fact, Németh et al. (2014) showed that the presence of {113} twins and {111} stacking fault in the shock-deformed meteoritic or synthetic diamonds can give rise to features that have been often misinterpreted as lonsdaleite [312]. Another important evidence for shock transformation of graphite to diamond is the presence of compressed graphite. However, the compressed graphite might also form from the graphitization of diamond. In any case, most of the studies supporting a shock origin of diamond in ureilites have only considered samples with nanometric diamond crystallites and cannot be easily extended to the large diamonds we have studied.

Shock durations in laboratory experiments last up to few microsecond, but for natural impacts in the Solar System, they range from milliseconds to few seconds for large objects [314]. This duration is not long enough to grow a 100 μ m diamond crystal. Indeed, the grain sizes reported for the shock produced diamonds are of the order of a few nanometers up to a few tens of nanometers [311, 313, 315]. Natural diamond aggregates can reach up to several



Figure 3.7: a) optical image and b) TEM BF image of the diamond aggregates from Popigai craters. The crystallite size of these shock-induced diamonds are below 50 nm. After [313].

hundreds of micron in diameter in the exceptional cases such as in the Ries and Popigai craters (figure 3.7), where the graphitic precursor and its shock-induced transformation to diamond is known. Nevertheless, the size of individual diamond crystallites is never greater than ~150 nm (figure 3.7) [313, 315, 316]. Moreover, it is noteworthy here that the mere existence of diamond inclusions is not consistent with the formation of diamond by shock, because the encapsulation of mineral grains is unlikely to occur in the short duration of the shock event. This reasoning is also true for the CVD diamond growth, where the crystallite sizes are limited to below 10 nm [317].

As a consequence, the only mechanism left for the the origin of diamonds of this size in ureilite, is the growth of diamond at the high-pressure and high-temperature conditions inside the UPB. According to the carbon phase diagram, the minimum pressure required for diamond formation is ~2 GPa [318, 319]. Hence, considering the diamond formation at the core-mantle boundary, the UPB should have been at least ~1000 km in diameter [147].

3.3.3 Diamond inclusions

Diamonds are the hardest known natural materials. Due to their high mechanical, chemical, and thermal stability, diamonds act as capsules that entrap and preserve materials from their growth environment as inclusion. Since natural diamonds are often formed at static high pressures deep inside the Earth, inclusions can provide information about the depth and conditions of their crystallization as well as the mineralogy and composition of the Earth interiors [320, 321]. In fact, these inclusions are the only direct samples from the depths of over few hundreds of kilometers inside the Earth. Thus, they are very precious subject of studies in Earth sciences. The same role could be given to the inclusions in the extraterrestrial diamonds. However, inclusion have been never found before in the meteoritic diamonds. This is mainly



Figure 3.8: HAADF image and Fe-S EDX map of Fe-S type inclusion in the diamond matrix. Kamacite and troilite are shown as light blue and reddish-pink, respectively (from the EDX coloring of Fe as blue and S as red). In c) the P is also added which shows the shreibersite phase.

because of the shock-induced origin of most of the diamonds reported in the literature. Even if some samples included pristine diamonds, they were never reported. Shock diamonds are too small and formed in a time too short to expect the inclusions inside them. Another reason is that the recently developed powerful characterization instruments and techniques were not previously available.

In this work, we have observed diamond inclusions in all five prepared TEM specimens from Almahata Sitta MS-170. These inclusions were structurally and chemically characterized by electron diffraction and EDX spectroscopy. Three different types of inclusions have been detected, all of which have euhedral shapes indicating that they were trapped inside the diamond as solid phases rather than liquids. The overwhelming majority of these inclusions have a Fe-S composition (figure 3.8). This type of inclusions can be found as isolated grains with sizes up to a few hundreds of nanometers. However, they are mostly observed in the vein-like trails of small particles with sizes ranging from \sim 60 nm down to few nanometers. The other two types of inclusions are chromite with grain sizes of a few hundreds of nanometers and phosphate that are \sim 20 nm or smaller (figure 3.14). These last two types of inclusions are rare and only few of them have been found in our samples. The detailed characteristic of the inclusions is discussed below.

Fe-S type inclusions

The Fe-S inclusions have complex chemistry and they show signs of breakdown to low-pressure phases similar to the high-pressure mineral inclusions in deep terrestrial diamonds [320] (figure 3.8). Each Fe-S inclusion consists of three phases, namely: kamacite (Fe, Ni), troilite (FeS), and minor schreibersite ((Fe,Ni)₃P) (figures 3.8 and 3.9). The metallic phase is an iron phase with an average nickel content of 5.4 (\pm 1.5) atomic% (table 3.1). Electron nano-



Figure 3.9: HAADF image and Fe-S, P, Ni, and Cr EDX maps of Fe-S type inclusion in the diamond matrix. In small inclusions, such as this one, shreibersite is seen as the P enrichment in the grain boundaries.



Figure 3.10: Electron diffraction patterns from zone axes in the chromite, troilite, and kamacite structures.

diffraction confirms the body-centered cubic (BCC) structure of this phase that is attributed to kamacite (figure 3.10). The sulfide phase has an Fe/S ratio equal to 1.03 (\pm 0.01) and electron diffraction indicates that it is troilite (table 3.1 and figure 3.10). Schreibersite is too small and always overlapping with the other two phases. Thus, we could not verify its structure with electron diffraction. However, its composition, as indicated in table 3.1, agrees with (Fe,Ni)₃P. This phase can be easily distinguished in the relatively large grains (figure 3.8c), but in the small grains we can see it only as a P (and Ni) enrichment at the boundaries (figure 3.9). Chromium is also detected in the composition of the inclusions and it segregates to the grain boundaries (figure 3.9). Nevertheless, the total Cr content of the inclusion (<0.3 atomic%) is below the accuracy of our measurement, and therefore, it is negligible (table 3.1).

In this study, more than 100 inclusions have been qualitatively examined by EDX and kamacite, troilite, or schreibersite have never been found as isolated mono-mineralic inclusions in diamond (figure 3.8). Moreover, they were always together inside a polyhedral grain with sharp facets. These arguments stand for the entrapment of the inclusions as a single phase mineral crystallite that has later undergone chemical dissociation. This parent phase should be a high pressure iron-sulfide that is richer in iron than troilite. There are two iron-rich sulfide that form at high pressure, namely: F_3S_2 and F_3S . These phases have been synthesized by Fei et al. (1997 and 2000) at pressures above 14 GPa and 21 GPa, respectively [322, 323]. To identify the parent phase, we need to know the total composition of individual inclusions. However, most of this inclusions could have been cut during the TEM section preparation in

Table 3.1: Composition of phases in the Fe-S type inclusions as well as the total composition of these inclusions (indicated as $(Fe,Ni)_3(S,P)$ phase) obtained from the complete inclusions. The error are given as standard deviation. The Cr and P composition in the troilite or Cr composition in total inclusions ((Fe,Ni)_3(S,P) phase) are written in parentheses because their existence and exact concentration in these phases are precise enough from the measurements.

Phase	Fe	Ni	S	Р	Cr
Kamacite	94.6 (±1.5)	5.4 (±1.5)	-	-	-
Troilite	50.7 (±0.3)	-	49.3 (±0.3)	(<0.7)	(<0.2)
Schreibersite	52.9 (±0.8)	22.1 (±0.3)	-	$25.0(\pm 0.5)$	-
$(Fe,Ni)_3(S,P)$	69.6 (±2.7)	5.1 (±0.8)	22.2 (±2.2)	3.1 (±0.7)	(<0.3)



Figure 3.11: The plot show the formation pressure of $Fe_3(S, P)$ phase versus the P/(S+P) molar ratio. When this ratio is below 0.2, the $Fe_3(S, P)$ forms only above 21 GPa. Replotted after [325].

one surface or both surfaces of the sample. Thus, tilt-series of HAADF images are acquired from the inclusions in several regions and we used electron tomography to identify intact inclusions in the diamond matrix. Then, the composition of these inclusions are obtained by EDX. The average value of (Fe+Ni)/(S+P) molar ratio measured for 30 inclusion is 2.98 (± 0.36) (table 3.1). This confirms that the inclusions have a parent phase with a stoichiometric (Fe, Ni)₃(S, P). It is noteworthy that the the $(Fe,Ni)_3P$ -schreibersite and Fe₃S phases have the same space group (tetragonal I4). Also, their lattice parameters are very close. Hence, at high pressures, they can form (Fe, Ni)₃(S, P) solid solution across the entire compositional S-P joint [323, 324].

The Fe₃S phase is table above 21 GPa to at least 80 GPa [323, 326], whereas the (Fe,Ni)₃P-schreibersite phase is stable from ambient pressure to at least 50 GPa [324]. Thus, the formation pressure and stability of Fe₃(S, P) solid solution depends on the concentration of phosphorous in this phase. Gu et al. (2006) demonstrated that the lower pressure limit for the formation of this phase increases with the decrease the P/(S+P) ratio according to figure



Figure 3.12: HAADF image and Fe-S EDX map from diamond and graphite. Note the morphology pf inclusions in the diamond and graphite. The arbitrary shape on inclusions and chemical separation to Fe-rich and S-rich region is a sign of melting.

3.11 [325]. Nevertheless, for P/(S+P) smaller than 0.2 molar ratio, the Fe₃(S, P) phase forms only above 21 GPa (figure 3.11)[325]. This ratio for the inclusion in our samples is 0.12 (\pm 0.02) (table 3.1). The Ni₃S phase forms above 5.1 GPa, and therefore, the nickel content can affect the formation pressure of (Fe, Ni)₃(S, P) solid solution [327]. However, the Ni/(Fe+Ni) molar ratio in the inclusions is 0.07 (\pm 0.01), and the possible effect of such a small amount of Ni is negligible (table 3.1). Therefore, we deduce that the (Fe, Ni)₃(S, P) inclusions are formed above 21 GPa.

Inclusions in graphite and dissociation of (Fe, Ni)₃(S, P)

In contrast to the polyhedral shapes and the homogeneous bulk composition of inclusions in diamond that indicates their origin as uniform single crystalline grains, their morphology in the adjacent graphite bands shows the signs of melting. As shown in figure 3.12, the inclusions in graphitic materials are forming S- and Fe- bearing phases of varying compositions and arbitrary shapes that are dispersed in the graphitized area. This often includes separated regions of Fe-rich and S-rich phases. In figure 3.13, graphitization took place around an inclusion. The shape of the inclusion inside the graphitized region is curved and spread. Moreover, EDX analysis show that the Fe-S-containing material has diffused inside the graphite (figure 3.13). These features attest the melting of inclusions at the same time of or after the graphitization, and is yet another evidence the graphitization to take place after the diamond formation. The most likely event responsible for the melting of the inclusions is a shock event after diamond crystallization. The melting usually involves some volume change that increases the stress concentration around the inclusions and assist the graphitization in these regions.



Figure 3.13: STEM BF and Fe-S EDX map from an inclusion in the graphitized region. The edge of inclusion in the diamond part is still sharp, whereas the other part in graphite is rounded. The green arrows show this rounded region as well as the Fe-S materials distribution in the graphitized area.

In addition, melting provides a convincing explanation for the dissociation of the parent (Fe, Ni)₃(S, P) phase. The liquid with this composition will crystallize as kamacite, troilite and schreibersite at low pressure, while the inclusions, still confined in diamond matrix, will preserve their original polyhedral shape. The temperature for melting should have reached the Fe-S eutectic temperature (~1250 K at ambient pressure[111]). Also, The absence of a F_3S_2 phase indicates that the crystallization after melting occurred at pressures below ~14 GPa[322].

Chromite and phosphate inclusions

The chromite Cr_2FeO_4 has the composition: 64 atomic% Cr, 33.4 atomic% Fe, 1.8 atomic% Zn, and 0.8 atomic% V (oxygen is excluded from quantification because of its low atomic number). Electron diffraction shows that it has a spinel structure, in which Cr^{3+} and Fe^{2+} occupy the octahedral and tetrahedral sites, respectively. Zinc and vanadium are commonly found in the chromite composition where they substitute in the tetrahedral site (like zincochromite Cr_2ZnO_4) and the octahedral site (like coulsonite V_2FeO_4) of the spinel structure, respectively. The deviation of $(Cr+V)/(Fe+Zn) \approx 1.85$ ratio from the stoichiometric value of 2 could arise from the EDX quantification errors or the presence of Fe^{3+} in the composition which substitutes the Cr^{3+} in the octahedral sites of spinel structure (like magnetite Fe_3O_4). Chromite, similar to other spinel minerals, transforms to other polymorphs at high pressures [328, 329, 330]. The exact pressure of phase transformations strongly depends on the composition. According to the phase diagram obtained by Ishi et al. (2014), the spinel Cr_2FeO_4 -chromite will transform to a $CaFe_2O_4$ -type (CF-type) structure above ~18 GPa in the temperature range of about 1050-1550 K [330]. If the chromite is formed at the same condition as the Fe-S inclusions (above



Figure 3.14: HAADF image and Fe, Cr, P, and Ca EDX maps from chromite and phosphate inclusions. . The slight bright contrast of P and Ca EDX maps in the chromite grain is the result of high background counts in that region and there is no actual P or Ca peak in chromite spectrum.

21 GPa), it is expected to have a CF-type structure. The CF-type phase is not quenchable and it transforms to a modified CF-type structure upon quench [330]. However, the diamonds and inclusions in these sample are annealed at above 1250 K temperature and below 14 GPa pressure, which is in the stability field of spinel. Thus, even if the chromite originally had CF-type structure, it would transform to spinel when the Fe-S inclusions have melted (figure 3.10).

Chromite is a common mineral found in various families of meteorites. They often have Mg^{2+} and Al^{3+} in their composition substituting for Fe^{2+} and Cr^{3+} , respectively. The chromites in ureilite samples have the Fe/(Fe+Mg) molar ratio ranging from ~0 to ~0.6 and Al/(Al+Cr) molar ratio ranging from ~0.5 to~0.8 [331]. On the other hand, the chromites found in pallasites (iron-stony meteorites) are richer in iron and the Fe/(Fe+Mg) ratio can reach ~0.85 [332, 333]. The Al concentration in the pallasite chromites is low [332, 333]. However, the iron-rich and Mg-free end member of the chromite composition, similar to the chromite inclusions in this study, is only observed in iron meteorites [333, 334, 335]. It has been suggested that these chromites form from a metallic liquid close to the Fe-FeS joint with low Cr and O concentration [336]. This indicates that the chromite inclusions in the studied diamonds are crystallized in an iron-rich environment without interaction with silicates.

The phosphate inclusions are only examined with qualitative EDX because of their small size (<20 nm) and their overlapping with the other phases (figure 3.14). The few phosphate inclusions observed in the sample are Ca-Fe phosphates, but their compositions are not the same. Some of the phosphate inclusions are also rich in Na and contain low concentration of K. Although we could not exactly identify the mineralogy of these inclusions, the phosphates in this range of compositions are often found in iron meteorites, where they are common



Figure 3.15: Fe-C binary phase diagram at ambient pressure and Fe-S binary phase diagram at 21 GPa. Orange color in Fe-C diagram shows the composition range where graphite is the first liquidus phase. Graphite will be replaced by diamond at higher pressures. In the Fe-S phase diagram orange color shows the composition range where Fe₃S is the first liquidus phase. After [338] and [323].

companion of chromites [337].

3.3.4 Formation of diamonds in UPB

Warren et al. (2006) noted the abundance of highly siderophile elements in ureilites and showed that the differentiation started with the segregation of S-rich metallic liquid (close to Fe-S eutectic composition) at the eutectic temperature of the Fe-S binary system (1250 K at ambient pressure, 1350 K at 21 GPa) [125]. The S-rich iron liquid percolates to form a core even when its volume fraction is small (5 vol%) [17]. The S-rich core formation in UPB has also been confirmed by Barrat et al. (2015) [127], but no samples of the core have been found. The temperature was increased in the UPB to melt about 20-30 vol% of the silicate too. However, the temperature increase did not continue enough to induce an efficient separation of iron. Fe₃S is the S-rich eutectic phase in the Fe-S phase diagram above 21 GPa and its composition is close to the eutectic point (figure 3.15) [323]. Moreover, the Mg-free chromite inclusions can only crystallize in a very Fe-rich environment (and likely a Fe-S melt) where there is no Mg to substitute fro iron. Thus, the composition of inclusions suggests that they have formed from a segregated Fe-S melt in the UPB either at the core-mantle boundary or before the melt reached the core.

The Fe-C binary system has also a eutectic point in the Fe-rich side of the phase diagram (figure 3.15) [338]. One of the eutectic phases in this system is metallic iron. The other stable eutectic phase is graphite or diamond (figure 3.15) that can be replaced with metastable iron-carbides (Fe₃C or Fe₇C₃) under the experimental conditions [338]. The eutectic temperature in this system is about ~ 1400 K [338], which is close to the solidus temperature of silicates [112]. Hence, for a carbon-rich body like the UPB, we can expect the formation of a Fe-C



Figure 3.16: Low magnification STEM BF image of a TEM section and high magnification HAADF image from the inclusion vein indicated by green rectangle in the BF image.

liquid. Fe-C and Fe-S liquids are immiscible at ambient pressure and will thus separate to S-rich and C-rich metallic liquids [339, 340, 341]. However, this miscibility gap closes through increasing the pressure above 4-6 GPa (depending on the composition), and they form a single Fe-S-C melt [339, 340, 341]. It has been shown that diamonds can crystallize from this liquid [321, 342, 343]. In fact, a recent study by Smith et al. (2016) found Fe-Ni-S-C inclusions in large terrestrial diamond that were trapped as a liquid, and concluded that these diamonds were formed from a Fe-S-C melt (with low concentration of Ni and P) [321]. At constant temperature, diamonds can crystallize from the Fe-S-C liquid through dissolution of supersaturated carbon or by increasing the S content of the melt that decreases the C solubility. On the other hand, diamonds can also form by decreasing the temperature below liquidus in the C-rich side of Fe-C eutectic where the diamond is the first liquidus phase at high pressures (figure 3.15) [338, 339]. In addition, considering that Fe_3S and diamond are the first crystallizing phases from the liquid on the Fe-poor side of their respective eutectic points in the Fe-S and Fe-C systems above 21 GPa (figure 3.15), there can be a three phase region in the Fe-S-C ternary diagram where these two solid phases are in equilibrium with the liquid. The Fe-S-C system has been studied only up to 20 GPa [339], and the possibility of simultaneous crystallization of Fe₃S and diamond requires further experimental investigations.

The evidence for crystallization of diamond and inclusions from a melt comes from the distribution of Fe-S inclusions in the sample. All the diamond have Fe-S inclusions, which shows that the Fe-S material was present everywhere in the carbonaceous materials. This is unlikely to happen with the diffusion of the Fe-S materials into solid graphite or diamond. More importantly, the localization of the inclusions is not uniform and they are mostly arranged in vein-like trails (figure 3.16). The vein morphology is an indication for the presence of the melt (figure 3.16). Consequently, we suggest that the diamonds and their inclusions are formed from an Fe-S-C melt (with small Ni and P content) below the liquidus where both Fe₃S and diamond crystallize together from the liquid.

3.3.5 Implication for the size and formation of the UPB

Previous size estimates for UPB varies from a few hundreds of kilometers up to ~700 km [118, 126]. In a recent study, Miyahara et al. (2016) estimated the lower size limit to be 1000 km in diameter considering the formation of large diamonds [147]. Here, we conclude that the inclusions can only form above 21 GPa, which implies a significantly larger body than in previous estimates. Assuming the diamond formation at the core-mantle boundary of the UPB, its size should be about that of Mars to exert the required pressure. Even if we assume 21 GPa to be the pressure at the center of the parent body, the lower limit of the size of the UPB should be about that of Mercury.

Although this is the first physical compelling evidence for such a large body, their existence in the inner Solar System has been predicted both in classical and modern planetary formation models [41]. Runaway and oligarchic growth of planetesimals resulted in the formation of Moon- to Mars- sized protoplanets, called planetary embryos, in about 10⁵ to 10⁶ years [41, 43, 47]. The terrestrial planets are formed later through the accretion of these protoplanets [41]. Nevertheless, not all the protoplanets accreted into planets. Indeed, in the classical model, some of these large objects, located in the asteroid belt, are excited by the fast growing Jupiter and got ejected from the Solar System or absorbed by the Sun [70]. On the other hand, in the modern "Grand Tack" scenario, these object are excited and cleared out of the asteroid belt through the migration of Jupiter toward the Sun [81]. Mars is believed to be a planetary embryo that has survived in the Solar System [344]. Also, Mercury was, probably, about the same size if its had had an initial composition close to that of the other terrestrial planets [344]. Another Mars-sized object, based on the simulations, could be the moon-forming giant impactor "Theia" [156]. Thus, the Mars-sized objects were common in the first few million years of the Solar System [344, 345]. Our results indicate that the diamonds and their inclusions could have formed in a Mars-sized planetary body. Ureilite meteorites are the surviving fragments of the UPB in the Solar System after its collision with planetary objects. This collision was likely a cataclysmic event that destroyed the UPB.

3.4 Conclusion

We have studied diamonds in the Almahata Sitta MS-170 ureilite meteorite. They showed a high density of crystalline defects, especially {111} twins, as a result of shock deformation. Moreover, these twins are occasionally graphitized upon intersection with diamond inclusions. Morphological features of the graphite bands and inclusions in the diamond crystallites, argue for a shock-induced graphitization of diamonds. On the other hand, large sizes of diamonds observed in this sample exclude the formation of diamond through shock-induced mechanisms. Therefore, the diamond are pristine and formed inside the UPB.

We have found three types of inclusions in the diamonds, namely: Fe-S type, chromite, and phosphates. Most of the inclusions were from the Fe-S type, and each inclusion consists of kamacite, troilite, and schreibersite phases. The well-defined polyhedral shape and uniform



Figure 3.17: Schematic summary of the formation of diamond and Fe_3 inclusions from the melt inside the UPB. Diamonds have been fragmented by graphitization during the shock event. Also, the inclusions are molten as a result of shock-induced temperature increase, and then crystallized as Fe and FeS at low pressure.

total composition of individual inclusions suggest that they formed as a single solid crystalline phase at high pressure and trapped inside the diamond. These inclusions have later decomposed into three phases likely as a result of shock-induced temperature increase. The parent phase is determined as $(Fe_{0.93}, Ni_{0.07})_3(S_{0.88}, P_{0.12})$ with EDX analysis. This phase can only form above 21 GPa. For the UPB to generate such a pressure at its core-mantle boundary, it has to be at least about the size of Mars. This agrees with the typical size range estimated for the planetary embryos that were populating the early inner Solar System.

Moreover, the existence of Fe-rich chromite end-member together with phosphate inclusions, similar to those found in the iron meteorites, point to the formation of diamonds and inclusion from a metallic melt. In addition, the arrangement of the Fe-S inclusion in a vein-like morphology attest to the presence of a melt during their formation. Therefore, it is proposed that the diamond and inclusions have crystallized from a Fe-S-C melt with small amounts of Ni and P. This idea is compatible with the segregation of a Fe-S core in the UPB. The complete scenario has been schematically shown in figure 3.17.

4 3D analytical investigation of melting in lower mantle conditions

4.1 Introduction

Earth, as other terrestrial planets, went through giant impacts during its growth [41]. Such an impact between the proto-Earth and a Mars-sized object is believed to be at the origin of the Moon formation [230, 155]. Previous studies have shown that the mantle was extensively or completely molten as a result of a giant impact which is also advocated to explain the core formation of the Earth as well as the similar isotopic composition between the Earth and the Moon [346]. The solidification and fractional crystallization of the resulting magma ocean has tremendous effects on the chemical distribution of elements in the Earth. Moreover, greater S-wave velocity decrease (up to \sim 30%) compared to P-wave velocity decrease (up to \sim 10%) is taken as an evidence for the presence of melt in the ultra low-velocity zones (ULVZs) just at the bottom of the mantle in present days [245, 347]. Depending on the melt geometry, 5-30 vol% of partial melt is suggested to explain the seismic velocity drop in these deep and dense regions [245, 347]. The possible partial melting at the core-mantle boundary (CMB) depends on the solidus temperature of the mantle materials and the CMB temperature. The solidus temperature of peridotite and chondritic primitive mantle composition is reported to be ~4150 K (±150) using the x-ray diffraction to determine the onset of melting [250, 348]. The CMB temperature based on the melting temperature of iron in the outer core, considering the depression of this temperature due to the alloying with light elements, is estimated to be ~4000 K (\pm 500), close to the temperature allowing low degree of partial melting of the mantle rocks [349, 350]. Other studies have suggested subducted basalts could partially melt at CMB due to a lower solidus temperature, measured to be ~3800-4000 K at corresponding pressure (~135 GPa) [252, 351]. However, more recent experiments on pyrolitic composition showed lower solidus temperature of 3570 K (±200) using textural and chemical analysis of the quenched samples to determine the onset of melting [352]. This also implies lower CMB temperature since there is no extensive melting in this region [352]. The variability in the measurements of mantle solidus temperature and CMB temperature mainly arises from the melting criteria for low degree of partial melting and from the uncertainty in the nature and content of light elements in the outer core, respectively. To conclude, the likelihood of partial

Chapter 4. 3D analytical investigation of melting in lower mantle conditions



Figure 4.1: Schematic view of Earth in the basal magma ocean scenario. The mantle is fully molten after the giant impact, and solidification starts from the middle of mantle upward. The basal magma ocean solidifies slowly and the residual iron-rich melt or iron-rich crystals remain at the bottom of the mantle to form the ULVZs.

melting in the CMB is still a matter of debate. On the other hand, seismic data collected from the ULVZs could also be explained by dense solid phases without the requirement of partial melting [246]. Iron-rich phases, post-perovskite or magnesiowüstite, have been suggested to be present in the ULVZs [247, 248].

Labrosse et al. (2007) starting from the close temperatures estimated for CMB and the mantle solidus, together with the core evolution and the amount of cooling required to preserve geodynamo through the Earth history, suggested that a ~1000 km thick melt layer, called basal magma ocean, existed at the bottom of mantle (figure 4.1). This layer has was slowly crystallized after the upper parts of the mantle (figure 4.1[249]). This was supported by the demonstration of steeper isentropic temperature for magma at high pressure than the liquidus temperature [353]. This implies a middle up solidification of the magma ocean (figure 4.1) contrary to previous models which relate to bottom up solidification. As a consequence, the melt at the base of the mantle progressively enriched in iron due the fractional crystallization of the basal magma ocean. This could explain the nature of ULVZs by the preservation of iron-rich melt or by the presence of iron-rich minerals crystallized from the melt at the CMB (figure 4.1).

The gravitational stability of melt at the bottom of the mantle in the basal magma ocean scenario as well as in the partial melting scenario will depend on the density difference between the solid and the melt. Several experimental and computational studies have shown that the volume change during melting of silicates decreases with increasing pressure. At CMB condition the MgSiO₃ crystals (either bridgmanite or post-perovskite as the first liquidus phase) are only slightly denser than the melt (1.6-4%) [353, 354, 355, 356]. Therefore, the density relation between the solid and the liquid phase will be determined only by chemistry, particularly by the partitioning of iron. Nomura et al. (2011) and Tateno et al. (2014) showed strong incorporation of iron in the melt [288, 357]. This supports the gravitational stability

of the melt at the lowermost mantle. On the other hand, Andrault et al. (2012) measured higher partitioning of iron into the bridgmanite phase and concluded that iron partitioning is not strong enough to make the melt denser than the solid at CMB conditions [251].

To further study the possible existence and crystallization of a basal magma ocean, the chemical evolution of the melt should be considered in more details. This has been studied through simulation [358], but we still lack the experimental demonstration of melting and subsequent fractional crystallization in lower mantle conditions. In this study, San Carlos olivine with the simple composition of (Mg, Fe)₂SiO₄ is used as mantle analogue. Olivine breaks down to ferropericlase and bridgmanite phases above ~23 GPa similar to more complex mantle composition. We have conducted melting experiments in diamond anvil cell (DAC) and followed the evolution of melt during fractional crystallization by changing the heating time from 1 to 6 minutes at 45 GPa. The change in the temperature profile and gradient in the course of laser heating with time will lead to a chemical evolution of the melt. Such a scenario is schematically shown in figure 4.2, where the peak temperature is constant but the profile changes and becomes narrower with increasing heating time. This narrowing induces crystallization in the molten part of the sample.

We have also heated two samples at 30 GPa and 71 GPa for ~3 minutes to investigate the pressure effects on melting in the DAC. Most importantly, for the first time, dual beam (ion and electron) system in combination with transmission electron microscopy (TEM) is used to obtain both 3D model and high resolution chemical analysis of melting in laser-heated diamond anvil cell (LH-DAC).

4.2 Methods

4.2.1 High pressure and high temperature experiments

Diamond anvil cells with the culet size of 300 μ m were used in this study. Re gaskets were indented at around 20 GPa to obtain a flat surface with a thickness of ~40 μ m. The pressure during the pre-indentation was determined by ruby fluorescence spectrum. A circular hole with ~120 um diameter was then drilled with a laser in the center of the indentation mark to be used as the sample chamber.

Sample chamber was loaded with San Carlos olivine powder. San Carlos olivine was selected as the starting material because not only it has a similar composition to the inner mantle of the Earth but also it has been widely studied before. Diamond anvil cells were then closed and the pressure was increased to the desired value. To avoid any contamination from the ruby chips we did not use them and, instead, the pressure was measured by the shift of the Raman spectra of diamond at center of the culet [270]. Samples are heated with a Nd:YAG near infrared laser beam through the diamonds either from one side or from both sides. Three samples are melted at ~45 GPa for 1, 3 and 6 minutes by double-sided heating to investigate the effect of heating time on the final morphology and chemical distribution in the samples.





Figure 4.2: The image shows the effect of possible changes in the temperature profile in the sample during laser heating. The molten region of the sample consists of a liquid phase and the first liquidus crystals. Due to the variation in the temperature gradient with increasing the time the liquid phase starts to crystallize.

Two other samples were heated from both sides for ~3 minutes at 31 GPa and 70 GPa to study the effect of pressure. One additional sample was single-side heated at 45 GPa for ~3 minutes to compare the single-sided and double-sided laser heating methods. All the samples were melted at about 3000-3500 K. Pressure was released slowly after quench to recover the samples for characterization.

4.2.2 3D EDX acquisition and analysis

For the first series of samples (three samples: 45 GPa heated for 6 minutes and 3 minutes both single-sided and double-sided), gaskets were extracted and directly glued to scanning electron microscope (SEM) sample holders with carbon paste. The holder was bent before inserting into the focused ion beam (FIB) instrument to avoid shadowing caused by diamond trace on the Re gasket. This process resulted in a too complex geometry of the sample and the shadowing could not be completely removed. Hence, for the rest of the samples the thin pre-indented part of the gasket was cut out with the laser drilling system and then stuck on a GaAs substrate with a conductive glue. Consequently, the GaAs substrate was glued to the SEM sample holder with carbon paste. Zeiss NVision 40 and Zeiss X540 dual beam instrument (FIB/SEM) were used in this study. Both instruments are equipped with Oxford Instruments energy dispersive X-ray (EDX) detector. Sample was brought up to the crossbeam level and tilted to be perpendicular to the ion beam. The interested area of the sample was initially coated with Pt. After milling the correction lines, the Pt coating was covered with a carbon



Figure 4.3: The elemental intensity maps obtained from SEM EDX are combined into RGB images using Fe, Si, and Mg maps as red, green and blue channels respectively. Also, the volume of the studied region is rendered using these maps, which shows the 3D model of Mg-rich, Fe-rich and Si-rich regions. This example is from the sample melted by single-sided laser heating at 45 GPa.

layer. This gives a clear reference mark on the coating that is used for drift correction after the whole set of measurements. The front edge of the zone of interest was milled away until the melted part was reached. The materials next to the coated area toward the EDX detector was also removed to avoid any blocking and shadowing effect. 3D tomography and x-ray acquisition was started after having cleaned the surface. For each slice a secondary electron image and an EDX map was recorded by INCA software from Oxford Instruments and then one slice with the thickness between 50-150 nm (depending on the sample) was removed. The electron beam high voltage was set between 4 and 7 kV. This high tension range is enough to record O L line at 0.54 keV, Si K line at 1.8 keV, Mg K line at 1.3 keV and Fe L line at 0.7 keV. About half of the heated area was used for slicing to produce 3D chemical model of the volume and the phases.

MultiStackReg and Template Matching plugins in ImageJ (Fiji) were used on the secondary electron image stacks to correct the drift based on the marker lines in the platinum deposition





Figure 4.4: The quantified elemental maps are used for segmentation and phase separation. The images show the 3D reconstruction of the whole sample as well as for the ferropericlase (Fp-I) phase, bridgmanite (Brg) phase, and the molten core. Sample is heated for 1 minute at 45 GPa.

as a reference. Then, a transformation matrix or a small ImageJ macro was used to impose the same alignment for elemental maps. The intensity maps are combined in 2D as RGB images with red, green, and blue channels being Fe, Si, and Mg maps (figure 4.3). Moreover, the intensity maps are used to reconstruct the 3D volume of the molten region (figure 4.3). Then, all the acquired maps were quantified with INCA software. AutoIt script was written to facilitate the quantification for all the slices on INCA software and to save quantified elemental maps with atomic percentage for Mg, Si, Fe and O. In the reported chemical formulas Fe, Mg, and Si atomic percentages are from the quantification but oxygen amount was written according to the stoichiometry of the predicted phase. The reason is that oxygen quantification with EDX method is not reliable due to oxygen's low atomic number and x-ray yield. The quantified elemental maps were loaded to Mathematica for further image analysis and phase identifications. Segmentation was done by separating the image pixels based on the expected phase composition to make 3D representation for each phase. At the end, Avizo software from FEI was used to visualize the 3D maps. The segmented phases are shown in figure 4.4.

4.2.3 TEM section preparation

The other half of the samples were used to make thin sections for transmission electron microscopy with the FIB lift-out technique. The front of the sample was empty after the 3D acquisition. The bulk of material behind the thin section , intended to be lifted-out, was milled away and the thin sections were transferred and glued to a copper probe with ion beam induced carbon deposition. The samples were then thinned with 30 kV ion beam with currents ranging from 700 pA down to 80 pA. The final polishing was done with 5 kV and 30 pA ion beam to obtain thicknesses of around 100 nm. The TEM samples were about 20 μ m in length and width which made them difficult to thin evenly. Therefore, we always had uneven thickness in different parts of the TEM lamella.

4.2.4 STEM EDX

Tecnai Osiris scanning transmission electron microscope (STEM) from FEI equipped with four windowless Super-X SDD EDX detectors from Bruker was used for chemical analysis of the samples. The microscope was operated at 200 kV high tension in STEM mode to obtain bright field (BF) and high-angle annular dark field (HAADF) images. The EDX maps were acquired with 50-100 μ s dwell time for 400-1000 seconds to have a sufficient amount of counts. Quantification was done with Espirit 1.9 software provided by Bruker using the Cliff-Lorimer method. K lines were used for quantification of all the elements. Similar to the SEM EDX, oxygen atomic percent reported in the chemical formulas are derived from the stoichiometry of the predicted phases rather than from the EDX quantification. EDX quantification is not accurate for light elements.

4.2.5 EELS

Electron energy-loss spectroscopy (EELS) was performed with FEI Titan Themis microscope operating at 300 kV both in STEM and TEM modes. In TEM mode, entrance, condenser (C2), and objective apertures are set to 2.5 mm, 70 μ m, and 70 μ m respectively to obtain the iron L₂₃-edge spectra with the screen current of 2.5-5 nA. The acquisition times were in the range of 20-500 seconds. The STEM EELS maps were recorded for 6-29 minutes using a camera length of 115 mm and a screen current of 2.5-4.8 nA. Drift tube was set to the 690 eV for all the measurements to record the iron white lines. Fe₂TiO₃ and Fe₂O₃ are used as Fe²⁺ and Fe³⁺ standards with Fe L₃ line at 709.4 eV and 711.1 eV, respectively.

The quantification was done by fitting the mineral L₂₃-edge spectra with the standard spectra with a Mathematica code following the method proposed by van Aken and Liebscher (2002) [359]. In this method, the pre-edge background was first subtracted with a power function in the form of $f(\Delta E) = k(\Delta E)^c$. The k and c parameters were obtained by fitting the logarithm of 6-22 eV pre-edge spectra to a linear function. Then, the post-edge background was subtracted using an arctan function given below (eq. 2.1) [359]:

$$f(\Delta E) = \frac{h_1}{\pi} (\arctan(\pi(\Delta E - E_1)) + \frac{\pi}{2}) + \frac{h_2 - h_1}{\pi} (\arctan(\pi(\Delta E - E_1)) + \frac{\pi}{2})$$
(4.1)

Where h_1 and h_2 are energy corresponding to the minimum intensity of the spectra after the L_3 and L_2 peaks, respectively. E_1 and E_2 are fixed energies of the inflection points which are set to be 710.55 and 723.55 by adjusting values reported in the literature to our spectrum peaks. This function bring the minima of the post-edge spectra to zero. Each spectrum was, then, normalized by its integral in the energy range of 705-728 eV corresponding to the beginning and the end of the L_{23} -edge. This procedure was repeated for all the quantified spectra as well as for the standard spectra for Fe²⁺ and Fe³⁺. Afterward, the mineral spectrum was linearly

fitted according to equation (2.2) [359]:

$$S_{exp} = k_1 S_{Fe^{2+}} + k_2 S_{Fe^{3+}} \tag{4.2}$$

Where the S_{exp} , $S_{Fe^{2+}}$, and $S_{Fe^{3+}}$ are the normalized spectrum from the mineral, Fe₂TiO₃, and Fe₂O₃ respectively. Therefore, the Fe³⁺/ total Fe will be given by $k_2/(k_1+k_2)$. This method was tested by quantifying the Fe³⁺/ total Fe ratio in Fe₃O₄ standards at the obtained value was equal to 69.9% which is ~3.3% higher than the actual value, but it is acceptable for our purpose.

4.3 Results and discussion

4.3.1 Single-sided laser heating

One sample was melted at 45 GPa during 3 minutes by single-sided laser heating to compare the morphology and texture of the heated zone with that obtained in double-sided laser heating experiments. Figure 4.3 shows the SEM EDX maps and the volume reconstruction of the sample. We observe an oval molten zone surrounded by a ferropericlase shell. However, the symmetry is broken at the top and there is a mixture of phases expelled out of the oval zone in the direction of "cold diamond", i.e. the one through which the laser beam does not pass. Iron-rich oxides are observed in the center of the laser heated zone, but iron has also been segregated in the cold zone outside the oval shape. This indicates substantial thermal gradient in the sample. Figure 4.5 shows the schematic temperature gradient in this sample based on figure 4.3. The temperature gradient in the radial direction remains symmetrical similar to the double-sided laser heating (figure 4.5). But the peak temperature shifts toward the laser heating side, and thus the the gradient in axial direction (direction of pressure and laser heating) is not symmetrical (figure 4.5). Nowadays, almost all the LH-DAC experiments are performed with the double-sided laser heating. Accordingly, the rest of the samples reported in this study are all heated from both sides.

4.3.2 Evolution of melt with time at 45 GPa

3D EDX

In all samples 3D reconstructions of the molten zone show three main regions: a ferropericlase shell surrounding the whole molten region (Fp-I), a bridgmanite (Brg) region just inside the ferropericlase shell and an iron-rich melt core in the center of approximately spherical molten volume (figure 4.4 and 4.6). Figure 4.6 shows the 3D reconstructions of the molten volume for samples heated at 45 GPa for different durations (1, 3, and 6 minutes). For the sample heated for 1 minute we only observe the three main regions (core, Brg, and Fp-I).


Figure 4.5: Schematic view of the single-sided laser heating in DAC and the resulting temperature gradient. The temperature gradient remains symmetrical in radial direction, but the peak temperature shift towards the laser heating side in the axial direction.

When the heating time is increased to 3 minutes, an additional ferropericlase phase (Fp-II) appears around the core (figure 4.6). As seen table 4.1, this Fp-II phase is richer in iron than the Fp-I one. This indicates that Fp-II crystallizes later from a more iron-rich melt. Compared to the previous sample the changes in the composition of Fp-I and Brg are insignificant. However, the volume of bridgmanite has increased, and the melt core has shrunk and has became richer in iron and poorer in Si and Mg.

In the sample heated for 6 minutes, the Fp-II phase has grown to create a complete shell around the melt core, separating it from the Brg region (figure 4.6). It is also richer in iron than Fp-II in the sample heated for 3 minutes, indicating crystallization from a more iron-rich melt. Fp-I and Brg phases still have composition similar to those observed in the samples heated for 1 and 3 minutes, which confirms that the outer shell (Fp-I) and the outer parts of the Brg region are the first to crystallize. Then, the melt and crystalline phase evolve towards the center of the heating. The Brg region in the sample heated for 6 minutes represents up to ~ 60 vol% of the molten volume, in contrast to the 24 vol% for the sample heated for 1 minute. Consequently, the volume fraction of melt core decreases from ~50% down to ~2% by increasing the heating time from 1 minute to 6 minutes. Since the iron favorably partitions to the melt, the core in the sample heated for 6 minutes is more iron-rich than the other samples heated for shorter duration at 45 GPa.



Figure 4.6: The images show the 3D reconstructed model as well as the 2D chemical distribution of the central slice for the sample heated at 45 GPa for 1, 3, and 6 minutes (from top to the bottom of the image). Fp-I, Brg, Fp-II and the Core are representing the ferropericlase shell, bridgmanite region, ferropericlase surrounding the Core, and the molten core respectively. Fe bleb is the small metallic iron region inside the core of the sample heated for 6 minutes.

TEM analysis and compositional gradient of the iron

Scanning transmission electron microscopy and energy dispersive x-ray analysis show details of the samples with higher resolutions as well as better accuracy for chemical analysis. Figure 4.7 shows the change in the iron content (Fe/(Fe+Mg+Si)%) of the melt core for the samples melted at 45 GPa for 1, 3 and 6 minutes. By increasing the heating time the iron content of the melt core increases while its size decreases. We observe a discrepancy between the

Table 4.1: Composition of phases for the samples heated at 45 GPa for 1, 3, and 6 minutes (SEM EDX and TEM EDX methods). The errors indicated for the compositions are the standard deviation. MgO, FeO, and SiO₂ are representative of Mg/(Fe+Mg+Si), Fe/(Fe+Mg+Si), and Si/(Fe+Mg+Si) in atomic% respectively. Therefore, the FeO depicts the total iron composition including Fe²⁺, Fe³⁺, and metallic iron. The dash (-) is used when that particular element is not expected in the phase, and N/A is used when the data is not available from that phase.

Sample	Phase		SEM EDX			TEM EDX	
		MgO	FeO	SiO ₂	MgO	FeO	SiO ₂
45 GPa	Fp-I	93.5 (±0.7)	6.5 (±0.7)	-	93.2 (±0.7)	$6.8 (\pm 0.7)$	-
1 min	Brg	48.9 (±1.2)	$4.7 (\pm 1.9)$	46.4 (±2.9)	46.1 (±0.4)	2.1 (±0.2)	51.8 (±0.5)
	Core	48.3 (±0.7)	18.1 (±1.4)	33.6 (±0.7)	50.5 (±0.5)	$10.0 (\pm 0.3)$	39.5 (±0.2)
45 GPa	Fp-I	86.9 (±3.7)	13.1 (±3.7)	-	N/A	N/A	-
3 min	Brg	47.3 (±2.6)	4.2 (±2.8)	48.5 (±2.9)	N/A	N/A	N/A
	Fp-II	76.0 (±5.5)	$24.0 (\pm 5.5)$	-	N/A	N/A	-
	Core	39.8 (±0.7)	27.6 (±2.1)	32.6 (±1.5)	N/A	N/A	N/A
45 GPa	Fp-I	86.8 (±4.0)	13.2 (±4.0)	-	92.0 (±0.5)	8.0 (±0.5)	-
6 min	Brg	48.3 (±4.4)	6.3 (±2.4)	45.4 (±4.8)	47.2 (±0.2)	2.0 (±0.1)	50.8 (±0.2)
	Fp-II	61.1 (±1.4)	38.9 (±1.4)	-	66.5 (±0.3)	33.5 (±0.3)	-
	Core	28.9 (±1.0)	46.6 (±1.3)	24.5 (±0.8)	32.8 (±1.3)	37.5 (±0.3)	29.7 (±1.0)
	Fe bleb	1.5 (±0.2)	97.9 (±0.9)	0.6 (±0.8)	-	-	-

quantification results of SEM EDX and TEM EDX. In the SEM EDX low high tension (4kV-7kV) was used to be suitable for imaging. With this range of voltages we can only get L line of the iron x-ray emission spectrum and the quantification based on L line is prone to errors. In fact, all the results from SEM EDX quantification are biased to higher iron compared to the compositions obtained by TEM EDX. However, we can see in the figure 4.7 that the trend of variations in iron content with time is similar.

Figure 4.8 shows HAADF image and EDX map from the Fp-I shell and Brg region in the 45 GPa sample heated for 1 minute. We can see the presence of ferropericlase grains inside the Brg phase, sometimes elongated similar to the Fp-I shell. These ferropericlase grains are slightly richer in iron than the Fp-I, suggesting that they have crystallized later from the more iron-rich melt. Since the bridgmanite is in contact with the melt core, we can consider it as the last phase crystallizing from the liquid. The partitioning coefficient between bridgmanite and liquidus phase is defined as $K_{brg/liq} = \frac{X_{Fe}^{brg} X_{Mg}^{liq}}{X_{Fe}^{leq} X_{Mg}^{hrg}}$ and using the data shown in table 4.1 gives the value of ~0.21. This is in a close agreement with the value ($K_{brg/liq} = 0.22-0.29$) obtained by Nomura et al. (2011) in the pressure range 40-70 GPa using olivine as starting material [288]. On the other hand, this is about 3 times lower than the partitioning coefficient measured by Andrault et al. (2012) for the same pressure range using chondritic-type starting material [251]. Andrault et al. (2012) attributed this discrepancy to result from the presence of Al in their composition, which is believed to stabilize Fe³⁺ in the bridgmanite composition and, hence, increase its iron content [251]. However, later experiment by Tateno et al. (2014) on peridotite



Figure 4.7: Variation of Fe/(Fe+Mg+Si) atomic% with increasing heating time. Data obtained from both SEM EDX and TEM EDX are shown. The SEM EDX results are biased towards higher iron content. However, the trend of the variation is similar for the data obtained from two methods (see text for further explanation).

samples showed that the partitioning coefficient is ~0.3 for 30-60 GPa despite the presence of Al in the composition [357]. The difference in the degree of partial melting is also suggested to explain the discrepancy between the experimental results [360, 361]. Indeed, it has been demonstrated that the $K_{brg/liq}$ decreases with increasing degree of partial melting until it becomes constant above 10 wt% of melt. Contrary to previous experiment, in our study, the bridgmanite phase is not the remnant of partial melt rather the crystallization product from a liquid.

Figure 4.9 shows the melt core in the 45 GPa sample heated for 1 minute. There are three distinguishable phases in the quenched melt. Two phases are identified as bridgmanite and ferropericlase which are forming 10-30 nm thick alternating with a lamellar morphology typical of a eutectic structure [362]. The third phase appears as iron-rich nano particles of up to ~20 nm in diameter, sprinkled throughout the core. Characterization of these nano particles is not straightforward due to their small size and overlap with the eutectic matrix. Nevertheless, the slight decrease in oxygen x-ray peak as well as the Ni enrichment in these nano particles points to a Fe-Ni metallic alloy. The ASTAR map was acquired from this region to identify the crystal structure of these particles. Although the indexing was not completely conclusive, the best match was found with FCC iron structure. Metallic iron forms by disproportionation of Fe²⁺ into Fe and Fe³⁺. Fe³⁺ is expected to be incorporated into the bridgmanite phase and its concentration in ferropericlase is negligible [208, 212].

Similar to the 1 minute sample, the sample melted at 45 GPa for 6 minutes has a second partial layer of ferropericlase shell. The composition of this shell is not homogenous, but it is always



Figure 4.8: HAADF image and the combined EDX maps of Fe, Mg, and Si in the 45 GPa sample heated for 1 minute. Fp-I, Brg, Fp, and core are representing the ferropericlase shell, bridgmanite region, ferropericlase grains and the melt pocket respectively. The solidus is the region that stayed below the solidus temperature and it has the starting material composition that has breakdown to ferropericlase and bridgmanite.

richer in iron than the Fp-I. The volume between these two shells is occupied by bridgmanite. Moreover, the bulk of the Brg region is filled with ferropericlase grains. Although these grains are not connected, their morphology looks like broken chain of ferropericlase connecting the Fp-I shell to the Fp-II shell and the melt core. Similar features have been seen by Fiquet et al. (2010) in molten peridotite samples [250].

Electron diffraction analysis confirm that all the oxide phases (Fp-I, Fp-II, and ferropericlase grains inside Brg) have NaCl structure. However, their compositions are different. Figure 4.10 shows ferropericlase grains in the Brg region in 45 GPa sample heated for 6 minutes. If we look to the composition of these particles with respect to their distance from the center of the heating zone, those which are closer to the core have a higher iron contents. Plot in figure 4.10 indicates the variation of Fe/Mg, measured by TEM EDX, versus the distance from the center of the heating zone. The iron content is decreasing almost linearly with distance. The bridgmanite around the more iron-rich ferropericlase particles (closer to the core) has also a higher average iron content than the bridgmanite phase that is far from the core. The exchange constant for Fe portioning defined as $K_{Brg/Fp} = \frac{X_{Fe}^{Brg} X_{Mg}^{Fp}}{X_{Fe}^{Fp} X_{Mg}^{Brg}}$) lies between 0.24 to 0.34 with the average at 0.29 which is fairly consistent with the previous studies in this pressure range [221, 222, 363]. Since the first liquidus phase changes from ferropericlase to bridgmanite in peridotite composition at 30-35 GPa [364, 250], the iron partitioning coefficient between



Figure 4.9: HAADF image and combined Fe, Mg, and Si EDX map as well as Ni EDX map from the melt pocket of the 45 GPa sample heated for 1 minute. The core has the eutectic morphology. Fp, Brg and Fe represent the ferropericlase, bridgmanite and iron nano particles.

ferropericlase and melt $K_{Fp/liq} = \frac{X_{Fe}^{Fp} X_{Mg}^{liq}}{X_{Fe}^{Fp} X_{Mg}^{Fp}}$ has only been measured for pressures lower than ~35 GPa in previous studies, and it was reported to be 0.6-0.7 at pressure range of 25-32 GPa [365, 288]. On the other hand, considering the $K_{Brg/Fp} = K_{Brg/liq}/K_{Fp/liq}$ relation and close value of $K_{Brg/Fp}$ and $K_{Brg/liq}$ from previous experiments, Boukare et al. (2015) speculated $K_{Fp/liq}$ to be about 1 in lower mantle pressures [358]. Assuming the maximum value of $K_{Fp/liq}$ to be ~1 at 45 GPa, the Fe/Mg ratio of ferropericlase grains plotted in figure 4.10 would be the lower limit of Fe/Mg in the melt front when these grains crystallized. Consequently, the upper limit of $K_{Brg/liq}$ will be equal to $K_{Brg/Fp}$ which lies in the range of 0.24-0.34. As discussed before this estimated $K_{Brg/Fp}$ is in a good agreement with previous studies [288, 357]. Through crystallization of ferropericlase and bridgmanite the melt core gets smaller and richer in iron as a result of the low $K_{Brg/liq}$. Thus, the grain crystallizing later from the melt have a higher iron content and they are also closer to the center of heated zone.

As previously mentioned, the liquidus phase in a peridotite composition has been shown to change from ferropericlase to bridgmanite. This has been often inferred from the sequence of phases with respect to the center in the quenched samples [288, 357, 364]. In this method, the closest phase to the melt pocket (in contact with the melt) is considered to be the first liquidus phase and the solidification sequence follows outwards from there. The logic behind this interpretation is the actual temperature gradient in the LH-DAC. Thus, the melt pocket forms in the highest temperature region in the center of heating and, then, the first liquidus phase crystallizes around it in lower temperatures. This sequence continues and the phases are crystallizing with decreasing the temperature as the distance from the center of the heating increases. Using this method, Nomura et al. (2011) stated, based on electron microprobe observations, that the liquidus phase of olivine composition changes to bridgmanite at 36 GPa

[288]. The corresponding sequence of phases is also observed in our sample. However, our results indicate that the ferropericlase grains are getting richer in iron closer to the melt core and, hence, their melting temperature is lower. In the sample heated for 6 minutes, the phase in contact with the melt pocket is Fp-II with Fe/Mg molar ratio of 49%, which means that it has melted at temperatures lower than for all the other phases outside the Fp-II shell. Even in the sample heated for 1 minute, although the bridgmanite phase is in contact with the melt pocket, it contains ferropericlase grains with higher iron content than the Fp-I shell. Therefore, we can conclude that ferropericlase is the first liquidus phase and, subsequently, the solidification continues at the eutectic point, or more precisely, in the cotectic curve of the FeO-MgO-SiO₂ system, where bridgmanite and ferropericlase crystallize together. In this scenario the crystallization would continue from the edge of the melt pool inward, due to the direction of the heat flux. This argument does not mean that the crystallization sequence is always the opposite of what has been believed before, but it demonstrates that other parameters affect the crystallization sequence of crystals in molten samples. When there is only one solid phase observed in the samples in equilibrium with the melt, it can be directly interpreted as the first liquidus phase for the samples in the composition range of the bridgmanite and ferropericlase joint. However, if there is more than one solid phase outside the melt pocket and in the molten region, it means that the crystallization continues on the eutectic line. In fact, Fiquet et al. (2010) found by in-situ x-ray diffraction that ferropericlase is the liquidus phase at 36 GPa for peridotite composition, and it changes to bridgmanite between 36 GPa and 61 GPa [250]. For olivine with Si/(Mg+Fe)=0.5 lower than that of peridotites (\sim 0.7), we expect a higher pressure to change the first liquidus phase. A recent study on MgO-MgSiO₃ system (using the phase sequence criteria), found the lower limit of eutectic composition to be Si/Mg = -0.6 (center of the composition range equal to Si/Mg=~0.68) at 45 GPa [366]. The presence of iron decreases the melting point of MgO [367] and, hence, shifts the Si/(Mg+Fe) ratio of eutectic composition to lower values. However, based on our result, we do not expect the eutectic point to be shifted enough to have bridgmanite at the liquidus for the olivine composition at 45 GPa.



Figure 4.10: Combined Fe, Si, and Mg EDX map from the bridgmanite region with the ferropericlase grains in the 45 GPa sample heated for 6 minutes. The schematic view indicates the position of this region in the sample with respect to the Fp-I and Fp-II. The plot below depicts the decrease in the Fe/Mg of the ferropericlase phase by increasing its distance from the center of molten region. The composition of ferropericlase grains are taken from the EDX map above.

Molten core and iron disproportionation

Figure 4.11 reveals the Fp-II boundary with the molten core. TEM studies show two additional layers in this region. Just after the Fp-II layer, there is another oxide layer with a higher iron concentration (Fe/Mg=1.27) and ~100 nm thickness, thus, we refer to it as magnesiowüstite (Mw). The presence of two iron-rich and magnesium-rich oxides in equilibrium at high pressure (above ~80 GPa) has been shown before and attributed to the phase transformation of iron-rich phase to rhombohedral structure [207]. However, in our sample both phases have NaCl structure with the same orientation. Therefore, the only difference is in the chemistry. Inside this layer, there is a Si-rich layer with Si:Mg:Fe ratio of 1:0.7:0.7 which has lower iron than the bulk core and its amorphous in the quenched sample. One possibility is that the iron-rich magnesiowüstite boundary between this Si-rich layer and Fp-II is forming due to the repelling of iron through the solidification of the Si-rich layer.



Figure 4.11: The figure shows BF image as well as Fe, Mg, and Si EDX maps in the 45 GPa sample heated for 1 minute. We can see a magnesiowüstite phase (Mw) with \sim 100 nm thickness surrounding the core. Inside that, there is an amorphous Si-rich layer followed by the core itself.

The core itself has a granular structure. The boundaries between the grains are wide (up to ~40 nm) and mainly composed of amorphous silicon oxide (stishovite?) and particles of iron oxide (figure 4.12). As shown in figure 4.12, individual grains in the core are chemically heterogeneous. There is an oxide phase at the center of each grain with a flower-like dendritic morphology. Fe/Mg ratio in this oxide is about 1 (±0.1). It is surrounded by a silicate phase rich in iron and magnesium. The Si:Mg:Fe ratio of this silicate phase is approximately measured to be $1:1.06(\pm 0.13):0.77(\pm 0.13)$. However, we should note that the spaces between the oxide dendrites are narrow and, therefore, we expect a strong overlap between these two phases inside a grain. This will result in inaccuracy of the EDX quantification. Thus, we also see a substantial difference among the compositions of silicate phase measured in different regions of a grain. In addition, we can also see metallic iron particles in many of core grains, which are distinct due to the strong Fe and Ni enrichment (figure 4.12).

We used electron diffraction to identify the structure of the phases in the core. In some grains, the silicate phase is amorphous and the diffraction pattern only shows the ferropericlase spots of the dendrite in the center of the grains. However, the whole grain is often crystalline and the diffraction patterns are indexed with spinel structure. Dark field imaging shows

Chapter 4. 3D analytical investigation of melting in lower mantle conditions



Figure 4.12: HAADF image, combined Fe, Mg, and Si EDX map as well as Ni and Ca maps from a core grain in the 45 GPa sample heated for 1 minute. Fp, Sp, St, Mag, and Fe represent the ferropericlase, spinel silicate, stishovite, magnetite and metallic iron phases respectively. Presence of Mg and Ca in the the grain boundaries along with stishovite and magnetite gives rise to the possibility of the formation of (Fe, Mg, Ca)Fe₂O₄ and CaSiO₃ (Ca-perovskite) phases.

that the dendrites are ferropericlase with NaCl structure and the spinel diffraction spots are originating from the silicate parts (figure 4.13). But since the two structures have the same exact orientation in the grains and, also, because the lattice parameter in spinel is approximately twice as large as the lattice parameter in ferropericlase, the diffraction spots from 2h2k2l planes in spinel partially overlap with the spots from hkl planes of ferropericlase structure (figure 4.13). High resolution Z-contrast images confirms the perfect orientational match between these phases. The common spinel phases with Mg-Fe-Si-O compositions are ringwoodite (Mg,Fe)₂SiO₄ and magnetite or magnesioferrite (Fe,Mg)Fe₂O₄. None of these spinel structures are stable in the pressure range of our experiments and they break down or transform to their high pressure polymorphs above 21-25 GPa [201, 202, 368, 369].

Figure 4.14 shows the distribution of Fe³⁺ in a core grain. The quantification of EELS spectrum shows that the ferropericlase has no Fe^{3+} in its composition (or below the detection limit) which is expected based on previous studies (figure 4.15) [208]. On the other hand, the silicate part shows a peak close to that of Fe₂O₃ standard and the quantification indicated the Fe³⁺/total Fe ratio of 60-100% (figure 4.15). Although the Si/(Mg+Fe) ratio of silicate phase is not far from that of ringwoodite, the high Fe³⁺ concentration excludes the ringwoodite. This is due to the fact that Fe^{3+} have to replace the Mg^{2+} and Si^{4+} as a pair and, considering this, the measured composition does not match with the ringwoodite phase. Fe³⁺/total ratio of iron oxide particles in the grain boundaries is about 70-100% (figure 4.15). This suggest the presence of magnetite Fe₃O₄ in the boundaries. Although spinel magnetite is not stable at 45 GPa, its high pressure polymorph is unquenchable to lower pressures. Therefore, it is possible to have magnetite in the sample. However, this is unlikely to be the explanation for the spinel structure in the silicate part. Moreover, the granular morphology of the core and the exact same orientation of the ferropericlase dendrites and the spinel phase inside the grains implies that there was a parent phase for the grains that has later decomposed to ferropericlase and spinel silicate. The MgO-FeO-Fe₂O₃-SiO₂ solid solution has been shown to form high pressure phases [370]. But we could not reconcile our observations with those phases. In-situ x-ray diffraction could help to understand the phase relationship in the quenched molten core.



Figure 4.13: The top row shows the BF, HAADF, and combined Fe, Si, and Mg EDX map for a core grain. In the bottom row we have the TEM BF, DF from (220) plane of the spinel, and DF from (440) plane of the spinel (same as (220) plane of ferropericlase) in the [332] zone axis. The DF images indicates that the ferropericlase and spinel have the same orientation.



Figure 4.14: HAADF image and the Fe³⁺ distribution map in a core grain.

Olivine has trace amount of Ni and Ca. The TEM EDX shows that the Ca strongly segregates to the core and, upon crystallization of the core, it segregates to the grain boundaries. The presence of Ca in the grain boundaries indicates the possible formation of Ca-perovskite (CaSiO₃) or CaFe₂O₄ in the core. Ni on the other hand preferentially partitions in ferropericlase rather than in bridgmanite, but it is mainly incorporated in the metallic iron particles.

Frost et al. (2004) have shown that for bridgmanite composition at lower mantle and in the presence of Al^{3+} , Fe^{2+} disproportionate into metallic Fe and Fe^{3+} [212]. In fact, it has been shown that Fe^{2+} and Al^{3+} substitutes for Mg^{2+} and Si^{4+} in bridgmanite [209, 210]. The disproportionation of iron in the lower mantle also indicates the presence of metallic iron there. In our experiment we have shown the iron disproportionation even when there is no Al^{3+} in the composition. EELS data from the Brg region show the clear peak shift of about +1.5 eV in iron L_3 peak indicating a large Fe^{3+} concentration. Due to the beam sensitivity



Figure 4.15: HAADF image and iron L-edge EELS spectra from the selected the spinel, magnetite and ferropericlase phases indicated by Sp, Mag, and Fp respectively.

of bridgmanite as well as its low total iron concentration, the quantification of EELS data were not accurate for this phase. Nevertheless, it showed $Fe^{3+}/total$ Fe is higher than 50%. Metallic iron has formed iron nano particles in the sample heated for 1 minute. Although these nano particles are present in the core of the sample heated for 6 minutes, they are much less frequent in this sample and the metallic iron forms a small bleb inside the core (figure 4.6). This could be explained by the reduction of the melt volume and, as a consequence, the increase in the volume fraction of the metallic iron which leads to the segregation into the Fe bleb. The existence of Fe^{3+} and metallic iron has been previously reported in the melting experiments and attributed to iron disproportionation during the temperature quench [288]. However, the high concentration of Fe^{3+} in bridgmanite. Moreover, although we cannot provide a quantitative partitioning coefficient for Fe^{3+} , the results show that the Fe^{3+} partitions between the melt and bridgmanite. During the fractional crystallization of the basal magma ocean, this could have promoted the formation of Fe^{3+} -rich phases and oxides at the bottom of the mantle.

Thermodynamic model

Boukare et al. (2014) have calculated the fractional crystallization of mantle minerals [358]. In their model, they have considered SiO_2 , MgO, and FeO components to be present in the liquid phase (all three oxides), bridgmanite (all three oxides with MgSiO₃ and FeSiO₃ as iron- and magnesium-rich end-members), ferropericlase (MgO and FeO as iron- and magnesium-rich end-members) and stishovite (SiO₂) [358]. Chemical potentials of solid species are taken

from Stixtrude and Lithgow-Bertelloni (2005) for SiO₂ and MgO [371], and from Fischer et al. (2011) for FeO [372]. Chemical potentials of MgO and SiO₂ in liquid are taken from DeKoker et al. (2013) [373]. The chemical potential of FeO is determined from its equation of state based on the Murnaghan expression [374]. The solid solutions in this model are considered to be ideal, and the non-ideality coefficients for liquid are derived by Margulas expansion. To obtain the parameters that describe chemical potential and activities of FeO, the model was fitted to the available experimental data, namely: the melting curve of FeO [375], the density of liquid Fe₂SiO₄ [376], and the iron partitioning coefficient between melt and bridgmanite or ferropericlase phases [288, 357] (as well as iron partitioning between ferropericlase and bridgmanite which are related to the liquid phase by $K_{Brg/Fp}=K_{Brg/liq}/K_{Fp/liq}$). Therefore, the minimum misfit for these data determined the parameters for thermodynamic model of FeO in the melt [358]. Consequently, the Gibbs energy minimization describes the phases and compositions for different pressure and temperature conditions [358].

This model was used to calculate the phase diagram at 45 GPa and compare the fractional crystallization of olivine composition with the obtained experimental results. Figure 4.16 shows the ternary diagram of MgO-FeO-SiO₂ at 45 GPa. As expected from the observation, the first solid in equilibrium with the liquid is ferropericlase. This phase corresponds to Fp-I in our data, the composition of which is almost constant for the samples heated for 1, 3, and 6 minutes. Fractional crystallization then continues on the liquidus surface (liquidus line for binary phase diagram) until it reaches the cotectic valley between bridgmanite and ferropericlase (eutectic point in binary diagram). The crystallization then follows the cotectic curve as shown in figure 4.16. The compositions of the central melt pocket obtained from SEM EDX measurements are shown on the phase diagram for three samples heated from 1 to 6 minutes and they all fall on the cotectic curve. The crystallization products would be bridgmanite and ferropericlase phases as observed in the Brg region of our samples. By progression of crystallization on the cotectic curve, the Fe concentration increases in the melt. Since FeO has the lowest melting point among the oxide species, it acts as an anti-freezing agent in the melt and decreases the melting point on the cotectic curve. On the other hand, it also shifts the eutectic point towards the Si-poor composition. Therefore, the equilibrium melt not only gets richer in the iron, but also shows a Si/(Mg+Fe) ratio decrease. Finally, the crystallization ends on the FeO-SiO₂ joint after all the MgO in the melt is exhausted. The phase diagram indicates that the crystallizing ferropericlase is getting more iron-rich by continuing the solidification process.

Figure 4.17 shows the composition of the melt, ferropericlase, and bridgmanite as estimated by the thermodynamical model at 45 GPa for the olivine composition as well as the measured values by SEM EDX. The measured experimental composition of the melt pocket for the samples heated for 1, 3, and 6 minutes are very close to the calculated composition during fractional crystallization at temperatures of ~3620 K, ~3530 K, and ~3440 K, respectively (figure 4.17). Although the reduction of temperature during the laser heating of our samples is not observed, the temperature is only measured in the center of the heated zone and, therefore, the temperature gradient and its variations are not known. The possible variation



Figure 4.16: Calculated ternary FeO-MgO-SiO₂ phase diagram at 45 GPa [358]. The yellow line indicates the crystallization path for the olivine composition, which starts from ferropericlase + liquid region (blue) and, then, follows the cotectic line between ferropericlase and bridgmanite. The melt compositions from SEM EDX are shown on the phase diagram. These compositions are in a good agreement with the simulations.

of the temperature profile with time can induce crystallization of the melt. Although the predicted temperatures in the models are higher than the actual temperatures of the samples (3000-3500 K), they are qualitatively in a good agreement with the heating temperature. We should also note that the SEM EDX results are biased towards the high iron composition. However, the variation slope for the melt composition obtained from SEM EDX is similar to that of TEM EDX. Since the TEM EDX data were not available for the sample heated for 3 minutes, the SEM EDX data were used for comparison with the model. The variation in pressure and temperature can explain the difference between simulated and experimental compositions. We note also that the solidus temperature estimated with this model has been shown to overestimate the experimental values [358].

4.3.3 Pressure effect on the melting

3D EDX

Two additional samples were pressurized at 30 GPa and 71 GPa and heated for ~3 minutes to study the effect of pressure change in the melting relations. Figure 4.18 shows the volume reconstruction of 30 GPa, 45 GPa, and 71 GPa heated for about the same duration with the laser. At 30 GPa, four different regions in the sample are visible; three region (Fp-I, Brg, and



Figure 4.17: Composition of liquid, ferropericlase (Fp) and bridgmanite (Brg) as predicted to evolve during the fractional crystallization by changing the temperature. The experimental composition of the same phases measured by SEM EDX are shown with the crosses on the graphs.

molten core) are similar to previous samples. However, another phase is observed around the core with the Si/(Mg+Fe) \approx 2 similar to the starting olivine. By increasing the pressure to 45 GPa, we have Fp-I, Brg, Fp-II and molten core as described before. The molten core in the 45 GPa sample is more iron-rich than the core in the 30 GPa sample. The measured compositions for 30 GPa and 71 GPa samples are given in the table 4.2.

When the pressure is increased to 71 GPa, we observe three main regions as before, namely: Fp-I shell, Brg region and the molten core. However, the Fp-I in this sample is connected to the molten core by continuous ferropericlase veins. Moreover, the molten core itself has become extremely iron rich with the Fe:Mg:Si ratio of 1:0.07:0.03. The variation in the molten core composition by increasing the pressure is shown in figure 4.19. Previous studies have shown iron enrichment in the melt with increasing pressure, although the degree and the slope of this enrichment varies substantially among the different sources [288, 357, 358, 251]. Both Nomura et al. (2011) and Tateno et al. (2014) observed a sharp decrease in the iron partitioning between bridgmanite and melt ($K_{Brg/liq}$) at about 60-75 GPa which was attributed to the spin transition of iron in the melt and partitioning of (Al^{3+}, Fe^{3+}) pairs into the melt instead of the bridgmanite, respectively [288, 357]. The iron enrichment observed in our 71 GPa sample is much higher than what was shown in the mentioned studies. However, this can be due to the prolonged heating time in our sample (~3 minutes) in contrast to the flash heating (~1 second) in those experiments. Moreover, Al is not present in our sample. Thus, the abrupt change in the iron partitioning into the melt could be the result of a spin transition of iron in the liquid phase similar to the sharp K_{Brg/Fp} change in the solid state at the pressures corresponding to the iron spin transition in the ferropericlase phase [217, 221, 222]. The pressure of ~ 70 GPa corresponds to the depth of \sim 1700 km in the Earth and it is close to the top of the basal



Figure 4.18: The images shows the 3D reconstructed models as well as the 2D chemical distribution of the central slice of the sample heated for ~3 minutes at 30 GPa, 45 GPa and 71 GPa (from top to the bottom of the image). The Fp-I, Brg, Fp-II and the Core are representing the ferropericlase shell, bridgmanite region, ferropericlase surrounding the core, and the molten core respectively.

magma ocean as previously estimated [249, 358]. Strong iron enrichment of the melt in this pressure range supports the gravitational stability of the melt at the base of the mantle. Also, it has been shown that the seismic properties of ULVZs could be explained by iron-rich oxide close to the wüstite (FeO) end-member [312]. The oxides crystallizing from the observed melt in 71 GPa sample, with the Fe/Mg ratio greater than 15, will be enough iron-rich to satisfy this condition.

TEM analysis

TEM EDX mapping of the 30 GPa sample (figure 4.20) shows that iron nano particles are distributed around and mainly outside of the Fp-I shell. The molten core in this sample is amorphous without any specific feature. Electron diffraction patterns from the phase surrounding the molten core are compatible with wadsleyite, also called β -olivine. This is also confirmed with its composition measured by TEM EDX. Wadsleyite is the product of phase transformation of olivine at ~14 GPa which is the widely accepted explanation for the 410 km



Figure 4.19: Variation of Fe/(Fe+Mg+Si) atomic% by increasing the pressure obtained from SEM EDX. The gray dashed line indicates the pressure correction for the 30 GPa sample considering \sim 7 GPa pressure drop necessary to explain the presence of wadsleyite. Although the SEM EDX results are biased towards the higher iron content, the variation trend is not expected to be different than the actual compositions.

seismic discontinuity at the beginning of the transition zone in the mantle [200]. This phase will then transform to ringwoodite (spinel) at ~17.5 GPa in the Earth [200]. High temperature could increase the stability pressure of wadsleyite. However, it will eventually break down to ferropericlase and bridgmanite at ~23 GPa and it is not expected to be present at the pressure of our experiment (figure 1.11) [201, 202]. On the other hand, we can clearly see the bridgmanite and ferropericlase phases outside the wadsleyite region where the temperature would be lower than in the wadsleyite region. This condition can only arise in the pressure range of about 22-23 GPa and temperature of around ~2500 K due to the positive Clapeyron slope of wadsleyite to ferropericlase plus bridgmanite phase transformation (figure 1.11) [377]. Therefore, the wadsleyite will be stable in high temperature region, while it will break down to ferropericlase and bridgmanite in the region with lower temperature. This sample has been observed to have high amount of cracks which can be the explanation of such a high pressure drop. Also, as we can see in figure 4.18, the melted zone in this sample is much less symmetrical than the other ones.

The molten core in 71 GPa sample was only few micrometer in diameter and, unfortunately, it was lost during the thinning of the thin section for TEM studies. As shown in figure 4.21, the ferropericlase and bridgmanite phases are intergrown and we cannot make a clear distinction between the ferropericlase shell and the ferropericlase grains in the bridgmanite regions like in the 45 GPa samples. This morphology resembles a eutectic structure [362], which implies that the composition was close to the eutectic point at that pressure. Moreover, a substantial volume in the bridgmanite region is occupied by ferropericlase veins, which is



Figure 4.20: HAADF image and Fe, Mg, and Si EDX maps in the 30 GPa sample heated for 3 minutes. Fe, Fp-I, Brg, Wad, and Core are representing the metallic iron, ferropericlase shell, bridgmanite region, wadsleyite and the melt pocket respectively. The solidus is the region that stayed below the solidus temperature and that has the starting material composition.

another indication that the eutectic point is shifted towards the Si-poor composition and, thus, the fraction of ferropericlase phase is increased at the eutectic point. The shifting of the eutectic point towards ferropericlase by increasing the pressure has been previously reported [366, 378], and is also evidenced by the change of the first liquidus phase from ferropericlase to bridgmanite at 30-35 GPa in peridotite composition [364, 250]. Naturally, this change will happen later for the olivine composition with lower Si/(Fe+Mg) ratio than the peridotites.

Unlike in the 45 GPa samples, we do not see a systematic change in the ferropericlase and bridgmanite composition at 71 GPa. In fact, the composition changes only slightly among the ferropericlase (Fe/Mg=0.14±0.03) and bridgmanite (Fe/Mg=0.04±0.01) grains throughout the sample. The iron partitioning between bridgmanite and ferropericlase ($K_{Brg/Fp}$) is ~0.28 which is in a good agreement with the values obtained from solidus experiments [221, 222]. The phase relations of this sample could not be reproduced by the thermodynamical model described in the previous section. However, we should note that in the model developed by Boukare et al. (2015) the possible discontinuity in the partitioning coefficient ($K_{Brg/liq}$) was not considered [358]. Hence, if the sharp increase in the iron enrichment in the melt is due to the spin transition of iron in the liquid phase, more sophisticated models should be developed to consider it.

4.3. Results and discussion



Figure 4.21: HAADF image and the Mg, Fe, and Si EDX maps in the 71 GPa sample heated for 3 minutes. Fp and Brg are representing the ferropericlase and bridgmanite phases respectively. The solidus is the region that remain below the solidus temperature and that has the starting material composition.

Table 4.2: Composition of the phases for the samples heated for ~3 minutes at 30 GPa and 71 GPa (SEM EDX and TEM EDX methods). The errors indicated for the compositions are the standard deviation. MgO, FeO, and SiO₂ are representative of Mg/(Fe+Mg+Si), Fe/(Fe+Mg+Si), and Si/(Fe+Mg+Si) in atomic% respectively. Therefore, the FeO content depict the total iron composition including Fe²⁺, Fe³⁺, and metallic iron. The dash (-) is used when that particular element is not expected in the phase, and N/A is used when the data is not available for that phase.

Sample	Phase		SEM EDX			TEM EDX	
		MgO	FeO	SiO ₂	MgO	FeO	SiO ₂
30 GPa	Fp-I	87.5 (±0.5)	12.5 (±0.5)	-	89.9 (±0.8)	10.1 (±0.8)	-
3 min	Brg	48.3 (±0.7)	3.0 (±0.2)	48.7 (±0.5)	47.4 (±0.4)	$1.6 (\pm 0.2)$	51.0 (±0.4)
	Wad	58.1 (±2.0)	10.1 (±1.6)	31.8 (±0.6)	59.3 (±0.8)	$5.6(\pm 0.4)$	35.1 (±0.4)
	Core	38.9 (±0.2)	21.8 (±0.1)	38.3 (±0.1)	43.3 (±0.2)	45.7 (±0.1)	11.0 (±0.3)
71 GPa	Fp-I	81.1 (±3.7)	18.9 (±3.7)	-	88.1 (±2.2)	11.9 (±2.2)	-
3 min	Brg	49.1 (±1.3)	$2.9 (\pm 0.8)$	$48.0 (\pm 0.7)$	46.4 (±1.2)	$1.7 (\pm 0.5)$	51.9 (±1.0)
	Core	5.9 (±0.5)	91.4 (±0.4)	2.7 (±0.1)	N/A	N/A	N/A

4.3.4 Thermo-chemical diffusion

The laser heating in the diamond anvil cell in accompanied by the generation of large temperature gradients up to 100s of kelvins per micrometer. This gradients gives rise to the thermo-chemical diffusion and separation of elements, also called Soret diffusion. This causes the elements or ions with larger radius to migrate down the thermal gradient and enrich the cold parts of the sample [286, 287]. Therefore, the most pronounced effect of Soret diffusion for mantle samples will be observed for iron. For silicate melts, the Soret diffusion is governed by the Z/r ratio with Z and r being the cation charge and ionic radius [286]. This behavior varies in the solid state sample for Mg, but iron has still shown to segregate into the coldest part [287]. One common effect related to the Soret diffusion is the appearance of metallic iron at the cold edges of the heated zone [379]. We have observed this effect in the single-sided laser heated sample (figure 4.3) with large temperature gradient. However, among the samples molten by double-sided laser heating, this has only been seen in the 30 GPa sample. This



Figure 4.22: HAADF image and the combined EDX maps of Fe, Mg, and Si from the solidus region of the 45 GPa sample heated for 1 minute. Fp and Brg e are representing the ferropericlase and bridgmanite phases respectively. The composition in this region is the same as starting composition.

sample has undergone ~7-8 GPa pressure drop due to the cracks and flaws in the sample and we observed the formation of wadsleyite around the molten core. Although the molten core is still the most iron-rich part of the sample, the presence of metallic iron nano particles in the cold edges of the molten regions indicates that Soret diffusion was active in this sample. However, we have seen no effect of thermo-chemical diffusion in other samples. In fact, the iron is consistently richer in the phases forming in the hotter region closer to the core due to fractional crystallization. This is in contrast with the previous experiments that reported high thermo-chemical diffusion even in the heating duration of 10 seconds [288].

The increase in the thermal gradient can enhance the Soret diffusion. TEM observations show that olivine has transformed to bridgmanite and ferropericlase immediately outside the Fp-I shell in all the samples. The texture in this region is the same as that of the samples heated below the solidus temperature (figure 4.22) [380]. Moreover, the chemical analysis of this region in 0.5*0.5 μ m² areas shows the same composition as the starting material (with less than 0.5 atomic% difference for Fe, Mg, and Si). This indicates that the partial melting started from the Fp-I shell and the melt had no interaction with the solid part outside this shell. Although the exact composition of the sample, especially the content of iron and presence of elements such as Al and Ca, can change the melting temperature, the solidus line of olivine will not change with a moderate change of the Si/(Mg+Fe) ratio due to the eutectic line. Therefore, assuming a similar solidus for olivine as the ones reported for peridotites and pyrolite, the temperature at the melting boundary for 45 GPa sample is close to 2600-3000 K [250, 348, 352]. The laser heating was performed at 3000-3500 K and the radius of the melted region is about 11-13 μ m. Thus, the temperature gradient in these sample is in the range of 30-80 K/ μ m. However, we should note that the fractional crystallization indicates that the temperature profile was changing by time during the laser heating despite the constant temperature measured in the center as demonstrated in the figure 4.23. In 4.23, we did not consider the temperature increase at the beginning of the laser heating. Recent calculation

estimated the time for this temperature increase to be up to \sim 5 ms which is negligible for our experiments [283]. Nevertheless, the Soret diffusion was insignificant or much weaker than the effect of fractional crystallization. This could be explained by efficient convection in the melt to homogenize the temperature [283]. In the solid part, the duration of the experiment is too short to observe a substantial Soret diffusion [287]. Even if we consider the influence of Soret diffusion, it means that the iron enrichment towards the center during the fractional crystallization would be stronger than what we observed in our experiments. Hence, it only strengthens the conclusions of this study.

4.4 Conclusions

In our studies, San Carlos olivine samples are pressurized at 45 GPa and laser heated for 1, 3 and 6 minutes. The ex-situ analysis of the sample with electron microscopy tool have shown that the melt, produced in the beginning of the laser heating, crystallizes over time despite the constant temperature in the center of the laser heating. These results are summarized in figure 4.23. This figure shows the schematic variation of the temperature profile in the molten sample during the laser heating. At the beginning of the laser heating, we expect to have a completely molten region (above liquidus) in equilibrium with the first liquidus phase at the edges of the molten region due to the temperature gradient. By increasing the heating time, the temperature profile has been tapered and, therefore, the melt crystallizes from its edge towards the center. The solidification front continues on the cotectic valley of the phase diagram between the bridgmanite and ferropericlase phases. Therefore, we observe both these phases in the sample. Due to the low iron partitioning coefficient between bridgmanite and melt (K_{Brg/liq}), the liquid gets richer in iron with time and, as a result, the phases formed later and closer to the center of heating are richer in iron. Although the melting will decrease the laser absorption, the iron enrichment in the center increases the absorption and, thus, stabilizes the peak temperature. On the other hand the tapering of temperature profile could arise from the decrease in the laser absorption and heat conductivity in the crystallizing materials. This procedure is important to note for the interpretation of the results in the melting experiment, especially considering the phase sequence in molten samples.

It has been shown that the volume change during melting decreases at lower mantle conditions with increasing pressure and , therefore, the density relation between the melt and the solid depends on the iron partitioning [353, 354, 355, 356]. The first liquidus phase for the mantle composition in most of the lower mantle pressure range, above 30-35 GPa, is expected to be bridgmanite. Our estimated $K_{Brg/liq}$ is in agreement with the lower range of the same value at ~45 GPa reported in the literature and does not changes substantially during the fractional crystallization. Moreover, the $K_{Brg/liq}$ in this study is obtained from the solidification of the liquid phase rather than the partial melting. This makes it more relevant to the crystallization of a magma ocean. Although the first liquidus for olivine composition is ferropericlase at 45 GPa, using the pyrolite or peridotite composition only increases the iron concentration in the melt at the beginning of the melting experiment and, eventually, it will fall on the cotectic

Chapter 4. 3D analytical investigation of melting in lower mantle conditions

valley and continue to crystallize under conditions similar to our experiments. Increasing the pressure to 71 GPa resulted in a sharp increase in the iron content of the melt. Similar increase has been reported before and attributed to the spin transition of iron in the melt. However, the iron partition drop between the solid and liquid observed here is much higher than reported ones [288, 357]. The determination of the exact pressure for this abrupt change and its nature requires more experiments. Nevertheless, since 71 GPa is in the range of the suggested pressure for the top of a basal magma ocean [249, 358], it supports a gravitational stability of the melt at the bottom of the mantle. The subsequent fractional crystallization would produce dense melt with a low melting temperature at the top of core-mantle boundary [249]. The remnant of this liquid or the iron-rich phases crystallizing from this liquid can be the origin of ULVZs observed by seismic surveys [232]. The presence of Fe³ + in the melt core of the sample also suggests the possible formation of Fe³ +-rich phases in the bottom of the mantle.



Figure 4.23: Schematic summary of melting experiments in the LH-DAC and its evolution with increasing heating time. The three columns are showing the temperature profile in LH-DAC, the view of the sample in the central cross section and the respective position of the solidification front on the phase diagram for $t_0 < t_1 < t_2 < t_3$. t_0 is the starting point of the laser heating where we have the melt and the first liquidus phase. In t_1 and t_2 the temperature profile gets narrower and, therefore, the melt crystallizes towards the center and follows the cotectic line between ferropericlase and bridgmanite. The crystallizing phases are getting richer in iron by increasing the time. Thus, there is a Fe composition gradient increasing toward the center of heating. At t_3 the sample is quenched and we have the final sample.

5 Spin and valence dependence of iron partitioning in Earth's deep mantle

5.1 Article

This chapter is the pre-submission version of the article titled "Spin and valence dependence of iron partitioning in Earth's deep mantle" authored by Hélène Piet, James Badro, Farhang Nabiei, Teresa Dennenwaldt, Sang-Heon Shim, Marco Cantoni, Cécile Hébert, and Philippe Gillet that has been published in *Proceeding of National Academy of Science (PNAS)* in 2016. Hélène Piet and James Badro lead the project and performed the high pressure experiments. They have also written the manuscript. The author of the thesis was responsible for STEM imaging as well as EDX mapping and quantification.

5.1.1 Introduction

The relative concentration (partitioning) of iron in minerals constituting mantle rocks is a critical parameter controlling their physical properties, and consequently the dynamical properties of the mantle. In a pyrolitic mantle, the lower-mantle mineral phase assemblage consists of bridgmanite (Brg) – which breaks down to form post-perovskite (PPv) from above 110 GPa [233, 381, 382, 383]– ferropericlase (Fp) and calcium silicate perovskite. Only Brg/PPv and Fp can accommodate significant amounts of iron in their structure. Density, elasticity, viscosity, and thermal or electrical conductivities, along with associated phase relations, melting temperatures, and relative melt/solid buoyancy are all linked to the concentration, speciation, and spin state of iron in lower mantle minerals. The seismic observation of global scale heterogeneities such as LLSVPs [232, 384], and that of experimental iron spin pairing in mantle minerals at lower mantle depths [217, 223], has fueled a number of investigation of Fe-Mg partitioning in the lower mantle [385, 386, 387, 388, 389, 390, 391, 392, 221, 363, 195, 228, 229].

Despite remarkable advances in experimental and analytical techniques in the last two decades (see section 5.2), stark discrepancies have been reported depending on the choice of starting material (San Carlos olivine vs. pyrolite), and those may be attributed to differences

Chapter 5. Spin and valence dependence of iron partitioning in Earth's deep mantle

in bulk composition as well as differences in iron speciation (Fe^{2+} and Fe^{3+}). San Carlos olivine has a molar (Mg+Fe)/Si=2 and contains only iron as Fe^{2+} , whereas pyrolite has a molar (Mg+Fe)/Si=1.4, contains Ca and Al, and iron exists in a range of Fe^{2+}/Fe^{3+} ratios [211], with 50:50 ratio being an average lower mantle value. Therefore, the parameters controlling iron partitioning in deep mantle conditions are complex [387], and hinder any attempts to infer large-scale geophysical of geochemical consequences on the mantle.

To disentangle redox [390, 211], spin [221, 222], and compositional [387] effects on iron partitioning, we measured iron concentration and iron speciation (Fe^{2+}/Fe^{3+} ratio) in Brg/PPv and Fp at lower mantle conditions, in two bulk compositions intermediate between the widely studied San Carlos olivine [385, 386, 392, 221, 363, 222, 393] and pyrolite [391, 228, 229]. These are (1) an alumina-bearing olivine and (2) a calcium-free pyrolite. Neither exist in nature, and were synthesized in the laboratory to be used as compositionally intermediate compounds: Al-bearing olivine is a San Carlos olivine (Mg#90) with the addition of 2 wt.% Al₂O₃, and has a Fe^{2+}/Fe^{3+} ratio similar to that of pyrolite (80:20 in most studies). Ca-free pyrolite has the same iron speciation as pyrolite, but contains no Ca eliminating CaPv from the phase assemblage; as CaPv contains negligible Fe it is not relevant to Fe partitioning at lower mantle conditions.

5.1.2 Materials and methods

Al-bearing olivine and Ca-free pyrolite glasses were produced in an aerodynamic levitation laser furnace, compressed in symmetrical diamond anvil cells at pressures between 28 and 120 GPa, and laser-heated from both sides to temperatures between 2100 K and 2500 K, sticking as close as possible to a mantle geotherm [394] (table 5.1). The samples were heated for 10 to 20 minutes in order to ensure full equilibration of the sample and to grow large enough crystal grains for accurate chemical quantification (figure 5.1). The samples were then quenched and decompressed, and thin sections suitable for analytical transmission electron microscopy analysis were prepared using the FIB lift-out technique (figure 5.3) using Zeiss Nvision 40 (CIME, EPFL) and Zeiss Auriga (IPGP) instruments. Quantitative chemical maps and analysis were obtained in STEM mode (figure 5.1) using energy dispersive x-ray (EDX) spectroscopy performed on a FEI Tecnai Osiris TEM (CIME, EPFL). Iron speciation (Fe²⁺ and Fe³⁺ distribution) was measured on aberration-corrected TEMs, with high spatial resolution and high analytical sensitivity, by electron energy loss spectroscopy (EELS) on a JEOL ARM 200 instrument (LeRoy Eyring Center for Solid State Science, ASU) using a Gatan Enfinium spectrometer and a FEI Titan Themis instrument (CIME, EPFL) using a Gatan GIF Quantum ERS high energy-resolution spectrometer. Quantitative chemical analysis of Brg and Fp phases are reported in table 5.1 for all runs, and more details about sample preparation, synthesis, recovery and analysis can be found in section 5.2.



Figure 5.1: STEM BF image and EDX chemical maps of a Brg and Fp assemblage heated for 15 min at 58 GPa and 2,400 K. Bright-field TEM image (A) of the assemblage and corresponding chemical maps for (B) iron, (C) silicon, and (D) magnesium. The geometry of Fp grains, as well as the identical composition of distinct grains across the sample, is indicative of equilibrium conditions. The central part of the sample shows smaller overlapping Fp and Brg grains; those were never used for quantification.

5.1.3 Results and discussion

The EELS measurements confirm that ferropericlase, like olivine at lower pressure conditions, does not accommodate ferric iron (table 5.1), and contains only Fe2+ as observed previously [390]. Bridgmanite, however, contains both Fe^{2+} and Fe^{3+} , consistent with previous observations [211, 395]. Post-perovskite also exhibits both species, albeit with a significantly lower Fe^{3+}/Fe^{2+} ratio. Ferric iron is therefore entirely contained in the silicate phase and doesn't exchange or partition between Brg/PPv and Fp, while ferrous iron is distributed between both silicate and ferropericlase through a Fe-Mg exchange reaction:

$$(\mathrm{Fe}^{2+})_{Sil} + (\mathrm{Mg}^{2+})_{Fp} \leftrightarrow (\mathrm{Mg}^{2+})_{Sil} + (\mathrm{Fe}^{2+})_{Fp}$$

This reaction describes Fe²⁺ partitioning between both phases, and is the exchange constant

Chapter 5. Spin and valence dependence of iron partitioning in Earth's deep mantle

 $K_D \text{ defined as } K_D = \frac{X_{Fe^{2+}}^{Sil} X_{Mg^{2+}}^{Fp}}{X_{Fe^{2+}}^{Fp} X_{Mg^{2+}}^{Sil}}, \text{ where X is the (molar) concentration of Mg and Fe^{2+} in Fp and Brg/PPv. The effective equilibrium constant <math>K_{eff}$ describes total iron (Fe²⁺+Fe³⁺) partitioning between the two phases, $K_{eff} = \frac{X_{Fe}^{Sil} X_{Mg}^{Fp}}{X_{Fe}^{Fp} X_{Mg}^{Sil}},$ where X is now the (molar) concentration of Mg and total Fe in Fp and Brg/PPv. K_{eff} is correlated with Fe enrichment in the silicate phases.

 K_{eff} is plotted in figure 5.2 along with LHDAC data from the literature obtained with other bulk chemistries (i.e. San Carlos olivine and pyrolite). Our measurements in both Al-bearing olivine and Ca-free pyrolite are fully consistent with the pyrolite dataset [391, 228, 229]. We can discriminate between two discernible behaviors in the comprehensive dataset: Al-free ferrous-iron bearing only systems (San Carlos olivine starting compositions, blue hues in figure 5.2) and Al-bearing systems, containing both ferrous and ferric species (pyrolite, Ca-free pyrolite, and Al-bearing olivine, orange hues in figure 5.2), that are more appropriate to serve as proxies of Earth's bulk lower mantle. Therefore, the long-standing systematic discrepancy in iron partitioning behavior between pyrolite and San Carlos olivine at all pressures is due to the presence of aluminum and to the ensuing Fe²⁺/Fe³⁺ speciation in the system.

At pressures up to 70 GPa K_{eff} is effectively constant (figure 5.2) in both systems, although Keff is roughly twice as high in the Al-bearing system. The invariance of Keff demonstrates that iron partitioning between lower mantle minerals is constant with depth down to about 1700-km depth, regardless of Al-content and iron speciation and is consistent with the absence of strong geophysical signature in the lower mantle to those depths [232, 257]. The relative enrichment of Fe in Brg in the Al-bearing system is the result of the coupled substitution $Fe^{2+}+Si^{4+} = Fe^{3+}+Al^{3+}$, stabilizing Fe^{3+} in that phase [209, 396]. 70 GPa corresponds to the onset of iron spin-pairing in Fp at room temperature [217, 220], where iron enrichment in Fp was predicted [216, 397]. This is indeed observed in both systems (figure 5.2) as a decrease in K_{eff} above 70 GPa, with a notable difference: the Al-free system shows a gradual and constant decrease in K_{eff} (in this case equal to K_D) with pressure up to 100 GPa, whereas the Al-bearing system shows a peculiar behavior, in which K_{eff} decreases to a minimum value at 85 GPa, and then increases up to 100 GPa. At higher pressures, Brg transforms to PPv [382, 383]. In the Al-bearing system, the transformation is accompanied by a sharp decrease in K_{eff}, while in the Al-free system the transformation is accompanied by a sharp increase in K_{eff} . The magnitude of these opposite behaviors is such that K_{eff} is identical in both systems. This particularity is preserved above the transition pressure in the PPv stability field, and both systems exhibit similar partitioning with Keff decreasing with pressure; it is noteworthy that this is the only pressure range, corresponding to the $D^{''}$ region, where both systems exhibit the same behavior.

Our data confirm that iron partitioning in the Al-bearing system is more complicated than that in the Al-free system. The mechanism is explained by changes in iron speciation in Brg/PPv at high pressure coupled with changes in spin state. Iron depletion in the silicate (Brg or PPv) is systematically associated with a drop in Fe³⁺ concentration in the Al-bearing system (figure 5.2), and conversely; the empirical curves describing the evolution of K_{eff} (figure



Figure 5.2: Fe-Mg exchange coefficient between silicate (BRG and PPV) and Fp at lower-mantle pressures and temperatures. Brg and PPv stability fields are separated by the vertical dashed line at ~115 GPa. (A) Effective exchange coefficients K_{eff} obtained from EDX analysis (yellow and purple filled circles) are plotted as a function of pressure. K_{eff} values from previous studies in the San Carlos olivine system [386, 392, 221, 363, 222, 393] and in the pyrolite system [228, 229, 391] are also plotted (see section 5.2 for details). The blue-shaded area delimits the K_{eff} range for Al-free systems, and the orange-shaded are delimits that of Al-bearing systems. Solid lines running through the data were obtained by linear least-squares regression, and the 95% confidence intervals were calculated from the linear model by propagating experimental uncertainties; these mostly serve the purpose of showing that K_{eff} variations above 70 GPa are statistically resolvable. (B) Fe³⁺ concentration in the silicate as a function of pressure from EELS measurements. The line is not fit to the data but is replicated from that obtained in A. The notable match is a strong indication that iron partitioning between lower-mantle minerals in an Al-bearing system follows the evolution of iron valence (i.e., Fe²⁺ and Fe³⁺) distribution in the silicate.

5.2) and that of Fe^{3+} concentration in the silicate (figure 5.2) are identical. A drop in Fe^{3+} implies an increase in Fe^{2+} concentration, and the latter has a strong affinity for Fp as shown by the partitioning behavior in the Al-free system, especially above 70 GPa when it turns to the low spin state in that phase. Therefore, iron depletion from the silicate is expected with decreasing Fe^{3+} and increasing Fe^{2+} concentration, due to the preferential partitioning of Fe^{2+} in ferropericlase; that partitioning is spin-state dependent, and becomes more extreme at pressures above 70 GPa, where iron becomes low-spin in Fp.

The combined dataset presented here clearly shows that iron partitioning in all Al-bearing systems (pyrolite, Ca-free pyrolite, Al-bearing olivine) is identical within uncertainties, regardless of bulk composition, and argues that our results are applicable to Earth's mantle. With Brg/PPv being the dominant interconnected phase in the lower mantle, their properties should strongly influence transport properties [398, 399, 400], and most notably viscosity [401].

Chapter 5. Spin and valence dependence of iron partitioning in Earth's deep mantle

While there is no applicable data on the composition dependence of Brg/PPv deformation, experiments on iron-bearing olivine have shown a clear inverse correlation between iron content and viscosity [402], with higher iron concentrations being less viscous. Assuming that the strength of Brg/PPv exhibits similar compositional dependence, an increase in K_{eff} should result in decreased viscosity. Therefore, high total Fe concentrations in Brg or PPv should result in reduced mantle viscosities [223]. We found a striking correlation between mantle viscosity profiles obtained either by geophysical inversion [403] or predicted by first principles [404], and iron partitioning (K_{eff}) between Brg/Pv and Fp; a viscosity maximum observed at 2000 km depth corresponds to a minimum in both K_{eff} and $Fe^{3+}/\Sigma Fe$ seen at 85 GPa, whereas the viscosity minimum at 2550 km depth fits with a maximum in both K_{eff} and $Fe^{3+}/\Sigma Fe$ at 100 GPa (figure 5.7). The lack of sensitivity below 2500 km precludes the accurate inference of viscosity from geophysical data, and the question remains open from the point of view of mineral physics. On the one hand, PPv is a weaker phase than Brg [400] and should be less viscous for a given composition; on the other we find that the Fe^{3+} content is very low in PPv, as well as the total iron content (figure 5.2), which would drive viscosity up. Additional experimental and DFT investigations are needed to resolve these competing effects.

It has been proposed that the viscosity high at 1000 km [403, 404, 405] is correlated with stagnating slabs and fast regions inferred from seismic tomography [406]. The strong viscosity contrast between 80 GPa and 120 GPa suggested here should strongly affect mantle dynamics below 1800 km, a depth coincidental with increasing chemical heterogeneities and the top of the LLSVP thermochemical piles. These structures are currently thought of as being primordial [384], dating back to the initial settling and freezing of Earth's Magma Ocean after accretion 4.5 Ga ago. The question of their stability [407], and how they anchor above the core-mantle boundary over geologic time, is still unsolved. We propose that a weak lowermost mantle (below 2000 km) topped by a stiffer mantle (1800-2000 km) could dynamically decouple the base of the mantle from the overlying mantle, which would in turn stabilize large structures, such as LLSVPs, below 2000 km depth.

5.2 Supplementary information

5.2.1 Experimental and analytical procedure

starting material preparation

High purity powders of MgO, FeO, and SiO₂ were finely ground and mixed together under ethanol to produce a natural San Carlos olivine composition (9.6 wt.% FeO). High purity alumina powder was added to the mix to obtain a total Al₂O₃ concentration of 2.0 wt.% (table 5.1). The powders were dried and pressed into pellets, and then fused at 2100 °C for 60 seconds in an aerodynamic levitation laser furnace [408] using argon carrier gas. Temperature was quenched at 1000 K/s to obtain a glass. A chip from each sample was then imaged with backscattered electrons using a field-emission scanning electron microscope. The sample was homogeneous and contain no grains at any scale; further energy dispersive x-ray analysis of the starting material were performed, and revealed no chemical heterogeneities in the sample for all elements.

High-pressure and high-temperature synthesis

Chips of the glassy starting material were pressurized in symmetrical diamond anvil cells, in a laser-drilled rhenium gasket (30-45 μ m thick, 70-150 μ m diameter hole). Flat 300 μ m, 200 μ m, and beveled 300/150 μ m diamond culets were used. Pressure was measured from the Raman shift of previously calibrated diamond anvils [409]. The samples were then laser-heated from both sides using a 200 W infrared fiber laser, to temperatures between 2100 K and 2450 K, sticking as close as possible to a mantle geotherm [394] (table 5.1). Temperatures were measured by spectroradiometry [273]. The samples were heated for 10 to 20 minutes in order to ensure full equilibration of the sample and to grow large enough crystal grains for accurate chemical quantification. After laser-heating the samples were instantly quenched by switching off laser power. The samples were then decompressed and prepared for subsequent microanalysis.

Sample preparation for TEM analysis: the FIB technique

Thin sections suitable for TEM analysis were prepared using the FIB lift-out technique (figure 5.3). We used Zeiss Nvision 40 (CIME, EPFL, Lausanne) and Zeiss Auriga (IPGP, Paris) instruments. We first deposited a 1.5 μ m thick carbon or platinum layer on top of the sample, in the zone corresponding to the center of the laser-heated area (figure 5.3). This prevents the sample from ion beam damage during excavation by milling around. Sample was excavated around the carbon deposit (figure 5.3) using a focused gallium ion (Ga⁺) beam operated at 30 kV and different currents in the 1-27 nA range. A (15x20x2) μ m section was then extracted with a micromanipulator and transferred to an omniprobe TEM copper grid for further thinning (figure 5.3). We then switched to a lower range of currents (80-700 pA) for thinning the sample down to electron transparency. TEM analysis require a thickness of the sample between 50-100 nm. Given the uncertainty in thickness measurements while in ion imaging, we thinned the sample until we reached electron transparency in SEM imaging with the electron beam operated at 4 kV. This was enough to provide good quantitative analysis for the two quantitative techniques used and described hereafter (TEM-EDX and EELS). Final polishing of the thinned area was performed operating the ion beam voltage of 5 kV with a current of 30 pA to remove the deposition from the milling process.

Chemical analysis by EDX spectroscopy

Chemical analysis were obtained by energy dispersive x-ray (EDX) spectroscopy and performed using Analytical TEM (ATEM), on a FEI Tecnai Osiris (CIME, EPFL, Lausanne) operated





Figure 5.3: a) Optical image of the sample viewed through the diamond anvils in-situ at high pressure. The dark area represents the transformed and equilibrated (laser-heated) area. b) Secondary electron image of the sample after decompression. c) Gallium ion image of excavation, obtained after milling around the center of the heated spot, and protected on top by a carbon or a platinum layer. d) Secondary electrons image of transferred sample on a TEM Cu grid. The thin section is thinned to electron transparency (thickness < 100 nm) for EDX and EELS TEM analysis.

at 200 kV to image the sample in Bright-Field (figure 5.1) as well as High Angle Annular Dark Field modes. Typical EDX spectra are shown in figure 5.4. Chemical maps were acquired in STEM mode for 500 to 1000 seconds to minimize analytical uncertainties (figure 5.1). Quantitative measurements were then performed on individual grains by deconvolution of selected areas, after Bremsstrahlung background subtraction, using Fe, Mg, Si, O and Al K alpha lines. A TEM thin section from the starting glass material was also prepared by FIB technique to provide the precise composition of the starting material, using the same quantification protocol as the high-pressure samples (table 5.1).

Characterization of iron valence state

The ARM200 was operated in a TEM mode at 120 kV. In order to avoid electron beam induced sample damage, particularly changes in the oxidation state of Fe, we expanded the electron beam (up to ~200 nm in diameter, but smaller than the size of individual grains). With similar concerns regarding sample damage, the Titan showed optimal performance when operated at 300 kV in STEM mode. On both microscopes, spectra were acquired for 10 to 30 s preventing beam damage of the silicate matrix and ensuring a signal good enough for deconvolution of



Figure 5.4: EDX spectrum obtained from Fp (left) and Brg (right). Energy distribution corresponding to x-ray emissions from characteristic chemical elements. Peak height is correlated to element concentration in the investigated zone. The spectrum for ferropericlase shows no peak for Si and Al, in good agreement with the absence of these two elements in the mineral structure.

spectral features from acquired spectra.

The energy resolution was < 1 eV, estimated from the full width at half maximum of the zeroloss peak. The fraction of ferric iron was determined by the EELS analysis methods in van Aken [359]. In the analysis, we used the EELS spectra of olivine and pyroxene as a ferrous iron standard and the EELS spectrum of andradite as a ferric iron standard, all of which are measured using the instrument in the same analytical conditions as when measuring the samples. We subtracted the background following the method described in van Aken [359]. The spectra were then fitted by minimizing (least squares) the residual of the linear combination of ferrous and ferric iron standard spectra (figure 5.5).

5.2.2 Results

TEM imaging and EDX mapping (figure 5.1) reveal that mineral assemblages are mainly composed of Fp grains embedded in an amorphous Brg matrix, in equal proportions as it is usually observed for samples equilibrated from olivine [221, 222]. Ferropericlase grains size ranges between 50 and 400 nm, with a texture characteristic of full chemical equilibration and growth [221, 390]. We observe no significant chemical heterogeneities among minerals investigated in different areas of the samples. These observations preclude any substantial chemical diffusion (Soret) during laser-heating that could have biased the chemical analysis. Fp grains used for quantification are essentially Si-free (figure 5.1) ensuring no contamination from overlap with Brg in chemical analysis (table 5.1).

Iron partitioning at lower mantle conditions has been thoroughly investigated in the simple San Carlos Olivine [385, 386, 392, 221, 363, 222, 393] and the complex pyrolite [391, 228, 229] systems. Besides the clear discrepancy in iron partitioning between these two systems (figure

Chapter 5. Spin and valence dependence of iron partitioning in Earth's deep mantle



Figure 5.5: EELS spectra of Fp (left) and Brg (right) in ALOL-86. The black dots are measurements on the sample, whereas the red and blue curves are the measurements from the standards (olivine for pure Fe²⁺, and andradite for pure Fe³⁺, respectively. The green curve is the calculated spectrum obtained by a least-squares fit using the two standards. The thin black line is the residual of the fit. The red and blue vertical bars show the energies of the Fe³⁺ and Fe²⁺ peaks, respectively. a) Ferropericlase shows no Fe³⁺ signature and is hence only composed of Fe²⁺ iron, b) while bridgmanite (here at 86 GPa) has a Fe³⁺/ Σ Fe value of 0.19 ± 0.03.

5.2), discrepancies are also reported amongst data sets treating identical bulk compositions. In figure 5.2 we show only the experimental values of K_{eff} that were not affected by experimental artifacts, and are thus consistent with P, T conditions along the lower mantle geotherm. We discuss the robustness of these data in the next section and refer to measured data as K_{eff} values. In following sections, we discuss observed changes in Fe³⁺ content of the silicate with increasing pressure and the effect on mantle rheology.

Iron partitioning data from the literature

The San Carlos olivine system

Two studies [221, 222] report an increase of iron content in Fp from 70 to 100 GPa, which they associate with the spin transition of ferrous iron from high spin to low spin state [217, 216]. A volume collapse of iron following the spin transition indeed favors the incorporation of low spin species into Mg-sites, resulting in an increased affinity of iron for Fp (figure 5.2). However, other studies on iron partitioning in the olivine system do not report this effect [363, 392].

Kobayashi et al. [392] report values of K_{eff} (below 0.2) in the Brg stability field systematically lower than all other studies; this could be due to the choice of low equilibration temperatures, several hundred Kelvin below the other studies (and far from a plausible mantle geotherm). For this reason, their data was discarded from our subsequent analysis. Sinmyo et al. [363] report strong heterogeneities in Fp compositions caused by extensive iron diffusion (Soret) towards the edges of the heated zone where temperatures are highest. Such non-equilibrium conditions preclude the use of such data for a proper thermodynamic quantification, as suggested by the authors. Hence, the data from that study was also discarded from subsequent analysis. Iron diffusion during laser heating is almost inevitable, but our samples only show minor iron depletion (less than 10% total iron loss).

Sakai et al. [393] report two significantly different values of K_{eff} measured in the same sample at 140 GPa. The sample experienced iron depletion in one part ($K_{eff} = 0.44 \pm 0.13$) and iron enrichment in another part ($K_{eff} = 0.04 \pm 0.01$) producing markedly different values due to accordingly different Fp compositions. Hence, that point was discarded from the dataset.

Auzende et al. [221] also measure an anomalously high K_{eff} value (0.66 ± 0.05) at 115 GPa compared to other data from the literature (K_{eff} below 0.5). They estimate the silicate to be PPv, despite the absence of XRD analysis. However all subsequent measurements on the PPv phase showed markedly lower partitioning values. Hence, that anomalous point was discarded from the author's dataset.

The pyrolite system

The high value of K_{eff} (0.90 ± 0.14) at 114 GPa from Sinmyo and Hirose [228] is intriguing. In the study of Sinmyo et al. [410] that same sample was characterized as Brg, and pressure was estimated at 93 GPa (20 GPa lower), a difference which easily spans the Brg/PPv transition. Moreover, the K_{eff} value of ~1.12 in 2011 was recalculated at 0.90 in 2013. Such uncertainties on the conditions of synthesis preclude any use of that point in the global model. For the same reasons, the value of Sinmyo et al. [410] for PPv at 135 GPa (K_{eff} = 0.22) was also scraped.

Prescher et al. [229] report a silicate phase as Brg though very clearly in the PPv stability field (130 GPa, 2500 K), probably indicating metastable conditions during synthesis. The data point was also discarded. Our data above 110 GPa lack in-situ characterization of the silicate structure (Brg vs. PPv). However, our measured K_{eff} values are identical to those observed by Sinmyo et al. [363], Sakai et al. [393], Kobayashi et al. [392] and Murakami et al. [391] where the silicate is confirmed as PPv by XRD. Low ferric iron contents in PPv (25% ferric iron vs. 40% on average in Brg) are another argument supporting the PPv structure in our silicates at the highest pressures.

Iron valence state in bridgmanite

The respect of charge neutrality of a crystallographic structure rules the possible cation substitutions in cation sites. In bridgmanite, Fe^{2+} for example, simply exchanges with Mg^{2+} in dodecahedral sites. On the other hand, the stabilization of Fe^{3+} in the structure is less straightforward, and aluminum is found to play a key role [211, 390]. Amongst all possible substitution mechanisms investigated by Richmond and Brodholdt [209], the 1:1 coupled substitution of Fe_{3+} and Al_{3+} , respectively in the dodecahedral Mg-site and the octahedral Si-site, is the mechanism that requires the minimal amount of energy and hence the most

favorable:

$$Fe_{A-site}^{2+} + Si_{B-site}^{4+} \rightarrow Fe_{A-site}^{3+} + Al_{B-site}^{3+}$$

$$(5.1)$$

A-site and B-site stands respectively for the dodecahedral Mg-site and the octahedral Si-site.

In Al-free systems or if Al content is too low to satisfy the conditions of eq. 5.1, the incorporation of Fe^{3+} similarly involves the substitution of two Fe^{3+} in both the dodecahedral and the octahedral sites:

$$Fe_{A-site}^{2+} + Si_{B-site}^{4+} \rightarrow Fe_{A-site}^{3+} + Fe_{B-site}^{3+}$$

$$(5.2)$$

charge balancing the electronic structure of the mineral. In the case where Al^{3+} is in excess over Fe³⁺, the incorporation of Al^{3+} follows the same mechanism:

$$Mg_{A-site}^{2+} + Si_{B-site}^{4+} \rightarrow Al_{A-site}^{3+} + Al_{B-site}^{3+}$$

$$(5.3)$$

entering adjacent dodecahedral and octahedral sites. These mechanisms do not involve the creation of oxygen vacancies.

At pressures below 75 GPa, Al/Fe^{3+} ratios in the silicate are close to unity implying that ferric iron incorporation mainly occurs following the coupled substitution of the two species in eq. 5.1 (figure 5.6). However, above 75 GPa, Al/Fe^{3+} ratios significantly exceed one, implying incorporation of excess aluminum through the mechanism described in eq. 5.3.

Viscosity in the lower mantle

Experimental estimates of the viscosity of mantle minerals can be obtained by deformation experiments at high P and T. Such measurements on lower-mantle mineral assemblages have only been performed, to date, to pressures up to 28 GPa [401].

Figure 5.7 shows that the trend of K_{eff} in the Brg stability field (figure 5.2) is strongly anticorrelated with the radial viscosity profile determined by Forte and Mitrovica [403]. This corroborates the idea that variations of the iron content in Brg are responsible for rheological variations observed in the mantle. Indeed, a decrease of iron content in Brg could make the material stronger, as is the case for olivine[402] and Fp [411], which might, in turn, affect the viscosity of the whole mantle. The rheological properties of a PPv-dominated mantle, on


Figure 5.6: Substitution mechanisms for incorporation of Fe^{3+} in the silicate structure. The most energetically favorable mechanism for stabilizing Fe^{3+} in the silicate structure is through the coupled substitution of Fe^{3+} in the dodecahedral site and Al^{3+} substitution in the octahedral site (eq. 5.1). This reaction takes place along the black dashed line and requires equal amounts of Fe^{3+} and Al^{3+} in the silicate. When ferric iron (orange spheres) or aluminum (blue spheres) are in excess in the system, their incorporation in the silicate is possible via a similar mechanism (respectively eq. 5.2 and 5.3) where they charge balance each other in adjacent sites.

the other hand, would most likely be different from that of a Brg-dominated mantle, given the structural change and the different intrinsic viscosity of the mineral. However, the lack of sensitivity of the radial viscosity models at those depths does not allow estimation of any possible viscosity change associated with the phase transition in the silicate.

Chapter 5. Spin and valence dependence of iron partitioning in Earth's deep mantle

Table 5.1: Synthesis conditions of phase assemblages and corresponding chemical analysis. Temperature is determined from the average temperature over the entire run, and the value in parentheses corresponds to the maximum temperature variation during heating (this is not the 1-sigma standard deviation). Pressure is measured from the first order Raman peak of the anvils [409]. Chemical composition of the starting material (SM) and of equilibrated samples of ferropericlase (fp) and silicate (sil: Brg or PPv), measured by TEM-EDX. Element concentrations for the silicate and ferropericlase are given in cations per formula units; standard deviations are in parentheses. OL stands for the Al-rich olivine composition while PYR corresponds to the Ca-free pyrolite composition. Fe* is the total iron.

Run	SM-OL		SM-PYR		OL-28		OL-36		PYR-40		OL-45	
P (GPa)					28 (1)		36 (2)		40 (2)		45 (2)	
T (K)	oxides (wt.)	%)	oxides (wt.9	6)	2100 (100)		2400 (200)		2150 (125)		2200 (100)	
Phase					sil	fp	sil	fp	sil	fp	sil	fp
Mg	41.7 (11)		37.7 (12)		0.87 (7)	0.83 (9)	0.89 (2)	0.85 (8)	0.87 (2)	0.80 (3)	0.93 (3)	0.82 (15)
Fe *	9.9 (7)		8.2 (7)		0.077 (9)	0.14 (2)	0.074 (3)	0.13 (1)	0.091 (11)	0.17 (1)	0.071 (5)	0.14 (3)
Si	45.9 (6)		48.8 (6)		1.00 (5)	0.014 (5)	1.00 (2)	0.012 (2)	0.97 (2)	0.018 (1)	0.98 (2)	0.019 (8)
AI	2.5 (1)		5.2 (1)		0.038 (7)	0.002 (1)	0.031 (1)	0.002 (1)	0.062 (4)	0.002 (1)	0.030 (2)	0.003 (1)
K _{eff}					0.51 (9)		0.57 (5)		0.50 (6)		0.46 (6)	
Fe ³⁺ /∑Fe	0.25 (4)				-		-		-		0.38 (3)	ND.
Run	OL-58		OL-73		OL-86		PYR-93		PYR-116		OL-118	
P (GPa)	58 (3)		73 (4)		86 (4)		93 (5)		116 (6)		118 (6)	
T (K)	2400 (50)		2100 (50)		2400 (100)		2350 (150)		2450 (130)		2300 (75)	
Phase	sil	fp	sil	fp	sil	fp	sil	fp	sil	fp	sil	fp
Mg	0.91 (2)	0.83 (11)	0.92 (3)	0.80 (18)	0.92 (2)	0.84 (6)	0.96 (3)	0.87 (20)	0.89 (2)	0.79 (13)	0.93 (2)	0.84 (6)
Fe *	0.073 (3)	0.13 (2)	0.071 (6)	0.12 (3)	0.060 (5)	0.14 (1)	0.077 (10)	0.11 (3)	0.057 (2)	0.18 (3)	0.043 (3)	0.14 (1)
Si	0.99 (3)	0.017 (7)	0.99 (2)	0.041 (12)	0.99 (3)	0.009 (3)	0.94 (4)	0.008 (5)	0.98 (2)	0.014 (9)	0.99 (1)	0.008 (3)
AI	0.031 (1)	0.001 (1)	0.023 (5)	0.001 (1)	0.028 (2)	0.001 (1)	0.062 (3)	0.002 (1)	0.064 (2)	0.003 (1)	0.030(1)	0.001 (1)
K _{eff}	0.52 (4)		0.53 (6)		0.40 (4)		0.64 (11)		0.29 (2)		0.27 (3)	
Fe ³⁺ /∑Fe	0.39 (4)	ND.	0.41 (3)	ND.	0.19 (3)	ND.	0.43 (3)	ND.	0.23 (4)	ND.	0.20 (3)	ND.



Figure 5.7: Radial viscosity profile of Earth's lower mantle. Radial viscosity models proposed by Forte and Mitrovica [403] are plotted in gray. The orange curve is the superimposed iron partitioning (K_{eff}) evolution with pressure (from figure 5.2) for Al-bearing systems systems relevant to the lower mantle (the dashed part corresponds to the range without data). The blue-white color gradient is a visual representation of Fe concentration in the silicate phase. The figure shows a striking correlation between increasing viscosity above 75 GPa and iron depletion in the silicate at the same pressure. Above 110 GPa, however, the silicate structure changes from Brg to PPv where Fe concentration is even lower. However, the deformation mechanism as well as the very high anisotropy of the PPv phase precludes any simple assessment of the evolution of viscosity at this depth.

6 Composition and Pressure Effects on Partitioning of Ferrous Iron in Ironrich Lower Mantle Heterogeneities

This chapter is the submitted version of the manuscript titled "Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities" authored by Susannah M. Dorfman, Farhang Nabiei, Vitali B. Prakapenka, Marco Cantoni, James Badro, and Philippe Gillet that is currently under review for publication in Physics of Earth and Planetary Interiors (PEPI). Susannah Dorfman lead the project and performed the high pressure experiments. She has also written the manuscript. The author of the thesis was responsible for STEM imaging and EDX spectroscopy.

Introduction 6.1

Iron-enrichment has been suggested to explain seismic observations of dense regions in the deep lower mantle such as large low shear velocity provinces (LLSVPs) and ultra-low velocity zones (ULVZs) (e.g. [412, 248]). For LLSVPs, the difference in Fe/(Mg+Fe), or Fe#, relative to the surrounding mantle is inferred to be as much as 7% based on estimated chemical density differences up to 2% [413]. ULVZs may be more dramatically enriched in Fe to generate density differences of 10% or more. The origin of these regions is unknown, but possibilities include segregation of dense material in a basal magma ocean beneath the crystallizing early mantle [249] and accumulation of dense material from subducted slabs [414]. Understanding geophysical observations has motivated numerous studies on the dependence of physical properties including elasticity, rheology, and electrical and thermal conductivities on Fecontent of mantle phases. The compositions of mantle phases, and thus their properties, are moderated by partitioning.

Iron in Earths lower mantle is distributed between (Mg,Fe,Al)(Fe,Al,Si)O₃ bridgmanite (Bdg), its polymorph (Mg,Fe,Al)(Fe,Al,Si)O₃ post-perovskite (pPv), and (Mg,Fe)O ferropericlasemagnesiowstite (Mws). Partitioning between these phases is characterized by the exchange coefficient, K_D , between coexisting silicate and oxide, related to their compositions, X, in equilibrium, where values less than 1 indicate that iron favors the oxide, and values greater than 1 the reverse:

$$K_D = (X_{Fe}^{Silicate} / X_{Mg}^{Silicate}) / (X_{Fe}^{Mws} / X_{Mg}^{Mws})$$
(6.1)

Previous experiments have explored silicate-oxide partitioning behavior primarily using San Carlos olivine and pyrolite compositions as analogues for the mantle [388, 221, 415, 195, 416, 417, 386, 418, 229, 222, 393, 228, 363, 410]. Due to challenges entailed in modeling iron, computational studies using density functional theory have only recently begun to address partitioning in the lower mantle [419]. Previous studies found that K_D is ~0.2-0.3 in San Carlos olivine near 660-km depth, but substantially higher in pyrolite. The higher K_D in pyrolite is due to incorporation of Al and ferric iron in Bdg [380]. In ferrous-iron-bearing olivine compositions, K_D decreases or remains constant with pressure and increases with temperature and oxygen fugacity.

The dependence of the exchange coefficient on bulk iron content is key to understanding dense mantle heterogeneities. Studies of silicate-oxide iron partitioning in iron-rich compositions with Fe#>16 have found that the exchange coefficient decreases with increasing amounts of ferrous iron, but these studies have been limited to <50 GPa [417, 418, 420]. Effects of ferrous iron enrichment on partitioning have been examined to deep lower mantle conditions only in inhomogeneous samples affected by experimental thermal gradients [363] or in relatively iron-poor compositions [222, 393, 410]. However, partitioning in lower mantle minerals may change at pressures >50 GPa and high ferrous iron content due to composition-dependent structural and electronic changes in bridgmanite.

At the boundary between the transition zone and lower mantle, bridgmanite is stable with no more than 12 mol% FeSiO₃, but in the deep lower mantle the solubility limit increases to at least 75% FeSiO₃ [421, 422, 417, 420, 423]. An increase in solubility may be linked to structural distortion in Bdg and corresponding bonding changes for ferrous iron predicted by density functional theory [424] and confirmed by X-ray diffraction of single-crystals [425]. The increase in solubility of iron in Bdg in the deep mantle may also be due to composition-dependence of a high-to-low electronic spin transition in ferrous iron [426]. Since the discovery of pressure-induced spin transitions in ferropericlase [217] and bridgmanite [223], these electronic changes have been explored for their potential effects on partitioning (e.g. [221, 229]) as well as other mantle properties. Differences in Fe-content and Fe³⁺/ Σ Fe control the conditions at which spin transitions and partitioning changes occur in the mantle [216, 397]. In San Carlos olivine, ferrous iron undergoes a high-to-low spin transition in Mws but remains high-spin in Bdg throughout the lower mantle pressure range; whether this holds true for more iron-rich compositions has been unknown.

At conditions corresponding to the base of the lower mantle, post-perovskite has also been observed to incorporate at least 80% FeSiO₃ [427]. Most studies found that Fe-rich pPv is

Sample	Fa45		Fa72				
	Weight %	Formula	Weight %	Formula			
SiO ₂	35.59(14)	0.994(3)	33.00(16)	1.009(4)			
MgO	26.7(3)	1.112(11)	12.3(6)	0.56(2)			
FeO	38.6(4)	0.901(9)	55.5(6)	1.42(2)			
Total	100.9(4)	3.006(3)	100.8(4)	2.990(4)			
Fe/(Mg+Fe)		0.448		0.717			
(Mg+Fe)/Si		2.025		1.963			

Table 6.1: Microprobe results for compositions of synthetic olivine starting materials.

stable at lower pressures than Fe-poor pPv (e.g. [427]), suggesting that iron prefers pPv to Bdg. Partitioning of iron from Bdg into pPv is supported by observations of higher K_D for pPv-Mws than for Bdg-Mws when olivine is used as a starting material [221]. Conversely, diffraction and microscopy studies of coexisting Bdg and pPv have observed the reverse in pyrolitic starting materials: a preference of iron for Bdg over pPv [428, 423]. The conflict between these studies has been attributed to differences in speciation of iron. Partitioning of iron in bridgmanite and post-perovskite at these higher pressures determines whether Fe-enriched silicate phases can explain dense heterogeneities in a potentially SiO₂-rich deep lower mantle [196, 412].

Constraints on chemistry at extreme conditions are best obtained by a combination of in situ phase identification and ex situ composition measurements. In situ X-ray diffraction (XRD) is required to determine the high-pressure phase assemblage, as mantle silicates including Fe-rich Bdg and pPv become amorphous upon quench to ambient conditions. Compositions of all phases can be measured to percent-level under best conditions using a combination of focused ion beam (FIB) and analytical transmission electron microscopy (TEM) [429, 430]. The FIB allows extraction and polishing of samples synthesized in the diamond anvil cell for nm-scale compositional measurements in the TEM. In this study, we apply XRD, FIB and TEM techniques to the partitioning of Fe in Fe-rich mantle phase assemblages synthesized in the laser-heated diamond anvil cell at deep lower mantle conditions.

6.2 Methods

Synthetic fayalite-rich olivines with compositions $(Mg_{0.55}Fe_{0.45})_2SiO_4$ (Fa45) and $(Mg_{0.28}Fe_{0.72})_2SiO_4$ (Fa72) were used as starting materials. Olivines were synthesized from stoichiometric mixtures of MgO, SiO₂, FeO, and a small amount of Fe₂O₃ to compensate for nonstoichiometry in FeO. Oxide powder mixtures were reacted in a reducing graphite capsule in a piston-cylinder press (IPGP, Paris) at 1 GPa and 1200°C for 15 hours to produce ~300- μ m olivine crystals. Olivine compositions were determined with the JEOL 8200 Superprobe at the University of Lausanne (table 6.1).

Single olivine crystals were crushed into $3-10-\mu$ m-thick platelets and sandwiched between insulating platelets of NaCl or MgO. Materials were dried in a 120° C oven overnight to remove

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.1: Scanning electron micrograph of thin section extracted by focused ion beam (FIB) from Fa45 sample heated to 2000 K at 40 GPa at APS GSECARS.

moisture before loading. Sample assemblages were loaded in symmetric diamond anvil cells with $300-\mu$ m-diameter flat anvil culets or $100-150-\mu$ m-diameter beveled anvil culets. Gaskets were Re sheets indented to $\sim 25-\mu$ m thickness.

Samples were compressed to 33-128 GPa in the diamond anvil cell and laser-heated from both sides to 1900-3000 K. Pressures were determined at 300 K from the diamond anvil Raman peak at the sample position [409] or the equation of state of the NaCl medium [431]. Laser heating was performed for 15-60 min at beamline 13-ID-D of the GSECARS sector of the Advanced Photon Source or at the Earth and Planetary Science Laboratory at Ecole polytechnique frale de Lausanne (EPFL). The laser heating system at GSECARS provides a flat-top beam profile for minimal temperature gradients at the sample center [432] and was co-aligned with the ~3-4 micron focused synchrotron X-ray beam (37077 eV) by visually observing X-ray-induced fluorescence on each sample. The MAR-CCD imaging detector was used to record highresolution X-ray diffraction in situ at high-pressure and high-temperature conditions. In situ X-ray diffraction is not available during experiments at EPFL. The EPFL system uses a single 1070 nm wavelength, 200 W fiber laser in Gaussian mode divided for double-sided heating using a polarizing beamsplitter. The two sides are independently controlled with rotating wave-plates and focused with 60 mm achromatic lenses. For both GSECARS and EPFL systems the hot spot has a diameter of $\sim 20 \ \mu m$. Temperature was determined throughout heating by spectroradiometry [433] over 620-900 nm spectral range. Samples were quenched directly from lower mantle temperature conditions by zeroing the laser power.

Chemical analysis of the quench products of these experiments were obtained by electron microscopy. After recovery to ambient conditions, each sample was prepared for ex situ



Figure 6.2: Scanning electron micrograph of thin section extracted by focused ion beam (FIB) from Fa72 sample heated to 2000K at 52 GPa at EPFL.

imaging and sectioning. The NaCl medium was dissolved from the surface of each silicate sample with a droplet of deionized water. Each sample was then coated with 10-20 nm of carbon. Heated spots were identified by color (black and opaque, vs. transparent unheated olivine) and radially-symmetric topography. Although the diameter of the entire laser-heated area is ~20 μ m, the diameter of the hottest part of the sample is ~4 μ (figures 6.1-6.2). The hottest region exhibits voids at grain boundaries, due possibly to water or release of strain, and larger grain sizes and higher modal abundance of bridgmanite relative to cooler regions.

Thin sections of each heated spot were extracted and polished to electron transparency using a Zeiss NVision 40 dual-beam scanning electron microscope and focused Ga+ ion beam. To prevent damage by the ion beam, a protective layer of carbon 1-2- μ m thick was deposited over a ~2x20 μ m area across the center of each heating spot. Additional carbon patches were deposited to support particularly thin (~1- μ m-thick samples recovered from ~1 Mbar pressure) or fragile samples (with cracks or holes). Slices were milled to 1-2- μ m thick at 30 kV and 1.5-27 nA before transfer to TEM grid. The center of each slice was then polished to 100-200-nm thickness at 30 kV and 300 pA. Final cleaning and polishing was performed at 5 kV and 80 pA at a 5° angle to the surface. As in previous work [221], a few slices were lost during the lift-out procedure.

Sections were transferred to a FEI Tecnai Osiris analytical TEM for composition analysis. Accelerating voltage for these measurements was 200 kV. To avoid selective migration of elements from measurement spots [434], chemical measurements were obtained in scanning mode from maps. EDX maps were acquired at 10,000-50,000 (typically ~40,000) counts/second with pixel dwell time of 50 microseconds scanned over 1024x1024 pixels for total scanning

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities

time ~10 min. Compositions of individual grains were summed over selected ~100 nm regions within maps. In the hot spot centers, two samples had grain sizes smaller than the 100-200-nm thickness of the polished thin section and due to grain overlap were not suitable for composition analysis. Grain sizes decreased significantly at higher pressures, requiring longer heating times. We evaluated the quality of chemical measurements from the Si-content measured in oxide grains due to overlap with silicate grains. All measurements included in this study have less than 4% Si/(Mg+Fe+Si) measured in magnesiowstite. Compositions measured for samples obtained via EDX are listed in table 6.2 and table 6.3. Reported uncertainties are standard deviations of composition measurements for selected grains used for composition measurements in each sample.

6.3 Results

6.3.1 Phase identification

Phases and compositions were identified ex situ for all experiments as well as in situ for experiments conducted at GSECARS with X-ray diffraction. Diffraction patterns recorded at heating spot centers after temperature quench exhibited peaks corresponding to bridgmanite, magnesiowstite, stishovite, and a single peak attributed to CaIrO₃-type post-perovskite (figures 6.3-6.4). In the Fa45 composition from 40-89 GPa (all pressures studied with X-ray diffraction), all observed diffraction peaks match Bdg or Mws (figure 6.4). In Fa72 at 33 GPa, corresponding to the shallow lower mantle, stishovite is also observed (figure 6.5). The exsolution of stishovite indicates that bridgmanite cannot accommodate all available iron and breaks down to a mixture of bridgmanite, stishovite and magnesiowstite. At higher pressures, the solubility of Fe in Bdg increases [421, 420, 423], and the stishovite phase disappears. Identification of stishovite and magnesiowstite by EDX in recovered samples concurs with observations by X-ray diffraction. Pure SiO₂ regions were identified in composition maps of samples synthesized at higher pressures (figure 6.5, table 6.2).

Although Fe metal droplets have been observed in multiple previous studies of lower mantle phase assemblages [212, 221, 392], they were not typically present in samples analyzed in this work. In one sample Fe metal droplets were embedded in a large grain of nearly pure FeO (figure 6.6). Unlike these droplets, Fe-rich inclusions in Bdg grains were not typically depleted in oxygen (figure 6.7). In contrast to previous experiments on less Fe-rich compositions, we do not observe Fe metal grains within Bdg due to disproportionation. This lack of metallic Fe is evidence that iron remains ferrous after synthesis of the lower mantle phase assemblage.

Silicates bridgmanite and post-perovskite in recovered samples could not be distinguished due to amorphization. With one exception, Bdg was amorphous (e.g. figure 6.8); Bdg with high Fe-content (Fe#≥38) is not quenchable [421]. The amorphous silicate is the interconnected phase, as Bdg has been in previous studies [221]. Fe#4 Bdg in the sample loaded in MgO was successfully quenched, and crystalline Bdg was observed before composition mapping.



Figure 6.3: Diffraction patterns for phase assemblages synthesized from Fa72 at 33-89 GPa. Bdg=bridgmanite, pPv=post-perovskite, Wus=wstite, Sti=stishovite, N=NaCl medium. Reference stick patterns for Bdg and Sti are provided below. For these experiments, $\lambda = 0.3344$ Å.

Bridgmanite lattice planes subsequently disappeared after composition mapping due to damage by the electron beam. Crystalline (Mg,Fe)SiO₃ pPv is also not quenchable to ambient conditions, and we were thus unable to conclusively identify a pPv phase in recovered samples. A single amorphous silicate phase quenched from synthesis at 128 GPa is assumed to have been post-perovskite.

6.3.2 Compositions of coexisting phases and partitioning

The compositions determined from EDX mapping for bridgmanite and magnesiowstite are listed in table 6.2 and table 6.3. Listed uncertainties in measured compositions and partitioning coefficients were obtained from a standard deviation of compositions of multiple grains, and may still be an underestimate due to sample topography and matrix effects. The total Fe# of the phase assemblage is within 6 Fe# of the starting materials (note that for phase

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.4: Diffraction patterns for phase assemblages synthesized from Fa45 at 40-89 GPa. Bdg=bridgmanite, Mws=magnesiowstite, N=NaCl medium. Reference stick pattern for Bdg is plotted below. For these experiments, $\lambda = 0.3344$ Å.

assemblages that include substantial stishovite, the bulk Fe# is not the average Fe# of Bdg and Mws, but an average over the entire measured region), confirming that the sample center did not lose or gain Fe by Soret diffusion [287]. Bridgmanite compositions are Fe#16-18 for Fa45 and Fe#37-51 for Fa72 (figure 6.9a). Measured compositions of Bdg formed from Fa72 are slightly more Fe-rich than the maximum solubility of FeSiO₃ in Bdg measured at ~2000 K in multianvil press experiments to 50 GPa [420] (figure 6.9b). The consistently higher maximum Fe-content in Bdg in these experiments relative to Tange et al. (2009) [420] may be due to underestimation of temperature during laser heating, overestimation of Fe-content by EDX, or other experimental differences in deviatoric stresses, run time, and/or redox state. Magnesiowstites formed from Fe-rich olivines are extremely Fe-rich: Fe#64-75 in Fa45 samples and Fe#87-98 in Fa72 (figure 6.9b). Magnesiowustite with Fe#95 may adopt the B8 structure at the pressure conditions of these experiments [435], but the diffraction peaks observed from this phase are not resolved well enough to determine its structure (figure 6.3). Compositions measured by EDX for Bdg and Mws determine values for K_D that are lower than previous studies of less Fe-rich San Carlos olivine, decrease with pressure, and increase with temperature (figure 6.11). This is consistent with previous observations at lower pressures of stronger preference of ferrous iron for Mws in Fe-enriched bulk compositions [222, 363, 417, 418, 420]. The exchange coefficient decreases with pressure for the Fa72 composition. While partitioning appears flat with increasing pressure in the Fa45 composition, this is likely an effect of higher



Figure 6.5: Energy-dispersive X-ray maps with Mg, Fe, and Si concentrations in red, green, and blue respectively and corresponding spectra obtained from selected grains for a) Fa72 heated to 1980 K at 33 GPa and b) Fa72 from 48 GPa. Bdg=bridgmanite, Mws=magnesiowstite, Sti=stishovite.

temperatures during the higher pressure runs for this composition, and we may expect the exchange coefficient to decrease with pressure at a constant temperature. Post-perovskite at 128 GPa was measured to have Fe#59, higher than any Fe# measured for bridgmanite. This results in a higher post-perovskitemagnesiowstite exchange coefficient relative to bridgmanitemagnesiowstite (figure 6.11), in agreement with previous studies of San Carlos olivine by Auzende et al. (2008) [221] and Sakai et al. (2010) [393].

Lattice spacings of bridgmanite, magnesiowstite and post-perovskite, when resolvable, also provide estimates of the partitioning of iron. This analysis has previously been attempted for high-pressure diffraction data [388], but more recent studies offer much improved constraints on the equation of state of lower mantle phases, including effects of iron on the compressibility of bridgmanite and effects of the spin transition on ferropericlase. Recent compression measurements of single-phase Bdg with a wide range of Fe# synthesized in the laser-heated diamond anvil cell [421] were used to fit a pressure-lattice spacing-composition equation of state for quantitative analysis of composition. The equation of state calibrates composition as a function of pressure and the a lattice parameter of bridgmanite, the direction most sensitive to Fe-content. For lattice parameter data from three studies of Fe-bearing Bdg by powder diffraction in quasi-hydrostatic media [421, 436, 437], compositions indicated by this calibration scatter around known compositions of starting materials with a standard deviation of ~5% (figure 6.10b). Precision of composition estimates by XRD for this study and other typical partitioning studies will be lower due to the need to avoid internal pressure calibrates,

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.6: Analytical TEM images of Mws grain in Fa72 sample heated to 2000 K at 82 GPa at EPFL. a) STEM high-angle annular dark field b) Energy-dispersive X-ray map with Mg, Fe, and Si concentrations coded in red, green, and blue respectively c) Energy-dispersive X-ray map with O concentration coded in white.



Figure 6.7: Analytical TEM images of Fa72 sample heated to 2000K at 52 GPa at EPFL. a) STEM high-angle annular dark field b) Energy-dispersive X-ray map with Mg, Fe, and Si concentrations coded in red, green, and blue respectively c) Energy-dispersive X-ray map with O concentration coded in white.

which may complicate chemistry and/or result in Soret diffusion [287]. Lattice parameters of Bdg in olivine compositions in this work at pressures determined by the NaCl medium are consistent with Fe#0-20 in Fa45 and Fe#40-70 in Fa72 (figure 6.10, table 6.2). These values are consistent with EDX observations (figure 6.10) to ~20 Fe#.

At 89 GPa in Fa72, lattice parameters of bridgmanite indicate only Fe#31, likely due to partitioning of Fe into incipient pPv. The most prominent diffraction line of pPv, (022) is observed in this diffraction pattern. The lattice spacing indicated by this peak is large relative to that observed for Fe#40 pPv at similar pressures, supporting very high Fe-content [440], and inconsistent with the recently-discovered post-perovskite H-phase [244]. The initiation of the post-perovskite transition at only 89 GPa is compatible with the shallow, broad post-perovskite transition in Fe-rich (Mg, Fe)SiO₃ observed in previous studies [421, 427, 412].

At all pressures, observed unit cell volumes for magnesiowstite support Fe-enrichment relative to the starting composition. The composition of Mws is more difficult to model relative to unit cell volume than ferrous-iron-bearing Bdg due to the composition-dependent spin



Figure 6.8: TEM, STEM and EDX images of Fa45 sample heated to 2000 K at 40 GPa at APS GSECARS. a) STEM bright field low magnification b) STEM high-angle annular dark field low magnification c) Energy-dispersive X-ray map with Mg, Fe, and Si concentrations coded in red, green, and blue respectively d) TEM high magnification of sample center with euhedral grains e) TEM high magnification of sample center showing disordered lattice planes in Mws grains and amorphized Bdg grains.

transition. Qualitatively, Mws volumes in Fa45 samples fall between previous measurements of Fe#58 and Fe#100 (FeO) compositions (figure 6.12) [218, 372, 442]. The measured volume of magnesiowstite formed from Fa72 is consistent with nearly pure FeO, in good agreement with EDX measurements (figure 6.9b).

6.4 Discussion

6.4.1 Multivariable effects on partitioning

The experiments presented here examine substantially more Fe^{2+} -rich compositions than those explored in previous studies of partitioning in Earths deep lower mantle, and thus

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.9: Composition data obtained from partitioning studies in olivine compositions plotted with relevant phase stability data. Data from this study and those from Auzende et al. (2008) [221] and Nakajima et al. (2012) [418] were obtained by EDX in the TEM. Data from Mao et al. (1991) [437] are based on X-ray diffraction at ambient conditions. a) Compositions for bridgmanite synthesized from olivine starting materials. Gray shaded region marks solubility of Fe in bridgmanite at ~2000 K from previous studies in the multianvil press [420] and laser-heated diamond anvil cell [421]. b) Compositions of (Mg,Fe)O synthesized from olivine starting materials. Shaded regions show change in the pressure of the high-to-low spin transition with composition [218, 438, 439].

provide systematic constraints on effects of compositional differences on partitioning in iron-rich heterogeneities. Previous studies have observed two major trends of partitioning with increasing pressure/depth for different compositions [380]: in San Carlos olivine, with no Fe³⁺, silicate-oxide K_D is flat or decreases between 50-100 GPa and increases across the post-perovskite transition [221, 222, 363, 392, 393, 419], while pyrolite, with high Fe³⁺/ Σ Fe, K_D exhibits a more complex behavior in the Bdg stability field, and decreases across the pPv transition [195, 228, 229]. Below 50 GPa in other olivines, presumably with low Fe³⁺/ Σ Fe, K_D decreases with total Fe# [417, 418, 420], and this work demonstrates that the trend for iron-rich compositions at higher pressures continues to be shifted to lower K_D values relative to San Carlos olivine.

Differences in partitioning behavior between Fe-rich and Fe-poor compositions may be due to differences in the conditions at which high-to-low spin transitions occur in Fe-bearing mantle phases. The decrease in K_D in low Fe³⁺/ Σ Fe olivine was linked to the spin transition of Fe²⁺ in magnesiowstite [217]. In more Fe-rich olivine, any decrease in K_D can be expected to occur at higher pressures due to the increase in high-to-low spin transition pressure with Fe# in magnesiowstite [218, 438, 439]. The spin transition in Fe# \sim 70 magnesiowstite in Fa45 can be estimated to begin at \sim 80 GPa based on observations of similar compositions [218, 220, 439]. The spin transition in FeO does not occur until \sim 120 GPa, particularly at high temperatures corresponding to conditions during partitioning [443, 444, 445] (figure 6.9a). We can assume that in Fa72 samples, with magnesiowstite compositions close to pure FeO, the



Figure 6.10: a) Lattice parameter a of bridgmanite at 300 K after laser heating with values from previously-measured 300 K compression of (Mg,Fe)SiO₃ bridgmanite [421, 436, 437]. Curves are fits to a linearized Birch-Murnaghan equation of state [441] with K₀ fixed at 4: $P = 3/2 K_0(X_{Fe})[((a_0(X_{Fe}))/a)^7 - ((a_0(X_{Fe}))/a)^5]$, where P is pressure, X_{Fe} =Fe#, and a is the measured lattice parameter. The zero-pressure lattice parameter $a_o = 4.787+0.123 X_{Fe}$ and linear zero-pressure bulk modulus K_o = 212.2 + 8.5 X_{Fe}. b) Difference between Fe# determined by the P(a, $X_{Fe})$ equation of state and Fe# of starting materials (standard deviation ~Fe#5).

spin transition does not occur in magnesiowstite in the bridgmanite stability field. However, a gradual decrease is observed in K_D in Fa72 in this study (figure 6.11). This suggests that at high Fe-contents, a decrease in K_D may arise from pressure effects alone on thermoelastic properties of Bdg and Mws.

Spin transitions in bridgmanite may increase the partition coefficient, but this has been less clear due to multiple possible crystallographic sites and valence states for Fe [397]. Increases in K_D due to spin transitions in Bdg have been proposed due to either a high-to-low spin transition in Fe³⁺ at <30 GPa [216] or a controversial intermediate-to-low spin transition in Fe²⁺ at ~100 GPa [229]. Since olivine starting materials for these experiments are nominally Fe³⁺-free, a spin transition in Fe³⁺ will only have a significant effect on K_D if during Bdg/Mws synthesis a substantial amount of Fe²⁺ is oxidized to Fe³⁺. Oxidization of Fe²⁺ was limited in

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.11: Exchange coefficient between silicate and oxide phases at lower mantle conditions [221, 222, 393, 418]. Filled/open symbols indicate a bridgmanite/post-perovskite silicate phase. Data for which temperatures were not in the range 1850-2100 K are circled in gold and labeled. Light gray region indicates composition/pressure space with coexisting bridgmanite and post-perovskite. Values chosen for model compositions Fa10, Fa30, Fa50 and Fa70 at selected pressures 40, 60, 80, 100 and 125 GPa are shown in x symbols and lines.

Bdg and Bdg-Mws mixtures synthesized from ~100% ferrous starting materials under identical loading and heating protocols to experiments in this study, resulting in Fe³⁺/ Σ Fe of less than 13-25% [446]. In addition, substantial disproportionation of Fe²⁺ to Fe³⁺ and Fe⁰ metal is not supported by TEM observations detailed above. A high-to-low spin transition in Fe³⁺ is thus unlikely to significantly affect partitioning in these experiments. Although a high-to-low spin transition does not occur in Fe²⁺ at mantle-relevant pressures in bridgmanite with low Fe# [424], higher Fe-content may promote this transition in bridgmanite at lower pressures [447, 448, 426, 449]. For Fe#75, a fraction of Fe²⁺ in Bdg may adopt the low spin state by 80 GPa [426]. Although Bdg in Fa72 samples reaches Fe#>40, this is not sufficiently Fe-rich to promote a spin transition in Fe²⁺. The lack of effects of any spin transition in bridgmanite on partitioning is consistent with the strictly decreasing trend of K_D in Fa72 in the bridgmanite stability field (figure 6.11).

Observations of the partitioning of Fe between bridgmanite and magnesiowstite versus postperovskite and magnesiowstite provide important constraints on the post-perovskite transition in Fe-bearing compositions in the mantle and the D'' discontinuity. Most measurements of phase equilibria by X-ray diffraction support a lower-pressure, broader pPv transition in Fe-



Figure 6.12: Unit cell volumes of ferropericlasemagnesiowstite (Fp-Mws) phase at 300 K after quench of laser heated olivine samples with analogous measurements from San Carlos olivine composition by Andrault (2001) [388]. Open symbols are previously-measured 300 K volumes of (Mg,Fe)O [218, 372, 450, 442]. Curves are fits to the Birch-Murnaghan equation of state [451].

rich compositions [382, 421, 427, 412], which implies that Fe partitions from Bdg into the pPv phase. Partitioning of Fe from Bdg to pPv is also supported by observations of higher silicate-oxide K_D for pPv than for Bdg [221, 222, 393]. However, a few studies have suggested that Fe partitions in the opposite direction, based on a higher pPv transition pressure in the presence of Fe [423] and direct partitioning measurements between coexisting silicates [388, 428, 410]. The conflict has been attributed to differences in the Fe³⁺/ Σ Fe content of starting materials and synthesized silicates [397, 410], which is not well-known for all experiments and challenging to determine both in situ and ex situ. The experiments in this study support a higher K_D for post-perovskite-magnesiowstite relative to bridgmanite-magnesiowstite, suggesting a shallower, broader depth for the post-perovskite transition in iron-rich lower mantle heterogeneities.

6.4.2 Mantle partitioning model

The composition and pressure dependence of iron partitioning enable us to model the compositions of the major phases in the deep lower mantle for a heterogeneous lower mantle containing iron-rich regions. We estimate K_D as a function of Fe# and pressure based on experimental measurements shown in figure 6.11 [221, 222, 393, 418]. The model values for K_D for compositions with total Fe# 10, 30, 50 and 70 at selected pressures 40, 60, 80, 100 and 125 GPa (corresponding to depths of roughly 1050, 1470, 1870, 2250 and 2700 km, respectively) are also

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Figure 6.13: Densities at 300 K and selected lower mantle pressures 40, 60, 80, 100 and 125 GPa as a function of variable X_{Fe} =Fe/(Fe+Mg) for a) bridgmanite [421, 436] and post-perovskite [452, 453, 440] and b) ferropericlase-magnesiowstite [218, 220, 372, 454, 455, 456, 457, 438, 450, 458, 442, 459]. Curves are linear or quadratic least-squares fits at each pressure.

plotted in figure 6.11. Note again that these experiments all examine olivine starting materials, and thus represent low ferric iron and fixed ~peridotitic SiO_2 -content. We assume that K_D is independent of mol% SiO_2 , expressed as mol% bridgmanite in a bridgmanitemagnesiowstite phase assemblage.

Model compositions for variable Fe#, mol% SiO₂ and pressure are combined with measurements of physical properties of bridgmanite and magnesiowstite to determine the observable seismic properties of mantle heterogeneities. Recent experimental equation of state measurements over a wide range of compositions have confirmed that the densities of bridgmanite and post-perovskite vary linearly with Fe²⁺-content (figure 6.13) [413]. The Fe#- and pressuredependence of density of ferropericlase/magnesiowstite requires a more complex model due to the composition-dependent spin transition (e.g. [460]). Below the onset of the spin transition, oxide density varies linearly with Fe-content, but at higher pressures the spin transition results in systematically higher densities for ferropericlase relative to FeO. Equation of state data for Mws from previous studies [218, 220, 372, 454, 455, 456, 457, 438, 461, 450, 458, 442, 459] were interpolated at each model pressure using quadratic trends (figure 6.13). Densities of mantle phase assemblages at lower mantle pressures and room temperature (figures 6.14-6.15) were modeled as weighted means between the silicate and oxide densities. A room temperature density calculation ignores any difference in thermoelastic properties between Fe-poor



Figure 6.14: Density of a lower mantle phase assemblage comprising ferrous-iron-bearing bridgmanite, ferropericlase, and post-perovskite as a function of mol% silicate and pressure. Densities are calculated based on partitioning data in this study and equation of state data for bridgmanite [421, 436], ferropericlase [218, 220, 372, 454, 455, 456, 457, 438, 450, 458, 442, 459] and post-perovskite [452, 453, 440]. Filled symbols = bridgmanite and ferropericlase phase assemblage, open symbols = post-perovskite and ferropericlase. Compositions are modeled at pressures 40, 60, 80, 100 and 125 GPa (dotted lines = isobars) for fixed bulk Fe# a) Fe#10, representing average mantle, and b) Fe#30, representing dense mantle heterogeneity.

and Fe-rich systems, but requires minimal extrapolation from existing experimental data. This model also does not consider Fe³⁺-rich mantle compositions, in which K_D is substantially different both above and below the post-perovskite transition [397] and a spin transition in bridgmanite affects density (e.g. [227]). Another source of uncertainty in the model is limited experimental constraints on temperature-dependence of partitioning at deep mantle conditions, with 100s K differences in temperature between the experimental data (figure 6.11). However, modeled densities are not highly sensitive to uncertainty in partitioning: 50% error bars on K_D result in uncertainty in modeled density of the resulting assemblage of ~0.2-1% in the deep mantle.

While it is well-known that increasing Fe# of the mantle phase assemblage increases its density, the effect of variable SiO₂-content on mantle dynamics is perhaps less intuitive. In average lower mantle rock with Fe#10, the change in density due to difference in mol% SiO₂, $\partial \rho / \partial SiO_2$, is nearly zero (figure 6.14). Increasing the fraction of bridgmanite in the mantle slightly increases net density in the shallow lower mantle (40 GPa and lower pressures). With increasing pressure, differences in compressibility between bridgmanite and ferropericlase result in a slightly negative change in density with increasing bridgmanite fraction. The post-perovskite transition increases the density of the silicate and $\partial \rho / \partial SiO_2$ becomes slightly

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities



Mol fraction bridgmanite

Figure 6.15: At 80 GPa, modeled densities of lower mantle phase assemblages comprising ferrous-iron-bearing bridgmanite and ferropericlase. Model compositions (symbols) vary in mol% bridgmanite and bulk iron content. Dotted lines for constant bulk Fe# are provided as guides to the eye.

positive again at 125 GPa. Adding iron to the mantle not only increases the density, it also modifies $\partial \rho / \partial SiO_2$ (figure 6.14, figure 6.15). An Fe#30 dense mantle heterogeneity exhibits negative $\partial \rho / \partial SiO_2$ at all modeled pressures (figure 6.14). For very Fe-rich compositions at deep mantle pressures, $\partial \rho / \partial SiO_2$ becomes comparable in magnitude to $\partial \rho / \partial Fe$ # (figure 6.15). The depth- and composition-dependence of $\partial \rho / \partial SiO_2$ may provide a mechanism for compositional stratification in the mantle, leading to Fe-bearing, Si-depleted LLSVPs and ULVZs. Heterogeneous mantle SiO₂-content may also explain enigmatic differences in seismic velocities V_S and V_P in LLSVPs [462]. The deep lower mantle has been noted for anticorrelation of V_S and V_P, which neither thermal differences nor iron content alone can explain [413]. However, differences in Fe-content in combination with SiO₂-content produce complex effects on density and compressibility. Further studies on composition, pressure, and temperature dependence of thermoelastic properties will test whether dense heterogeneities such as LLSVPs are enriched or depleted in SiO₂.

6.5 Summary

In order to systematically investigate the effects of iron enrichment on the properties of dense LLSVPs and ULVZs, partitioning of iron between magnesiowstite, bridgmanite, and post-perovskite was examined in Fe^{2+} -rich olivine compositions, Fa72 and Fa45, at pressure and temperature conditions spanning the entire range for Earths lower mantle, 33-128 GPa and 1900-3000 K. Both in situ X-ray diffraction and ex situ transmission electron microscopy were used to determine synthesized phase assemblages and compositions of each phase. Experimental equations of state for bridgmanite can be used to determine composition within ~20 Fe# of the composition measured by EDX over a compositional range up to at least Fe#50. In all samples, magnesiowstite composition was enriched in Fe relative to the starting material, demonstrating that Fe favors the oxide over the silicate phase throughout the lower mantle. In Fa72 samples, both EDX and XRD indicate that magnesiowstite was within 5% Fe/(Mg+Fe) of pure FeO between 50-100 GPa. Fe-content in bridgmanite increases with pressure up to ~80 GPa, reaching a maximum Fe# of 51 in Fa72 at 82 GPa. At 128 GPa, the Fe-content of the silicate phase is higher than that measured at lower pressures due to the higher silicate-oxide partitioning coefficient of Fe into post-perovskite relative to bridgmanite. The observations show no evidence of increase in partition coefficient due to a spin transition either Fe^{3+} or Fe²⁺ in bridgmanite. Decrease of the partition coefficient from 60-100 GPa in Fa72 is unlikely to be related to a spin transition in magnesiowstite as the spin transition pressure in Fe#95-100 magnesiowstite is greater than 100 GPa. These results provide important constraints on the effect of Fe-content on partitioning of iron and resulting physical properties of iron-rich lower mantle heterogeneities. In iron-rich low shear velocity provinces, different effects of iron on densities of magnesiowstite and bridgmanite result in increased effect of SiO₂-content to reduce the density of the bulk phase assemblage. Dynamics of iron-rich regions over Earths history may have resulted in Si-depletion at the base of the mantle in LLSVPs and ULVZs.

Chapter 6. Composition and Pressure Effects on Partitioning of Ferrous Iron in Iron-rich Lower Mantle Heterogeneities

Table 6.2: Composition measurements by XRD and EDX and corresponding experimental conditions pressure (P), temperature (T), and duration (t). Uncertainties are taken from statistical error in EDX quantification. *=Laser heating and X-ray diffraction conducted at APS beamline 13-ID-D. Missing data: NR=Lattice parameters not resolvable from diffraction data, NA=No diffraction available, TS=grain sizes too small for EDX measurements. Phases: Bdg=bridgmanite, pPv=post-perovskite, Mws=magnesiowstite, and Sti=stishovite.

Sample	P (GPa)	T (K)	t (min)	Phases	$\begin{array}{c} X^{Bdg}_{Fe} \\ (\text{XRD}) \end{array}$	X_{Fe}^{Bdg}	X ^{Mws} _{Fe}	K _D
Fa45*	40	2000	10	Mws, Bdg, Sti (1 grain)	25±5	17.9±1.9	74.7±1.8	0.074±0.018
Fa45*	46	2050	20	Mws, Bdg	14±5			Recovery failed
Fa45*	62	2000	15	Mws, Bdg	27±5	16±3	73.6±1.1	0.07±0.03
Fa45*	66	2250	15	Mws, Bdg	21±5			Recovery failed
Fa45*	71	2440	20	Mws, Bdg	18±5		TS	
Fa45*	89	2600	15	Mws, Bdg	4±5	18±4	64±2	0.12±0.05
Fa72*	33	1980	15	Mws, Bdg, Sti	56±5	37±3	86.8±0.3	0.089±0.016
Fa72	39	2000	30	Mws, Bdg, Sti	69±5	47±7	92.4±1.2	0.07±0.04
Fa72*	48	1900	15	Mws, Bdg	NR	43±5	92.2±0.6	0.06±0.02
Fa72	52	2000	30	Mws, Bdg	NA	46.5±1.3	95.3±0.8	0.043±0.011
Fa72*	61	1850	20	Mws, Bdg	55±5		TS	
Fa72	82	2000	20	Mws, Bdg, Fe	NA	51±2	98.2±0.5	0.019±0.009
Fa72*	89	2200	35	Mws, Bdg, pPv	31±5	49±2	96.8±1.1	0.032±0.014
Fa72	128	2700	60	Mw, pPv	NA	pPv: 59.1±0.8	97±3	0.05±0.07
Fa72 in MgO	83	2200	45	Fp, Mws, Bdg	NA	4.2±0.7	21.9±0.9, 96.4±0.5	

Table 6.3: Composition measurements and calculated partition coefficient obtained from energy-dispersive X-ray spectroscopic maps for each sample. Atomic percents of each element are averaged over pixels obtained from multiple grains. Bdg=bridgmanite, Mws=magnesiowstite.

K_D		deviation	standard	grain	Fe# grain-	Fe/(Mg+Fe)	i)	Si/(Mg+Fe+S	Ratio:	Ga	С	Cu	C	Na	0	Si	Fe	Mg	Atomic %:	Pixels	Total #	# Grains		
0.074		1.9%				17.9%	51.5%						0.05	0.26	54.41	23.33	3.93	18.00		766		∞	Bdg	Fa45 4
		1.8%				74.7%	3.0%						0.06	1.38	43.10	1.68	40.20	13.59		212		6	Mws	10 GPa
0.069		3.4%				16.2%	51.8%						0.04	0.22	53.63	23.90	3.61	18.60		176		2	Bdg	Fa45 (
		1.1%				73.6%	0.7%						0.49	2.44	41.48	0.40	40.64	14.55		74		2	Mws	52 GPa
0.124		4.3%				18.2%	53.8%						0.20	0.57	56.58	22.94	3.59	16.12		1550		5	Bdg	Fa45 8
		2.4%				64.3%	2.5%						0.29	5.59	48.27	1.14	28.74	15.98		284		4	Mws	89 GPa
0.090		3.3%				37.2%	52.7%						0.05	0.17	55.49	23.32	7.81	13.16		642		4	Bdg	Fa72 3
		0.3%				86.8%	2.3%						0.13	1.91	44.95	1.20	44.97	6.84		122		3	Mws	3 GPa
0.072		7.3%				46.8%	49.9%			0.09	0.60		0.16	1.16	54.32	21.79	10.25	11.63		678		7	Bdg	Fa72 3
		1.2%				92.4%	0.7%			0.14	0.37		0.20	2.00	43.40	0.38	49.45	4.06		790		6	Mws	9 GPa
0.063		4.8%				42.5%	54.3%						0.10	0.38	58.04	22.54	8.06	10.89		686		5	Bdg	Fa72 4
		0.6%				92.2%	3.5%						0.17	1.19	49.04	1.75	44.10	3.74		122		з	Mws	18 GPa
0.043		1.3%				46.5%	52.0%				1.09	2.22	0.06	1.84	53.78	21.31	9.16	10.53		1346		4	Bdg	Fa72 5
		0.8%				95.3%	1.0%				0.33	4.25	0.12	0.41	43.66	0.49	48.37	2.38		40		З	Mws	2 GPa
0.019		2.4%				50.9%	55.1%				1.45	2.39	0.15	1.25	54.52	22.18	9.19	8.87		180		4	Bdg	Fa72 8
		0.5%				98.2%	1.7%				1.53	4.88	0.11	3.75	42.26	0.80	45.81	0.86		672		4	SMM	32 GPa
0.032		2.0%				49.4%	49.2%						0.21	0.82	59.20	19.55	9.99	10.22		580		4	Bdg	Fa72 8
		1.1%				96.8%	2.2%						0.30	2.85	50.87	1.01	43.54	1.44		128		ω	Mws	}9 GPa
0.046		0.8%				59.1%	48.3%				14.86	3.30	0.57	0.45	38.13	20.60	13.04	9.04		150		ω	рРи	Fa72 1
	87	3.5%				96.9%	3.5%				12.23	4.72	1.07	0.68	21.18	2.13	56.20	1.79		30		4	Mws	28 GPa

149

7 Carbonate stability in the reduced lower mantle

This chapter is the submitted version of the manuscript titled "Carbonate stability in the reduced lower mantle" authored by Susannah M. Dorfman, James Badro, Farhang Nabiei, Vitali B. Prakapenka, Marco Cantoni, Philippe Gillet that is currently under review for publication in *Earth and Planetary Science Letters (EPSL)*. Susannah Dorfman lead the project and performed the high pressure experiments. She has also written the manuscript. The author of the thesis contributed to this work through conducting the STEM imaging as well as EDX mapping and quantification. He also helped with the FIB sample preparation.

7.1 Introduction

Carbonates are the major minerals responsible for transportation of carbon from the Earths surface to its deep interior. Their behavior at depth is critical to the storage capacity and fluxes of the geologic carbon cycle. Recent estimates of the flux of carbon trapped in carbonate minerals that reach the deep Earth range from 0.0001 to 52 megatons annually [463, 464]. The uncertainty in this range hinges on poor constraints on the budget of carbon retained by subducting slabs. Transport of carbon to at least transition zone depths is demonstrated by carbonate inclusions in diamonds [465, 466, 467], but whether any carbonates remain in the lower mantle is controversial. Most subducted carbon is expected to melt and/or break down and return to Earths surface via volcanism [463, 464, 468]. However, relatively oxidizing conditions, low temperatures, and resulting slow kinetics within subducting slabs may result in transportation of carbonates magnesite, siderite, calcite, and their solid solutions to great depths [469]. Subducted carbonates in slabs that reach the base of the lower mantle will undergo multiple phase transitions and encounter reducing conditions, to be finally buffered by metallic iron at the CMB.

Carbon provides key constraints on the chemical evolution of the deep Earth through its role as a proxy for mantle redox conditions, as its speciation is largely governed by oxygen fugacity, or f_{O_2} [470]. Evidence of deep mantle chemistry [320] and redox state [321, 471] in local environments of diamond formation can likely be inferred from diamond inclusions.

Chapter 7. Carbonate stability in the reduced lower mantle

Diamonds and their inclusions indicate widely varying local f_{O_2} [320, 321, 465, 472, 471], though f_{O_2} is expected to generally decrease with mantle depth [470, 473]. Both isotopic evidence (e.g. [474, 475]) and carbonate inclusions in diamonds [476, 467] suggest that diamonds are (at least in part) formed by reduction of subducted carbonate minerals or carbonate melts. Reduction of carbonates to diamond takes place by interactions with mantle silicates [477, 478, 479, 476] or metal [343, 480, 481, 482]. These redox reactions contribute to the barrier to carbonate transport to the deep Earth [473, 468]. The key to determining the amount of oxidized carbon in the deep Earth is the dependence of both the thermodynamics and the kinetics of redox reactions in carbonates on temperature, pressure, and f_{O_2} .

Petrologic observations, experiments and computational studies on stability and breakdown kinetics of carbonates have determined that magnesite is the most stable carbonate phase throughout most of the mantle, but calcite and siderite polymorphs have also attracted interest. Magnesite is thought to be more likely to persist to transition zone depths based on its melting point [483, 484, 485, 486], which is higher than that of aragonite [487] or siderite [488]. Melting of carbonated peridotite systems confirms that calcium and iron carbonate components are more likely to enter a melt phase than magnesium carbonate [489, 468]. Both $MgCO_3$ [465, 490, 491, 471] and CaCO₃ [465, 492] have been observed in inclusions in diamonds, including ultra-deep diamonds from the transition zone or possibly the lower mantle [465]. These inclusions demonstrate that kinetic effects may preserve both MgCO3 and CaCO3 within cold subducting slabs, consistent with slow breakdown kinetics observed in experiments at transition zone conditions [469]. In the lower mantle, experiments on carbonate-silicate mixtures also support MgCO₃ as the dominant carbonate: the reaction CaCO₃ + MgSiO₃ \rightarrow MgCO₃ + CaSiO₃ was observed at lower mantle pressures up to 80 GPa [493, 494]. Due to its broad solid solution with siderite [495, 496], magnesite in the mantle may also host iron. An iron-rich carbonate in the lowermost mantle may have mixed redox state and coexist with diamond [497]. However, the relative stability of (Mg,Fe)CO₃ and CaCO₃ may change at depth due to polymorphism. If (Mg,Fe)CO₃ or CaCO₃ reaches the base of the lower mantle, density functional theory calculations [498, 499] and experiments [500, 501] suggest these carbonates will transform to tetrahedrally-coordinated structures. If the transition in CaCO₃ occurs at a shallower depth than the analogous transition in MgCO₃, as predicted by Pickard and Needs (2015) [499], CaCO₃ would be the denser and more energetically-favored carbonate in the deep lower mantle.

This study examines a Mg-Fe-Ca carbonate system in the petrologic context of an assemblage including metallic iron. Metallic iron may be present at the percent level throughout the mantle [212], and the outer core provides an unlimited reservoir of iron in contact with subducted carbonates reaching the core-mantle boundary [502, 503]. Previous studies of carbonates at lower mantle pressures have investigated mineralogical stability of single phases as a function of pressure and temperature alone [500, 483, 504, 486], or used mixtures of carbonates and silicates which complicate textural analysis of run products [493, 505]. In contrast, we examine reaction interfaces between multiple carbonates and iron; similar previous studies have been limited to transition zone conditions [469, 481]. We determine the



Figure 7.1: Backscattered scanning electron image recorded at 4 kV of dolomite-iron reaction interface in sample thin section recovered from 66 GPa and 1900-2200 K. The iron-rich region in the center appears brightest due to its high density. The extent of iron diffusion into and reaction with the Fe-poor carbonate is also evident based on density. A few micron offset in alignment of upstream and downstream lasers may be responsible for asymmetry of heated spot.

relative stability and metastability of Mg-, Fe-, and Ca-carbonates as host phases for oxidized carbon storage in the lower mantle and at the CMB.

7.2 Methods

To bring experimental petrology of carbonates to the Mbar pressures and 1000s K temperatures of the core-mantle boundary, experiments must be miniaturized: sample geometry must be controlled within the ~50x50x10-micron chamber of the laser-heated diamond anvil cell, and analysis must be performed with ~100-nm-scale spatial resolution of typical grain sizes of run products. Dolomite provides a unique advantage as a starting material as it has a mixed Mg-Fe-Ca carbonate composition homogeneous to <nm scale. Natural dolomite crystals with composition determined to be (Mg_{0.38}Ca_{0.59}Fe_{0.03})CO₃ by X-ray fluorescence spectroscopy and structure confirmed by X-ray diffraction were used as starting materials (tables 7.1 and 7.2). Single dolomite crystals were polished to ~10-micron thickness and dried in a 120°C oven overnight before loading. 3-micron thick 99.85% iron foil was machined into discs with a ps-pulsed 532-nm laser or cut with a razor blade. Iron foils were loaded sandwiched between dolomite crystals in symmetric diamond anvil cells. No other pressure standard or medium was loaded in order to prevent reactions with other components and contamination of the chemical system. Sample sandwiches were loaded within chambers cut in Re gaskets in

Table 7.1: Diffraction peaks observed from single-crystal carbonate starting material. Observed d-spacings correspond well to dolomite.

2 Theta	D	HKL
(Cu)		
31.0 (5)	2.88(4)	104
64.5 (5)	1.443(10)	208
106.5 (5)	0.961(3)	3 0 12

Table 7.2: X-ray fluorescence composition analysis of single-crystal carbonate starting material. Measurements were performed at 10 kV and 200 μ A.

Element	Counts	Weight %	Weight % Error	Atomic %
Mg	160	26.29	3.38	38(5)
Са	8660	68.10	1.04	59.0(9)
Fe	448	5.62	0.41	3.5(3)
Total		100.00		

diamond anvil cells. Diamond anvils with flat culets of 200 micron diameter or beveled culets of 150 micron diameter were chosen to generate pressures corresponding to the lower mantle.

Samples were compressed to pressures of 51, 66, 77, and 113 GPa, as determined by the equation of state of the iron foil [506] before laser heating (table 7.3). Pressures were not measured during heating due to chemical reaction of the iron foil with the dolomite, but were likely ~7-10 GPa higher than those reported here due to thermal pressure. Laser heating was performed with in situ X-ray diffraction at the GSECARS sector of the Advanced Photon Source [432]. The laser spot was focused to a diameter of ~10 microns with a flat-top beam shape. Each sample was heated for 10-20 min at 1800-2500 K.

After recovery to ambient conditions, each heated spot was sectioned using a Zeiss NVision 40 dual-beam scanning electron microscope and focused Ga^+ ion beam (Centre Interdisciplinaire Microscopie de Electronique (CIME), EPFL). Each sample was coated with 15 nm Au to reduce charging in the scanning electron microscope. To protect the samples from damage by the Ga^+ ion beam, an additional ~1-2 micron thick layer of Pt or C was deposited across the centers of heated spots. Thin sections of each heated spot were extracted and polished to electron transparency (~100 nm thickness).

Imaging of recovered thin sections was performed with scanning transmission election microscopy (S/TEM) and energy-dispersive X-ray spectroscopy (EDX) in a FEI Tecnai Osiris Table 7.3: Pressure, temperature, and heating duration for all experiments. Pressures given were obtained before heating from the equation of state of the iron foil [506]. Temperature differences between downstream and upstream sides were typically observed to be ~100 K and varied by ~100 K over the heating duration.

Pressure before heating	Temperature (K)	Duration (min)		
(GPa)				
51	1800-2050	15		
66	1900-2200	10		
77	1900-2200	20		
113	2400-2500	10		

analytical TEM (CIME, EPFL). Accelerating voltage for these measurements was 200 kV. The Osiris TEM is equipped with four wide-solid-angle detectors for high-speed chemical measurements by EDX spectroscopy. EDX maps were scanned over 1024x1024 pixel areas with pixel dwell time of 50 microseconds. Typical count rates were ~40,000-50,000 counts per second. Chemical mapping prevents migration of elements due to damage by the electron beam. Uncertainties in compositions were determined from standard deviations of EDX measurements obtained from selected regions within multiple grains.

7.3 Results

Laser-heating dolomite-iron sandwiches from both sides produces a lens-shaped heated zone (figure 7.1), as predicted by models [280, 281] and measurements [278] of thermal diffusion in the diamond anvil cell. Laser absorption and diffraction indicate that the sample reaches a steady state within a few minutes. The hottest region of the sample is the laser-absorbing central iron layer. The insulating dolomite layers experience both axial and radial temperature gradients, with highest temperatures at the contacts with the iron foil and lowest temperatures at the diamond anvil surface. High-resolution TEM inspection of recovered thin sections indicates that grain sizes decrease away from the surface of the iron foil, consistent with this thermal gradient (figure 7.1). At the cool upper and lower edges of the heated spot, ribbons of magnesium and calcium carbonate exsolve from the dolomite (figure 7.2), as has been observed at lower pressures [507, 508].

Both EDX analysis of recovered thin sections in the TEM (figures 7.1, 7.3, and 7.4) and diffraction patterns obtained during and after sub-solidus laser heating (figure 7.5b) show that the metallic iron at the sample center reacts completely with the dolomite to generate a mixture of FeO and Fe₇C₃. The iron layer thus exhibits oxidation which must be compensated by



Figure 7.2: EDX map of a) exsolution of two carbonates from dolomite at 51 GPa and b) formation of $Fp + C + CaCO_3$ at 113 GPa. Elements color-coded as follows: red=iron, blue=calcium, green=magnesium, white=carbon.

reduction of the carbonate. Within the carbonate layer near the hot interface with the iron foil, three phases are found in all samples: diamond, Mg-bearing ferropericlase, and CaCO₃ (figures 7.3 and 7.4). The diffusion of iron from the sample center propagates breakdown of the magnesium carbonate to diamond and ferropericlase. Due to diffusion, this ferropericlase has much more MgO than the FeO at the sample center (figure 7.6 and 7.7). Unlike MgCO₃, CaCO₃ exsolves from the dolomite but is never observed to break down. EDX composition analysis confirms that the CaCO₃ phase retains both O and C within measurement error and there is no evidence for measurable Ca in any other phase (figure 7.7). At the pressures examined here, the stable polymorph of CaCO₃ is the post-aragonite phase [504]. Post-aragonite-type CaCO₃ is observed in diffraction patterns after heating (figure 7.5b), along with unreacted dolomite. These experiments show that in reducing conditions in the presence of metallic iron, post-aragonite-type CaCO₃ is a more stable form of carbonate than MgCO₃ throughout the lower mantle pressure range.

7.4 Discussion

The mixture of (Mg,Fe)O, diamond, Fe_7C_3 and $CaCO_3$ is produced by redox coupling between the iron and carbon and breakdown of the MgCO₃ component. The following reactions explain these observations:

 $MgCO_3 + 2Fe \rightarrow C + MgO + 2FeO$

 $3MgCO_3 + 13Fe \rightarrow Fe_7C_3 + 3MgO + 6FeO$

In the center of the sample, the system is saturated in iron, leading to a mixture dominated



Figure 7.3: Composition measurements for dolomite-iron sample recovered from 113 GPa and 2400-2500 K. a) Energy-dispersive X-ray map with elements color-coded as follows: red=iron, blue=calcium, green=magnesium, white=carbon. b) Examples of EDX spectra obtained for each phase.

by Fe₇C₃ and FeO. In the region where the carbonate breaks down, the carbon/iron ratio is higher, and reduced carbon is found in diamonds rather than carbides. The breakdown of MgCO₃ is favorable in all heated regions in the presence of iron. The stable host phase for carbon is controlled by the Fe/MgCO₃ ratio of reactants. Recent studies have largely focused on (Mg,Fe)CO₃ as a host phase for oxidized carbon in the deep Earth, as the melting point of magnesite or ferromagnesite is higher than that of CaCO₃ in the transition zone. However, (Mg,Fe)CO₃ is much more susceptible to redox breakdown than CaCO₃.

Previous studies have suggested that carbonates are stable to great depths in the mantle based on diamond inclusions (e.g. [467]) and experiments on single-component systems [483, 485]. Under favorable redox conditions, MgCO₃ and CaCO₃ do not decompose at high temperatures below their melting points [509, 483, 486, 487, 505], which are far above a 1600 K adiabatic geotherm [510]. However, for carbonate mixtures, the eutectic melting point is substantially lower [505], and comparable to the geotherm investigated in these experiments. Although no evidence is observed for melting of the carbonate in this work, eutectic melting has been argued to effectively block carbonate transport to the lower mantle [468]. Moreover, geotherms both for the average mantle (e.g. [348, 352, 510]) and subducting slabs (e.g. [252]) remain highly uncertain. The key question is whether, for realistic subducted carbonates, the melting point of the mixture is high enough relative to the temperature in the slab to prevent diamond formation. With temperature uncertainties of at least 100s K, in addition to potential kinetic effects on the efficiency of carbonate reduction and melting [469], preservation of some carbonates in the lower mantle cannot yet be ruled out.

In addition to melting, f_{O_2} provides a major control on carbonate reduction to diamond. Reducing agents relevant to carbonate stability at different stages of Earths chemical evolution

Chapter 7. Carbonate stability in the reduced lower mantle



Figure 7.4: Energy-dispersive X-ray image of center of heated spot recovered from 66 GPa. Elements color-coded as follows: red=iron, blue=calcium, green=magnesium, white=carbon.

include graphite [511], H₂ [477], Si metal [343], and Fe metal. This study and others have shown that diamonds nucleate and grow directly from carbonates at subsolidus, reducing conditions. In a mixture of carbonate and Fe-Si alloy, Si and C were oxidized, producing a mixture in which diamonds coexist with metallic iron [343]. Other studies have suggested either that pure iron and pure carbon should not coexist in equilibrium [482, 512] or that iron carbides and diamond compete as hosts of reduced carbon [513]. In this study, no metallic iron is left, indicating that the system is oversaturated in carbon. Because the mantle has been suggested to be a highly reducing environment, saturated in metallic iron [212, 470, 514, 473], carbonate in this system will be susceptible to redox breakdown at subsolidus temperatures.

Reduction of subducted carbonates by interaction with metallic iron was previously explored at relatively modest depths [515, 516, 517, 476]. Most previous studies were conducted at pressures reaching ~6 GPa [515, 516, 517], too low to model the depths at which metallic iron becomes available to react with subducted carbonate. Metallic iron may also be present in the lower mantle due to charge disproportionation in silicates [212, 514], mixing at the CMB [502, 503], or residue of magma ocean solidification [518]. Recently, iron-magnesite mixtures were examined at 16-45 GPa and 1500-1700 °C, corresponding to transition zone to lower mantle depths [476]. At these conditions, diamonds are observed to coexist with magnesite, ferropericlase and carbon-free iron-iridium alloy. The Ir alloy was used to determine that f_{O_2}



Figure 7.5: X-ray diffraction patterns observed before and after transforming samples of dolomite (d) and iron foil (Fe) to magnesiowstite and ferropericlase (gold Mw and Fp), Fe₇C₃ (red), and post-aragonite-type CaCO₃ (blue) at pressures 51-113 GPa and temperatures 1800-2500 K in the laser-heated diamond anvil cell. Additional diffraction peaks from high-pressure polymorphs of dolomite are labeled dII and dIII. For these experiments λ =0.3100 Å.

was ~3 log units above the iron-wstite buffer. The breakdown of magnesite observed here may imply lower f_{O_2} conditions, perhaps due to the sample environment in the diamond anvil cell or higher pressures.

Spin transitions in ferromagnesite have recently been studied for their potential to affect carbonate stability [495, 496]. The spin transition results in a ~8% unit cell volume collapse for (Mg_{0.35}Fe_{0.65})CO₃ [495] and would thus be expected to have a significant effect on phase equilibria. As the minimum pressure examined in these experiments is above the spin transition pressure, we are unable to evaluate whether the spin transition is related to the observed breakdown of (Mg,Fe)CO₃. The susceptibility of (Mg,Fe)CO₃ to disproportionation at low f_{O_2} suggests that low-spin iron-bearing carbonates are unlikely to be stable in Earths mantle.

Observations in this and other experimental studies challenge interpretation of oxide inclusions in identified in diamonds. While traditionally (Mg,Fe)O inclusions have been considered to be a smoking gun for formation in the Earths lower mantle, as a leftover from the breakdown of Mg₂SiO₄ to lower mantle bridgmanite [472], carbonate disproportionation is another possible mechanism for oxide formation [475, 468]. Direct observation of lower mantle silicates of appropriate compositions is necessary to confirm ultra-deep diamond origin.

Chapter 7. Carbonate stability in the reduced lower mantle



Figure 7.6: Compositions for observed phases obtained from EDX spectra plotted on Mg-Fe-Ca ternary diagrams.

7.5 Conclusions

Unlike magnesite-siderite carbonates, post-aragonite-type CaCO₃ is a likely host phase for carbonate in the deep lower mantle. While CaCO₃ undergoes more pressure-induced polymorphic transitions than (Mg,Fe)CO₃ in the deep mantle and may be more likely to react with lower mantle silicates, relative to (Mg,Fe)CO₃ it is less likely to participate in redox reactions. A low f_{O_2} environment in the lower mantle [470, 473] will promote breakdown of ferromagnesite but CaCO₃ will remain stable to pressure, temperature and redox conditions near the base of the lower mantle. The stability of CaCO₃ as an accessory phase in a silicate-dominated phase assemblage has been doubted based on reaction observed between CaCO₃ and MgSiO₃ [493, 494], but future studies will be needed to reassess this reaction under variable f_{O_2} conditions. A carbonate-rich region at the base of the mantle would thus be a high-pressure marble, with CaCO₃ associated with diamonds formed by breakdown of MgCO₃.

Diamond-bearing marble in the lower mantle is not likely to be directly observable by seismic tomography, but could impact observations of heterogeneous redox conditions at depth due to mantle convection and subduction and/or signatures of Earths chemical evolution. As a carbonate-rich region would be much less dense than the surrounding mantle phase


Figure 7.7: Observed unit cell volumes for Mw (black) and Fp (green) in this study plotted relative to previously-measured equations of state for Fp-Mw compositions with different Fe# = Fe/(Mg+Fe) [218, 372, 450]. Pressures for data in this study are assumed to be the same as pressures obtained from the Fe foil before heating. (Mg,Fe)O diffraction peaks are split, indicating unit cell volumes consistent with coexistence of FeO at the sample center and ~(Mg_{0.6}Fe_{0.4})O produced by breakdown of the dolomite. A decrease in unit cell volume observed in both oxides between 66 and 77 GPa is consistent with the spin transition in iron-rich Mw and structural change in FeO under these conditions.

assemblage, entrainment in slabs to the deep lower mantle would require small lateral scale below the resolution of seismic imaging. However, heterogeneous oxygen fugacity at depth is evident in diamond inclusions [320, 321, 465, 472, 471] as well as chemical variation in both mid-ocean ridge basalts due to relative contributions of depleted and primitive mantle sources [519] and ocean island basalts potentially sourced from the core-mantle boundary [520]. The interpretation of available redox proxies for the deep mantle over deep time, particularly presence of carbonate (e.g. [465]) and speciation of iron [470], must be evaluated in the light of the multivariable dependence of stability of MgCO₃ and CaCO₃ on temperature, bulk composition of the phase assemblage and f_{O_2} .

8 Conclusions and perspectives

8.1 Diamonds and their inclusions from a Mars-sized planet

We have studied the diamonds in Almahata Sitta MS-170 meteorites that is classified as a ureilite. Diamonds show substantial deformation as evidenced by large number of dislocation, stacking faults and mechanical twins. The twins are formed parallel to 111 planes, and are sometimes graphitized upon intersection with inclusions. The morphology of graphite bands in the diamond matrix indicates that they have been generated as a result of shock-induced diamond to graphite transformation. This process is assisted by the stress concentration around the inclusions, particularly because the inclusion have melted during the shock event. This point to the existence of large diamond crystallites, up to 100 μ m, those are impossible to grow during the shock-event or through CVD mechanism. Therefore, the diamond are formed in the high pressure condition inside the ureilite parent body (UPB).

In addition, we have detected three different types of the inclusion in diamonds. The vast majority of these inclusions are Fe-S type. All these inclusions have polyhedral shapes pointing to their entrapment as solid crystals. However, the chemical analysis shows that these inclusions have broken to three phases, namely: kamacite (Fe, Ni), troilite (FeS), and schreibersite ((Fe, Ni)₃P). It is noteworthy that none of these phases are found as isolated inclusions and they are always together in an individual inclusion. The parent phase is determined to be (Fe, Ni)₃(S, P) through measuring the composition of intact inclusions. Considering the low P concentration of inclusions, this phase can only form above 21 GPa. That is to say the UPB has to be at least about a Mars-sized body to generate this pressure at its core-mantle boundary. Interestingly, this size is similar to the speculated size of planetary embryos at the aftermath of runaway and oligarchic growth. In fact, the Mars-sized bodies such as Mars, Mercury, and Theia are thought to have been common in the early inner Solar System.

The second type of inclusions is chromite, Cr_2FeO_4 . This is a common mineral in many meteoritic groups. However, the Al- and Mg- free end-member of chromite has only been seen in iron meteorites. If the chromite has grown with any interaction with silicates, the Mg is expected to partially substitute iron in its structure. Thus, the Fe-rich end-member

of chromite is speculated to form from an Fe-S liquid. The third type of inclusions is Ca-Fe phosphates that are also similar to the phosphate found in the iron meteorites alongside the chromite. This is an evidence that the diamond and inclusion are crystallized in an iron-rich environment. UPB is known to be partially differentiated. The differentiation started with the segregation of S-rich iron melt to form the core. Our results suggest that the diamonds and their inclusions are formed from Fe-S (with small P, Ni, Cr, and O concentration), possibly in the composition, pressure and temperature condition where the diamond and Fe₃S are both in equilibrium with the melt in the Fe-S-C phase diagram.

It should be noted that the Fe₃S is stable above 21 GPa, while the Fe-S-C phase diagram has been only studied up to ~20 GPa. To probe the possibility of the simultaneous crystallization of diamond and Fe₃S phase, it is necessary to extend the pressure range of these experiment above 21 GPa. Both diamond anvil cell (DAC) and multi-anvil apparatus are suitable for this pressure range. Also, the temperature should be controlled around 1500 K, above the eutectic temperature, to ensure the equilibrium.

Moreover, if the inclusions and diamonds re the remnant of the differentiated melt, it is interesting to measure the isotopic composition of metallic species in them. Although this is not an straightforward experiment due to the small grain size of the inclusion, it might be possible with atom probe tomography.

8.2 3D analytical investigation of melting in lower mantle conditions

In this study, we have investigated the sample molten at 30 GPa to 71 GPa in the laser-heated diamond anvil cell (LH-DAC). San Carlos olivine is selected as starting material because of the simplicity of the system and its similarity to the mantle composition. One sample was heated with single-sided laser heating. The 3D chemical analysis show that the temperature gradient is symmetrical in radial direction but unsymmetrical in the axial direction, whereas it is symmetrical in both direction for the double-sided laser heating (5 samples). Three distinct regions of ferropericlase shell (Fp), bridgmanite layer (Brg), and Fe-rich molten core has been observed in all samples. Transmission electron microscopy (TEM) and energy-dispersive x-ray (EDX) spectroscopy show that the core is getting richer in iron with increasing heating time. Moreover, the individual phases have higher iron content when they are formed closer to the core. This demonstrates that the temperature gradient is shrinking with increasing the heating duration from 1 to 6 minutes at 45 GPa and, as a result, the solidification continues toward the center and falls on the cotectic line of the Fe-Mg-Si ternary phase diagram. In this condition the Fp and Brg are crystallizing together and because of the preference of iron to partition into the melt, the iron concentration in the melt is increasing.

The iron enrichment in the melt is also enhanced with increasing the pressure from 30 GPa to 71 GPa. Indeed, a sharp change in the iron partitioning is seen at 71 GPa sample, where the

melt core is almost entirely made of Fe and O. Our results show that through increasing the pressure or continuation of the fractional crystallization, the melt can be rich enough in iron to have higher density than the solid and sink down to the bottom of the mantle. The higher iron content will also decrease the melting temperature that prolongs the crystallization of this melt. Hence, the remnant of this liquid in the bottom of the mantle or iron-rich oxide phases crystallizing from it can explain the presence of ultra-low velocity zones in the core-mantle boundary. Moreover, we have seen the partitioning of Fe³⁺ between silicates and the melt. Although the partitioning coefficient could not be determined, the presence of Fe³⁺ in the melt could give rise to the crystallization of Fe³⁺-bearing phases and oxides in the bottom of the mantle.

The abrupt change in the iron partitioning between solid and melt has been shown at \sim 70 GPa for the compositions related to the mantle. However, the exact mechanism of this variation is still not clear. In order to determine the nature of this discontinuity, we have synthesized additional samples in this pressure range. The analysis of these samples is still on going. It would be curious to repeat this experimental the more complicated systems such as pyrolite that has mantle composition (or very close).

Moreover, we have shown a procedure for complete ex-situ characterization of LH-DAC sample. The 3D chemical analysis using focused iron beam (FIB) and scanning electron microscopy (SEM) gives the the overview of the heating zone and enables us to qualitatively discuss the temperature gradient. Then, the transmission electron microscopy (TEM) is used to measure the accurate composition and identify the structure of phases down to nanometer scale (EDX and electron diffraction). In addition, the electron energy-loss spectroscopy (EELS) makes it possible to measure the valence state of iron on the same sample. This procedure can be combined with the in-situ x-ray diffraction techniques to ensure the thorough characterization of the samples.

- [1] Thomas Duffy. Earth science: Crystallography's journey to the deep Earth. *Nature News*, 506(7489):427, February 2014.
- Frank H. Shu, Fred C. Adams, and Susana Lizano. Star Formation in Molecular Clouds: Observation and Theory. *Annual Review of Astronomy and Astrophysics*, 25(1):23–81, 1987.
- [3] Christopher F. McKee and Eve C. Ostriker. Theory of Star Formation. *Annual Review of Astronomy and Astrophysics*, 45(1):565–687, 2007.
- [4] Sean M. Andrews and Jonathan P. Williams. High-Resolution Submillimeter Constraints on Circumstellar Disk Structure. *The Astrophysical Journal*, 659(1):705, 2007.
- [5] Sean M. Andrews and Jonathan P. Williams. Circumstellar Dust Disks in Taurus-Auriga: The Submillimeter Perspective. *The Astrophysical Journal*, 631(2):1134, 2005.
- [6] C. Hayashi, K. Nakazawa, and Y. Nakagawa. Formation of the solar system. pages 1100–1153, 1985.
- [7] Lee Hartmann, Paola D'Alessio, Nuria Calvet, and James Muzerolle. Why Do T Tauri Disks Accrete? *The Astrophysical Journal*, 648(1):484, 2006.
- [8] James Muzerolle, Kevin L. Luhman, César Briceño, Lee Hartmann, and Nuria Calvet. Measuring Accretion in Young Substellar Objects: Approaching the Planetary Mass Regime. *The Astrophysical Journal*, 625(2):906, 2005.
- [9] O. Krauss, G. Wurm, O. Mousis, J.-M. Petit, J. Horner, and Y. Alibert. The photophoretic sweeping of dust in transient protoplanetary disks. *Astronomy & Astrophysics*, 462(3):977–987, February 2007.
- [10] John A. Wood. Pressure and Temperature Profiles in the Solar Nebula. *Space Science Reviews*, 92(1-2):87–93, April 2000.
- [11] Joseph C. Weingartner and B. T. Draine. Dust Grain-Size Distributions and Extinction in the Milky Way, Large Magellanic Cloud, and Small Magellanic Cloud. *The Astrophysical Journal*, 548(1):296, 2001.

- [12] B. T. Draine. Interstellar Dust Grains. *Annual Review of Astronomy and Astrophysics*, 41(1):241–289, 2003.
- [13] Audrey Bouvier and Meenakshi Wadhwa. The age of the Solar System redefined by the oldest Pb–Pb age of a meteoritic inclusion. *Nature Geoscience*, 3(9):637–641, September 2010.
- [14] Yuri Amelin, Alexander N. Krot, Ian D. Hutcheon, and Alexander A. Ulyanov. Lead Isotopic Ages of Chondrules and Calcium-Aluminum-Rich Inclusions. *Science*, 297(5587):1678–1683, September 2002.
- [15] James N. Connelly, Martin Bizzarro, Alexander N. Krot, Åke Nordlund, Daniel Wielandt, and Marina A. Ivanova. The Absolute Chronology and Thermal Processing of Solids in the Solar Protoplanetary Disk. *Science*, 338(6107):651–655, November 2012.
- [16] T. S. Kruijer, M. Touboul, M. Fischer-Gödde, K. R. Bermingham, R. J. Walker, and T. Kleine. Protracted core formation and rapid accretion of protoplanets. *Science*, 344(6188):1150– 1154, June 2014.
- [17] Takashi Yoshino, Michael J. Walter, and Tomoo Katsura. Core formation in planetesimals triggered by permeable flow. *Nature*, 422(6928):154–157, March 2003.
- [18] Don Brownlee, Peter Tsou, Jérôme Aléon, Conel M. O'D Alexander, Tohru Araki, Sasa Bajt, Giuseppe A. Baratta, Ron Bastien, Phil Bland, Pierre Bleuet, Janet Borg, John P. Bradley, Adrian Brearley, F. Brenker, Sean Brennan, John C. Bridges, Nigel D. Browning, John R. Brucato, E. Bullock, Mark J. Burchell, Henner Busemann, Anna Butterworth, Marc Chaussidon, Allan Cheuvront, Miaofang Chi, Mark J. Cintala, B. C. Clark, Simon J. Clemett, George Cody, Luigi Colangeli, George Cooper, Patrick Cordier, C. Daghlian, Zurong Dai, Louis D'Hendecourt, Zahia Djouadi, Gerardo Dominguez, Tom Duxbury, Jason P. Dworkin, Denton S. Ebel, Thanasis E. Economou, Sirine Fakra, Sam A. J. Fairey, Stewart Fallon, Gianluca Ferrini, T. Ferroir, Holger Fleckenstein, Christine Floss, George Flynn, Ian A. Franchi, Marc Fries, Z. Gainsforth, J.-P. Gallien, Matt Genge, Mary K. Gilles, Philipe Gillet, Jamie Gilmour, Daniel P. Glavin, Matthieu Gounelle, Monica M. Grady, Giles A. Graham, P. G. Grant, Simon F. Green, Faustine Grossemy, Lawrence Grossman, Jeffrey N. Grossman, Yunbin Guan, Kenji Hagiya, Ralph Harvey, Philipp Heck, Gregory F. Herzog, Peter Hoppe, Friedrich Hörz, Joachim Huth, Ian D. Hutcheon, Konstantin Ignatyev, Hope Ishii, Motoo Ito, Damien Jacob, Chris Jacobsen, Stein Jacobsen, Steven Jones, David Joswiak, Amy Jurewicz, Anton T. Kearsley, Lindsay P. Keller, H. Khodja, A. L. David Kilcoyne, Jochen Kissel, Alexander Krot, Falko Langenhorst, Antonio Lanzirotti, Loan Le, Laurie A. Leshin, J. Leitner, L. Lemelle, Hugues Leroux, Ming-Chang Liu, K. Luening, Ian Lyon, Glen MacPherson, Matthew A. Marcus, Kuljeet Marhas, Bernard Marty, Graciela Matrajt, Kevin McKeegan, Anders Meibom, Vito Mennella, Keiko Messenger, Scott Messenger, Takashi Mikouchi, Smail Mostefaoui, Tomoki Nakamura, T. Nakano, M. Newville, Larry R. Nittler, Ichiro Ohnishi, Kazumasa Ohsumi, Kyoko Okudaira, Dimitri A. Papanastassiou, Russ Palma, Maria E. Palumbo,

Robert O. Pepin, David Perkins, Murielle Perronnet, P. Pianetta, William Rao, Frans J. M. Rietmeijer, François Robert, D. Rost, Alessandra Rotundi, Robert Ryan, Scott A. Sandford, Craig S. Schwandt, Thomas H. See, Dennis Schlutter, J. Sheffield-Parker, Alexandre Simionovici, Steven Simon, I. Sitnitsky, Christopher J. Snead, Maegan K. Spencer, Frank J. Stadermann, Andrew Steele, Thomas Stephan, Rhonda Stroud, Jean Susini, S. R. Sutton, Y. Suzuki, Mitra Taheri, Susan Taylor, Nick Teslich, Kazu Tomeoka, Naotaka Tomioka, Alice Toppani, Josep M. Trigo-Rodríguez, David Troadec, Akira Tsuchiyama, Anthony J. Tuzzolino, Tolek Tyliszczak, K. Uesugi, Michael Velbel, Joe Vellenga, E. Vicenzi, L. Vincze, Jack Warren, Iris Weber, Mike Weisberg, Andrew J. Westphal, Sue Wirick, Diane Wooden, Brigitte Wopenka, Penelope Wozniakiewicz, Ian Wright, Hikaru Yabuta, Hajime Yano, Edward D. Young, Richard N. Zare, Thomas Zega, Karen Ziegler, Laurent Zimmerman, Ernst Zinner, and Michael Zolensky. Comet 81p/Wild 2 Under a Microscope. *Science*, 314(5806):1711–1716, December 2006.

- [19] Michael E. Zolensky, Thomas J. Zega, Hajime Yano, Sue Wirick, Andrew J. Westphal, Mike K. Weisberg, Iris Weber, Jack L. Warren, Michael A. Velbel, Akira Tsuchiyama, Peter Tsou, Alice Toppani, Naotaka Tomioka, Kazushige Tomeoka, Nick Teslich, Mitra Taheri, Jean Susini, Rhonda Stroud, Thomas Stephan, Frank J. Stadermann, Christopher J. Snead, Steven B. Simon, Alexandre Simionovici, Thomas H. See, François Robert, Frans J. M. Rietmeijer, William Rao, Murielle C. Perronnet, Dimitri A. Papanastassiou, Kyoko Okudaira, Kazumasa Ohsumi, Ichiro Ohnishi, Keiko Nakamura-Messenger, Tomoki Nakamura, Smail Mostefaoui, Takashi Mikouchi, Anders Meibom, Graciela Matrajt, Matthew A. Marcus, Hugues Leroux, Laurence Lemelle, Loan Le, Antonio Lanzirotti, Falko Langenhorst, Alexander N. Krot, Lindsay P. Keller, Anton T. Kearsley, David Joswiak, Damien Jacob, Hope Ishii, Ralph Harvey, Kenji Hagiya, Lawrence Grossman, Jeffrey N. Grossman, Giles A. Graham, Matthieu Gounelle, Philippe Gillet, Matthew J. Genge, George Flynn, Tristan Ferroir, Stewart Fallon, Denton S. Ebel, Zu Rong Dai, Patrick Cordier, Benton Clark, Miaofang Chi, Anna L. Butterworth, Donald E. Brownlee, John C. Bridges, Sean Brennan, Adrian Brearley, John P. Bradley, Pierre Bleuet, Phil A. Bland, and Ron Bastien. Mineralogy and Petrology of Comet 81p/Wild 2 Nucleus Samples. Science, 314(5806):1735-1739, December 2006.
- [20] Kevin D. McKeegan, Jerome Aléon, John Bradley, Donald Brownlee, Henner Busemann, Anna Butterworth, Marc Chaussidon, Stewart Fallon, Christine Floss, Jamie Gilmour, Matthieu Gounelle, Giles Graham, Yunbin Guan, Philipp R. Heck, Peter Hoppe, Ian D. Hutcheon, Joachim Huth, Hope Ishii, Motoo Ito, Stein B. Jacobsen, Anton Kearsley, Laurie A. Leshin, Ming-Chang Liu, Ian Lyon, Kuljeet Marhas, Bernard Marty, Graciela Matrajt, Anders Meibom, Scott Messenger, Smail Mostefaoui, Sujoy Mukhopadhyay, Keiko Nakamura-Messenger, Larry Nittler, Russ Palma, Robert O. Pepin, Dimitri A. Papanastassiou, François Robert, Dennis Schlutter, Christopher J. Snead, Frank J. Stadermann, Rhonda Stroud, Peter Tsou, Andrew Westphal, Edward D. Young, Karen Ziegler, Laurent Zimmermann, and Ernst Zinner. Isotopic Compositions of Cometary Matter Returned by Stardust. *Science*, 314(5806):1724–1728, December 2006.

- [21] J. E. P. Matzel, H. A. Ishii, D. Joswiak, I. D. Hutcheon, J. P. Bradley, D. Brownlee, P. K. Weber, N. Teslich, G. Matrajt, K. D. McKeegan, and G. J. MacPherson. Constraints on the Formation Age of Cometary Material from the NASA Stardust Mission. *Science*, 328(5977):483–486, April 2010.
- [22] William F. Bottke, David Nesvorný, Robert E. Grimm, Alessandro Morbidelli, and David P. O'Brien. Iron meteorites as remnants of planetesimals formed in the terrestrial planet region. *Nature*, 439(7078):821–824, February 2006.
- [23] Jürgen Blum and Gerhard Wurm. The Growth Mechanisms of Macroscopic Bodies in Protoplanetary Disks. *Annual Review of Astronomy and Astrophysics*, 46(1):21–56, 2008.
- [24] Torsten Poppe, Jürgen Blum, and Thomas Henning. Analogous Experiments on the Stickiness of Micron-sized Preplanetary Dust. *The Astrophysical Journal*, 533(1):454, 2000.
- [25] S. J. Weidenschilling and Jeffrey N. Cuzzi. Formation of planetesimals in the solar nebula. pages 1031–1060, 1993.
- [26] Akira Kouchi, Tatsuyuki Kudo, Hideyuki Nakano, Masahiko Arakawa, Naoki Watanabe, Sin-iti Sirono, Michiya Higa, and Norikazu Maeno. Rapid Growth of Asteroids Owing to Very Sticky Interstellar Organic Grains. *The Astrophysical Journal Letters*, 566(2):L121, 2002.
- [27] Frank G. Bridges, Kimberly D. Supulver, D. N. C. Lin, Roberta Knight, and Mario Zafra. Energy Loss and Sticking Mechanisms in Particle Aggregation in Planetesimal Formation. *Icarus*, 123(2):422–435, October 1996.
- [28] Joseph A. Nuth, Otto Berg, James Faris, and Peter Wasilewski. Magnetically Enhanced Coagulation of Very Small Iron Grains. *Icarus*, 107(1):155–163, January 1994.
- [29] S. J. Weidenschilling. Aerodynamics of solid bodies in the solar nebula. *Monthly Notices of the Royal Astronomical Society*, 180(2):57–70, September 1977.
- [30] Jeffrey N. Cuzzi and Stuart J. Weidenschilling. Particle-gas dynamics and primary accretion. *Meteorites and the early solar system II*, 353, 2006.
- [31] V. S. Safronov. *Evolution of the protoplanetary cloud and formation of the earth and planets.* 1972.
- [32] Peter Goldreich and William R. Ward. The Formation of Planetesimals. *The Astrophysical Journal*, 183:1051–1062, August 1973.
- [33] S. J. Weidenschilling. Dust to planetesimals: Settling and coagulation in the solar nebula. *Icarus*, 44(1):172–189, October 1980.

- [34] Anders Johansen, Jeffrey S. Oishi, Mordecai-Mark Mac Low, Hubert Klahr, Thomas Henning, and Andrew Youdin. Rapid planetesimal formation in turbulent circumstellar disks. *Nature*, 448(7157):1022–1025, August 2007.
- [35] Anders Johansen, Andrew Youdin, and Mordecai-Mark Mac Low. Particle Clumping and Planetesimal Formation Depend Strongly on Metallicity. *The Astrophysical Journal Letters*, 704(2):L75, 2009.
- [36] Andrew N. Youdin and Jeremy Goodman. Streaming Instabilities in Protoplanetary Disks. *The Astrophysical Journal*, 620(1):459, 2005.
- [37] Jeffrey N. Cuzzi, Robert C. Hogan, and Karim Shariff. Toward Planetesimals: Dense Chondrule Clumps in the Protoplanetary Nebula. *The Astrophysical Journal*, 687(2):1432, 2008.
- [38] Jeffrey N. Cuzzi, Robert C. Hogan, Julie M. Paque, and Anthony R. Dobrovolskis. Sizeselective Concentration of Chondrules and Other Small Particles in Protoplanetary Nebula Turbulence. *The Astrophysical Journal*, 546(1):496, 2001.
- [39] J. E. Chambers. Planetesimal formation by turbulent concentration. *Icarus*, 208(2):505–517, August 2010.
- [40] Alessandro Morbidelli, William F. Bottke, David Nesvorný, and Harold F. Levison. Asteroids were born big. *Icarus*, 204(2):558–573, December 2009.
- [41] A. Morbidelli, J. I. Lunine, D. P. O'Brien, S. N. Raymond, and K. J. Walsh. Building Terrestrial Planets. *Annual Review of Earth and Planetary Sciences*, 40(1):251–275, 2012.
- [42] G. W. Wetherill. Formation of the Earth. *Annual Review of Earth and Planetary Sciences*, 18(1):205–256, 1990.
- [43] G. W. Wetherill and Glen R. Stewart. Accumulation of a swarm of small planetesimals. *Icarus*, 77(2):330–357, February 1989.
- [44] Richard Greenberg, John F. Wacker, William K. Hartmann, and Clark R. Chapman. Planetesimals to planets: Numerical simulation of collisional evolution. *Icarus*, 35(1):1–26, July 1978.
- [45] G. W. Wetherill and G. R. Stewart. Formation of Planetary Embryos: Effects of Fragmentation, Low Relative Velocity, and Independent Variation of Eccentricity and Inclination. *Icarus*, 106(1):190–209, November 1993.
- [46] Shigeru Ida and Junichiro Makino. Scattering of Planetesimals by a Protoplanet: Slowing Down of Runaway Growth. *Icarus*, 106(1):210–227, November 1993.
- [47] Eiichiro Kokubo and Shigeru Ida. Oligarchic Growth of Protoplanets. *Icarus*, 131(1):171– 178, January 1998.

- [48] Eiichiro Kokubo and Shigeru Ida. Formation of Protoplanets from Planetesimals in the Solar Nebula. *Icarus*, 143(1):15–27, January 2000.
- [49] Qingzhu Yin, S. B. Jacobsen, K. Yamashita, J. Blichert-Toft, P. Télouk, and F. Albarède. A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. *Nature*, 418(6901):949–952, August 2002.
- [50] M. Touboul, T. Kleine, B. Bourdon, H. Palme, and R. Wieler. Late formation and prolonged differentiation of the Moon inferred from W isotopes in lunar metals. *Nature*, 450(7173):1206–1209, December 2007.
- [51] Jr. Karl E. Haisch, Elizabeth A. Lada, and Charles J. Lada. Disk Frequencies and Lifetimes in Young Clusters. *The Astrophysical Journal Letters*, 553(2):L153, 2001.
- [52] M. Podolak and S. Zucker. A note on the snow line in protostellar accretion disks. *Meteoritics & Planetary Science*, 39(11):1859–1868, November 2004.
- [53] M. Lecar, M. Podolak, D. Sasselov, and E. Chiang. On the Location of the Snow Line in a Protoplanetary Disk. *The Astrophysical Journal*, 640(2):1115, 2006.
- [54] Eiichiro Kokubo and Shigeru Ida. Formation of Protoplanet Systems and Diversity of Planetary Systems. *The Astrophysical Journal*, 581(1):666, 2002.
- [55] Sarah E. Dodson-Robinson, Karen Willacy, Peter Bodenheimer, Neal J. Turner, and Charles A. Beichman. Ice lines, planetesimal composition and solid surface density in the solar nebula. *Icarus*, 200(2):672–693, April 2009.
- [56] Olenka Hubickyj, Peter Bodenheimer, and Jack J. Lissauer. Accretion of the gaseous envelope of Jupiter around a 5–10 Earth-mass core. *Icarus*, 179(2):415–431, December 2005.
- [57] E. W. Thommes, M. J. Duncan, and H. F. Levison. Oligarchic growth of giant planets. *Icarus*, 161(2):431–455, February 2003.
- [58] M. Lambrechts and A. Johansen. Rapid growth of gas-giant cores by pebble accretion. *Astronomy & Astrophysics*, 544:A32, August 2012.
- [59] A. Morbidelli and D. Nesvorny. Dynamics of pebbles in the vicinity of a growing planetary embryo: hydro-dynamical simulations. *Astronomy & Astrophysics*, 546:A18, October 2012.
- [60] Harold F. Levison, Katherine A. Kretke, and Martin J. Duncan. Growing the gas-giant planets by the gradual accumulation of pebbles. *Nature*, 524(7565):322–324, August 2015.
- [61] J. E. Chambers and G. W. Wetherill. Making the Terrestrial Planets: N-Body Integrations of Planetary Embryos in Three Dimensions. *Icarus*, 136(2):304–327, December 1998.

- [62] Sean N. Raymond, Thomas Quinn, and Jonathan I. Lunine. Terrestrial Planet Formation in Disks with Varying Surface Density Profiles. *The Astrophysical Journal*, 632(1):670, 2005.
- [63] Sean N. Raymond, David P. O'Brien, Alessandro Morbidelli, and Nathan A. Kaib. Building the terrestrial planets: Constrained accretion in the inner Solar System. *Icarus*, 203(2):644–662, October 2009.
- [64] J. E. Chambers. Making More Terrestrial Planets. Icarus, 152(2):205–224, August 2001.
- [65] G. W. Wetherill. Why Isn't Mars as Big as Earth? volume 22, March 1991.
- [66] E. Thommes, M. Nagasawa, and D. N. C. Lin. Dynamical Shake-up of Planetary Systems. II. N-Body Simulations of Solar System Terrestrial Planet Formation Induced by Secular Resonance Sweeping. *The Astrophysical Journal*, 676(1):728, 2008.
- [67] David P. O'Brien, Alessandro Morbidelli, and Harold F. Levison. Terrestrial planet formation with strong dynamical friction. *Icarus*, 184(1):39–58, September 2006.
- [68] Ryuji Morishima, Joachim Stadel, and Ben Moore. From planetesimals to terrestrial planets: N-body simulations including the effects of nebular gas and giant planets. *Icarus*, 207(2):517–535, June 2010.
- [69] G. A. Krasinsky, E. V. Pitjeva, M. V. Vasilyev, and E. I. Yagudina. Hidden Mass in the Asteroid Belt. *Icarus*, 158(1):98–105, July 2002.
- [70] J. E. Chambers and G. W. Wetherill. Planets in the asteroid belt. *Meteoritics & Planetary Science*, 36(3):381–399, March 2001.
- [71] Richard P. Binzel, Schelte J. Bus, Thomas H. Burbine, and Jessica M. Sunshine. Spectral Properties of Near-Earth Asteroids: Evidence for Sources of Ordinary Chondrite Meteorites. *Science*, 273(5277):946–948, August 1996.
- [72] Richard P. Binzel, Thomas H. Burbine, and Schelte J. Bus. Groundbased Reconnaissance of Asteroid 253 Mathilde: Visible Wavelength Spectrum and Meteorite Comparison. *Icarus*, 119(2):447–449, February 1996.
- [73] J. Gradie and E. Tedesco. Compositional Structure of the Asteroid Belt. *Science*, 216(4553):1405–1407, June 1982.
- [74] A. Morbidelli, J. Chambers, J. I. Lunine, J. M. Petit, F. Robert, G. B. Valsecchi, and K. E. Cyr. Source regions and timescales for the delivery of water to the Earth. *Meteoritics & Planetary Science*, 35(6):1309–1320, November 2000.
- [75] Masahiro Ikoma and Hidenori Genda. Constraints on the Mass of a Habitable Planet with Water of Nebular Origin. *The Astrophysical Journal*, 648(1):696, 2006.

- [76] Sean N Raymond, Thomas Quinn, and Jonathan I Lunine. Making other earths: dynamical simulations of terrestrial planet formation and water delivery. *Icarus*, 168(1):1–17, March 2004.
- [77] Craig Agnor and Erik Asphaug. Accretion Efficiency during Planetary Collisions. *The Astrophysical Journal Letters*, 613(2):L157, 2004.
- [78] Eiichiro Kokubo and Hidenori Genda. Formation of Terrestrial Planets from Protoplanets Under a Realistic Accretion Condition. *The Astrophysical Journal Letters*, 714(1):L21, 2010.
- [79] Erik Asphaug, Craig B. Agnor, and Quentin Williams. Hit-and-run planetary collisions. *Nature*, 439(7073):155–160, January 2006.
- [80] Brad M. S. Hansen. Formation of the Terrestrial Planets from a Narrow Annulus. *The Astrophysical Journal*, 703(1):1131, 2009.
- [81] Kevin J. Walsh, Alessandro Morbidelli, Sean N. Raymond, David P. O'Brien, and Avi M. Mandell. A low mass for Mars from Jupiter/'s early gas-driven migration. *Nature*, 475(7355):206–209, July 2011.
- [82] Alessandro Morbidelli and Aurélien Crida. The dynamics of Jupiter and Saturn in the gaseous protoplanetary disk. *Icarus*, 191(1):158–171, November 2007.
- [83] David P. O'Brien, Kevin J. Walsh, Alessandro Morbidelli, Sean N. Raymond, and Avi M. Mandell. Water delivery and giant impacts in the 'Grand Tack' scenario. *Icarus*, 239:74–84, September 2014.
- [84] Kevin J. Walsh, A. Morbidelli, S. N. Raymond, D. P. O'brien, and A. M. Mandell. Populating the asteroid belt from two parent source regions due to the migration of giant planets—"The Grand Tack". *Meteoritics & Planetary Science*, 47(12):1941–1947, December 2012.
- [85] Rogerio Deienno, Rodney S. Gomes, Kevin J. Walsh, Alessandro Morbidelli, and David Nesvorný. Is the Grand Tack model compatible with the orbital distribution of main belt asteroids? *Icarus*, 272:114–124, July 2016.
- [86] Michael K. Weisberg, Timothy J. McCoy, and Alexander N. Krot. Systematics and evaluation of meteorite classification. *Meteorites and the early solar system II*, 19, 2006.
- [87] A. N. Krot, K. Keil, E. R. D. Scott, C. A. Goodrich, and M. K. Weisberg. 1.05 Classification of Meteorites. In Heinrich D. Holland and Karl K. Turekian, editors, *Treatise on Geochemistry*, pages 1–52. Pergamon, Oxford, 2007. DOI: 10.1016/B0-08-043751-6/01062-8.
- [88] E. R. D. Scott and A. N. Krot. 1.2 Chondrites and Their Components. In Heinrich D. Holland and Karl K. Turekian, editors, *Treatise on Geochemistry (Second Edition)*, pages 65–137. Elsevier, Oxford, 2014. DOI: 10.1016/B978-0-08-095975-7.00104-2.

- [89] Edward R. D. Scott. Chondrites and the Protoplanetary Disk. *Annual Review of Earth and Planetary Sciences*, 35(1):577–620, 2007.
- [90] C. M. O'd Alexander, J. N. Grossman, D. S. Ebel, and F. J. Ciesla. The Formation Conditions of Chondrules and Chondrites. *Science*, 320(5883):1617–1619, June 2008.
- [91] Erik Asphaug, Martin Jutzi, and Naor Movshovitz. Chondrule formation during planetesimal accretion. *Earth and Planetary Science Letters*, 308(3):369–379, August 2011.
- [92] S. T. Dye, Y. Huang, V. Lekic, W. F. McDonough, and O. Šrámek. Geo-neutrinos and Earth Models. *Physics Procedia*, 61:310–318, January 2015.
- [93] Edward Anders and Nicolas Grevesse. Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta*, 53(1):197–214, January 1989.
- [94] Paul H. Warren. Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth and Planetary Science Letters*, 311(1):93–100, November 2011.
- [95] E. A. Worsham, C. Burkhardt, M. Fischer-Gödde, T. S. Kruijer, and T. Kleine. The cosmic mo-ru isotope correlation and the dichotomy between carbonaceous and noncarbonaceous meteorites. Accretion and Early Differentiation of the Earth and Terrestial Planets, Nice, 2017.
- [96] R. N. Clayton. Oxygen Isotopes in Meteorites. *Annual Review of Earth and Planetary Sciences*, 21(1):115–149, 1993.
- [97] Hisayoshi Yurimoto, Kiyoshi Kuramoto, Alexander N. Krot, Edward RD Scott, Jeffrey N. Cuzzi, Mark H. Thiemens, and James R. Lyons. Origin and evolution of oxygen isotopic compositions of the solar system. *Protostars and planets V*, pages 849–862, 2007.
- [98] Robert N. Clayton. Isotopes: From Earth to the Solar System. *Annual Review of Earth and Planetary Sciences*, 35(1):1–19, 2007.
- [99] Mark H. Thiemens. HISTORY AND APPLICATIONS OF MASS-INDEPENDENT ISOTOPE EFFECTS, April 2006.
- [100] Edward R. D. Scott and John T. Wasson. Classification and properties of iron meteorites. *Reviews of Geophysics*, 13(4):527–546, August 1975.
- [101] Richard Greenberg and Clark R. Chapman. Asteroids and meteorites: Origin of stonyiron meteorites at mantle-core boundaries. *Icarus*, 57(2):267–279, February 1984.
- [102] Harry Y. McSween, Richard P. Binzel, M. Cristina De Sanctis, Eleonora Ammannito, Thomas H. Prettyman, Andrew W. Beck, Vishnu Reddy, Lucille Le Corre, Michael J. Gaffey, Thomas B. McCord, Carol A. Raymond, Christopher T. Russell, and the Dawn Science Team. Dawn; the Vesta–HED connection; and the geologic context for eucrites, diogenites, and howardites. *Meteoritics & Planetary Science*, 48(11):2090–2104, November 2013.

- [103] Harold C. Urey. The cosmic abundances of potassium, uranium, and thorium and the heat balances of the Earth, the Moon, and Mars. *Proceedings of the National Academy of Sciences*, 41(3):127–144, 1955.
- [104] Ondřej Šrámek, Laura Milelli, Yanick Ricard, and Stéphane Labrosse. Thermal evolution and differentiation of planetesimals and planetary embryos. *Icarus*, 217(1):339–354, January 2012.
- [105] Nicholas Moskovitz and Eric Gaidos. Differentiation of planetesimals and the thermal consequences of melt migration. *Meteoritics & Planetary Science*, 46(6):903–918, June 2011.
- [106] Phonsie J. Hevey and Ian S. Sanders. A model for planetesimal meltdown by 26al and its implications for meteorite parent bodies. *Meteoritics & Planetary Science*, 41(1):95–106, January 2006.
- [107] S. Sahijpal, P. Soni, and G. Gupta. Numerical simulations of the differentiation of accreting planetesimals with 26al and 60fe as the heat sources. *Meteoritics & Planetary Science*, 42(9):1529–1548, September 2007.
- [108] Martin Bizzarro, Joel A. Baker, Henning Haack, and Kasper L. Lundgaard. Rapid Timescales for Accretion and Melting of Differentiated Planetesimals Inferred from 26al-26mg Chronometry. *The Astrophysical Journal Letters*, 632(1):L41, 2005.
- [109] Benjamin P. Weiss and Linda T. Elkins-Tanton. Differentiated Planetesimals and the Parent Bodies of Chondrites. Annual Review of Earth and Planetary Sciences, 41(1):529– 560, 2013.
- [110] Bernard J. Wood, Michael J. Walter, and Jonathan Wade. Accretion of the Earth and segregation of its core. *Nature*, 441(7095):825–833, June 2006.
- [111] B. Ryzhenko and G. C. Kennedy. The effect of pressure on the eutectic in the system Fe-FeS. *American Journal of Science*, 273(9):803–810, 1973.
- [112] Carl B. Agee. Melting temperatures of the Allende meteorite: implications for a Hadean magma ocean. *Physics of the Earth and Planetary Interiors*, 100(1):41–47, March 1997.
- [113] G. Jeffrey Taylor, Klaus Keil, Timothy McCoy, Henning Haack, and Edward R. D. Scott. Asteroid Differentiation: Pyroclastic Volcanism to Magma Oceans. *Meteoritics*, 28(1):34– 52, March 1993.
- [114] Lionel Wilson and Klaus Keil. Consequences of explosive eruptions on small Solar System bodies: the case of the missing basalts on the aubrite parent body. *Earth and Planetary Science Letters*, 104(2):505–512, June 1991.
- [115] R. Boehler. Temperatures in the Earth's core from melting-point measurements of iron at high static pressures. *Nature*, 363(6429):534–536, June 1993.

- [116] G. Jeffrey Taylor. Core formation in asteroids. *Journal of Geophysical Research: Planets*, 97(E9):14717–14726, September 1992.
- [117] Richard C. Greenwood, Ian A. Franchi, Albert Jambon, and Paul C. Buchanan. Widespread magma oceans on asteroidal bodies in the early Solar System. *Nature*, 435(7044):916–918, June 2005.
- [118] Cyrena Anne Goodrich, William K. Hartmann, David P. O'Brien, Stuart J. Weidenschilling, Lionel Wilson, Patrick Michel, and Martin Jutzi. Origin and history of ureilitic material in the solar system: The view from asteroid 2008 TC3 and the Almahata Sitta meteorite. *Meteoritics & Planetary Science*, 50(4):782–809, April 2015.
- [119] Cyrena Anne Goodrich. Ureilites: A critical review. *Meteoritics & Planetary Science*, 27(4):327–352, 1992.
- [120] Masamichi Miyamoto, Hiroshi Takeda, and Hiromi Toyoda. Cooling history of some Antarctic ureilites. *Journal of Geophysical Research: Solid Earth*, 90(S01):116–122, November 1985.
- [121] S. J. Singletary and T. L. Grove. Early petrologic processes on the ureilite parent body. *Meteoritics & Planetary Science*, 38(1):95–108, January 2003.
- [122] Cyrena Anne Goodrich, Edward R. D. Scott, and Anna Maria Fioretti. Ureilitic breccias: clues to the petrologic structure and impact disruption of the ureilite parent asteroid. *Chemie der Erde - Geochemistry*, 64(4):283–327, November 2004.
- [123] Cyrena Anne Goodrich, James A. Van Orman, and Lionel Wilson. Fractional melting and smelting on the ureilite parent body. *Geochimica et Cosmochimica Acta*, 71(11):2876– 2895, June 2007.
- [124] Cyrena A. Goodrich, Richard D. Ash, James A. Van Orman, Kenneth Domanik, and William F. McDonough. Metallic phases and siderophile elements in main group ureilites: Implications for ureilite petrogenesis. *Geochimica et Cosmochimica Acta*, 112:340– 373, July 2013.
- [125] Paul H. Warren, Finn Ulff-Møller, Heinz Huber, and Gregory W. Kallemeyn. Siderophile geochemistry of ureilites: A record of early stages of planetesimal core formation. *Geochimica et Cosmochimica Acta*, 70(8):2104–2126, April 2006.
- [126] Paul H. Warren. Parent body depth–pressure–temperature relationships and the style of the ureilite anatexis. *Meteoritics & Planetary Science*, 47(2):209–227, February 2012.
- [127] J. A. Barrat, O. Rouxel, K. Wang, F. Moynier, A. Yamaguchi, A. Bischoff, and J. Langlade. Early stages of core segregation recorded by Fe isotopes in an asteroidal mantle. *Earth and Planetary Science Letters*, 419:93–100, June 2015.

- [128] Paul H. Warren and Gregory W. Kallemeyn. Explosive volcanism and the graphite-oxygen fugacity buffer on the parent asteroid(s) of the ureilite meteorites. *Icarus*, 100(1):110–126, November 1992.
- [129] Lionel Wilson, Cyrena Anne Goodrich, and James A. Van Orman. Thermal evolution and physics of melt extraction on the ureilite parent body. *Geochimica et Cosmochimica Acta*, 72(24):6154–6176, December 2008.
- [130] Barbara A. Cohen, Cyrena A. Goodrich, and Klaus Keil. Feldspathic clast populations in polymict ureilites: Stalking the missing basalts from the ureilite parent body. *Geochimica et Cosmochimica Acta*, 68(20):4249–4266, October 2004.
- [131] J. L. Berkely and J. H. Jones. Primary igneous carbon in ureilites Petrological implications. volume 13, pages A353–A364, 1982.
- [132] Cyrena Anne Goodrich and John L. Berkley. Primary magmatic carbon in ureilites: Evidence from cohenite-bearing metallic spherules. *Geochimica et Cosmochimica Acta*, 50(5):681–691, May 1986.
- [133] Robert N. Clayton and Toshiko K. Mayeda. Formation of ureilites by nebular processes. *Geochimica et Cosmochimica Acta*, 52(5):1313–1318, May 1988.
- [134] Robert N. Clayton and Toshiko K. Mayeda. Oxygen isotope studies of achondrites. *Geochimica et Cosmochimica Acta*, 60(11):1999–2017, June 1996.
- [135] Richard C. Greenwood, Thomas H. Burbine, Martin F. Miller, and Ian. A. Franchi. Melting and differentiation of early-formed asteroids: The perspective from high precision oxygen isotope studies. *Chemie der Erde - Geochemistry*, 77(1):1–43, April 2017.
- [136] Edward D. Young and Sara S. Russell. Oxygen Reservoirs in the Early Solar Nebula Inferred from an Allende CAI. *Science*, 282(5388):452–455, October 1998.
- [137] Takayuki Ushikubo, Makoto Kimura, Noriko T. Kita, and John W. Valley. Primordial oxygen isotope reservoirs of the solar nebula recorded in chondrules in Acfer 094 carbonaceous chondrite. *Geochimica et Cosmochimica Acta*, 90:242–264, August 2012.
- [138] Paul H. Warren. Stable isotopes and the noncarbonaceous derivation of ureilites, in common with nearly all differentiated planetary materials. *Geochimica et Cosmochimica Acta*, 75(22):6912–6926, November 2011.
- [139] N. Dauphas, L. Remusat, J. H. Chen, M. Roskosz, D. A. Papanastassiou, J. Stodolna, Y. Guan, C. Ma, and J. M. Eiler. Neutron-rich Chromium Isotope Anomalies in Supernova Nanoparticles. *The Astrophysical Journal*, 720(2):1577, 2010.
- [140] L. Qin, L. R. Nittler, C. M. O'D. Alexander, J. Wang, F. J. Stadermann, and R. W. Carlson. Extreme 54cr-rich nano-oxides in the CI chondrite Orgueil – Implication for a late supernova injection into the solar system. *Geochimica et Cosmochimica Acta*, 75(2):629– 644, January 2011.

- [141] Joel A. Baker, Martin Schiller, and Martin Bizzarro. 26al–26mg deficit dating ultramafic meteorites and silicate planetesimal differentiation in the early Solar System? *Geochimica et Cosmochimica Acta*, 77:415–431, January 2012.
- [142] Der-Chuen Lee, Alex N. Halliday, Steven J. Singletary, and Timothy L. Grove. 182hf–182w chronometry and early differentiation of the ureilite parent body. *Earth and Planetary Science Letters*, 288(3):611–618, November 2009.
- [143] Elishevah M. M. E. van Kooten, Martin Schiller, and Martin Bizzarro. Magnesium and chromium isotope evidence for initial melting by radioactive decay of 26al and late stage impact-melting of the ureilite parent body. *Geochimica et Cosmochimica Acta*, 208:1–23, July 2017.
- [144] Michael E. Lipschutz. Origin of Diamonds in the Ureilites. *Science*, 143(3613):1431–1434, March 1964.
- [145] Y. Nakamuta and Y. Aoki. Mineralogical evidence for the origin of diamond in ureilites. *Meteoritics & Planetary Science*, 35(3):487–493, May 2000.
- [146] Kazuya Fukunaga, Jun-ichi Matsuda, Keisuke Nagao, Masamichi Miyamoto, and Keisuke Ito. Noble-gas enrichment in vapour-growth diamonds and the origin of diamonds in ureilites. *Nature*, 328(6126):141–143, July 1987.
- [147] Masaaki Miyahara, Eiji Ohtani, Ahmed El Goresy, Yangting Lin, Lu Feng, Jian-Chao Zhang, Philippe Gillet, Toshiro Nagase, Jun Muto, and Masahiko Nishijima. Unique large diamonds in a ureilite from Almahata Sitta 2008 TC3 asteroid. *Geochimica et Cosmochimica Acta*, 163:14–26, August 2015.
- [148] S. R. Taylor. Chondritic Earth Model. Nature, 202(4929):281–282, April 1964.
- [149] S. R. Taylor. Trace element abundances and the chondritic Earth model. *Geochimica et Cosmochimica Acta*, 28(12):1989–1998, December 1964.
- [150] M. Javoy, E. Kaminski, F. Guyot, D. Andrault, C. Sanloup, M. Moreira, S. Labrosse, A. Jambon, P. Agrinier, A. Davaille, and C. Jaupart. The chemical composition of the Earth: Enstatite chondrite models. *Earth and Planetary Science Letters*, 293(3):259–268, May 2010.
- [151] Caroline Fitoussi and Bernard Bourdon. Silicon Isotope Evidence Against an Enstatite Chondrite Earth. *Science*, 335(6075):1477–1480, March 2012.
- [152] Caroline Fitoussi, Bernard Bourdon, Thorsten Kleine, Felix Oberli, and Ben C. Reynolds. Si isotope systematics of meteorites and terrestrial peridotites: implications for Mg/Si fractionation in the solar nebula and for Si in the Earth's core. *Earth and Planetary Science Letters*, 287(1):77–85, September 2009.
- [153] Ian H. Campbell and Hugh St C. O'Neill. Evidence against a chondritic Earth. *Nature*, 483(7391):553–558, March 2012.

- [154] William K. Hartmann and Donald R. Davis. Satellite-sized planetesimals and lunar origin. *Icarus*, 24(4):504–515, April 1975.
- [155] A. G. W. Cameron and W. R. Ward. The Origin of the Moon. volume 7, March 1976.
- [156] Robin M. Canup and Erik Asphaug. Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature*, 412(6848):708–712, August 2001.
- [157] U. Wiechert, A. N. Halliday, D.-C. Lee, G. A. Snyder, L. A. Taylor, and D. Rumble. Oxygen Isotopes and the Moon-Forming Giant Impact. *Science*, 294(5541):345–348, October 2001.
- [158] A. G. W. Cameron and W. Benz. The origin of the moon and the single impact hypothesis IV. *Icarus*, 92(2):204–216, August 1991.
- [159] I. A. Franchi, I. P. Wright, A. S. Sexton, and C. T. Pillinger. The oxygen-isotopic composition of Earth and Mars. *Meteoritics & Planetary Science*, 34(4):657–661, July 1999.
- [160] Kaveh Pahlevan and David J. Stevenson. Equilibration in the aftermath of the lunarforming giant impact. *Earth and Planetary Science Letters*, 262(3):438–449, October 2007.
- [161] Robin M. Canup. Forming a Moon with an Earth-like Composition via a Giant Impact. *Science*, 338(6110):1052–1055, November 2012.
- [162] S. J. Lock, S. T. Stewart, M. I. Petaev, Z. M. Leinhardt, M. Mace, S. B. Jacobsen, and M. Ćuk. A New Model for Lunar Origin: Equilibration with Earth Beyond the Hot Spin Stability Limit. volume 47, page 2881, March 2016.
- [163] Simon J. Lock and Sarah T. Stewart. The structure of terrestrial bodies: Impact heating, corotation limits, and synestias. *Journal of Geophysical Research: Planets*, 122(5):2016JE005239, May 2017.
- [164] Matija Ćuk and Sarah T. Stewart. Making the Moon from a Fast-Spinning Earth: A Giant Impact Followed by Resonant Despinning. *Science*, 338(6110):1047–1052, November 2012.
- [165] Alex N. Halliday. A young Moon-forming giant impact at 70–110 million years accompanied by late-stage mixing, core formation and degassing of the Earth. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 366(1883):4163–4181, November 2008.
- [166] Seth A. Jacobson, Alessandro Morbidelli, Sean N. Raymond, David P. O'Brien, Kevin J. Walsh, and David C. Rubie. Highly siderophile elements in Earth/'s mantle as a clock for the Moon-forming impact. *Nature*, 508(7494):84–87, April 2014.
- [167] A. E. Ringwood. Composition and petrology of the earth's mantle. McGraw-Hill, 1975. Google-Books-ID: UmgSAQAAIAAJ.

- [168] V. Rama Murthy. Early Differentiation of the Earth and the Problem of Mantle Siderophile Elements: A New Approach. *Science*, 253(5017):303–306, July 1991.
- [169] John H. Jones and Michael J. Drake. Geochemical constraints on core formation in the Earth. *Nature*, 322(6076):221–228, July 1986.
- [170] Jie Li and Carl B. Agee. Geochemistry of mantle–core differentiation at high pressure. *Nature*, 381(6584):686–689, June 1996.
- [171] Julien Siebert, Alexandre Corgne, and Frederick J. Ryerson. Systematics of metal–silicate partitioning for many siderophile elements applied to Earth's core formation. *Geochimica et Cosmochimica Acta*, 75(6):1451–1489, March 2011.
- [172] D. C. Rubie, H. J. Melosh, J. E. Reid, C. Liebske, and K. Righter. Mechanisms of metal-silicate equilibration in the terrestrial magma ocean. *Earth and Planetary Science Letters*, 205(3):239–255, January 2003.
- [173] Kan Kimura, Roy S Lewis, and Edward Anders. Distribution of gold and rhenium between nickel-iron and silicate melts: implications for the abundance of siderophile elements on the Earth and Moon. *Geochimica et Cosmochimica Acta*, 38(5):683–701, May 1974.
- [174] A. Holzheid, P. Sylvester, H. St C. O'Neill, D. C. Rubie, and H. Palme. Evidence for a late chondritic veneer in the Earth's mantle from high-pressure partitioning of palladium and platinum : Article : Nature. *Nature*, 406(6794):396–399, July 2000.
- [175] Michael J. Drake, Horton E. Newsom, and Christopher J. Capobianco. V, Cr, and Mn in the Earth, Moon, EPB, and SPB and the origin of the Moon: Experimental studies. *Geochimica et Cosmochimica Acta*, 53(8):2101–2111, August 1989.
- [176] Julien Siebert and Anat Shahar. An Experimental Geochemistry Perspective on Earth's Core Formation. In James Badro and Michael Walter, editors, *The Early Earth*, pages 103–121. John Wiley & Sons, Inc, 2015. DOI: 10.1002/9781118860359.ch6.
- [177] J. Wade and B. J. Wood. Core formation and the oxidation state of the Earth. *Earth and Planetary Science Letters*, 236(1):78–95, July 2005.
- [178] Bernard J. Wood, Jon Wade, and Matthew R. Kilburn. Core formation and the oxidation state of the Earth: Additional constraints from Nb, V and Cr partitioning. *Geochimica et Cosmochimica Acta*, 72(5):1415–1426, March 2008.
- [179] David C. Rubie, Daniel J. Frost, Ute Mann, Yuki Asahara, Francis Nimmo, Kyusei Tsuno, Philip Kegler, Astrid Holzheid, and Herbert Palme. Heterogeneous accretion, composition and core–mantle differentiation of the Earth. *Earth and Planetary Science Letters*, 301(1):31–42, January 2011.
- [180] Julien Siebert, James Badro, Daniele Antonangeli, and Frederick J. Ryerson. Terrestrial Accretion Under Oxidizing Conditions. *Science*, 339(6124):1194–1197, March 2013.

- [181] Francis Birch. Elasticity and constitution of the Earth's interior. *Journal of Geophysical Research*, 57(2):227–286, June 1952.
- [182] James Badro, John P. Brodholt, Hélène Piet, Julien Siebert, and Frederick J. Ryerson. Core formation and core composition from coupled geochemical and geophysical constraints. *Proceedings of the National Academy of Sciences*, 112(40):12310–12314, October 2015.
- [183] P.S. Savage, F. Moynier, H. Chen, G. Shofner, J. Siebert, J. Badro, and I.S. Puchtel. Copper isotope evidence for large-scale sulphide fractionation during Earth?s differentiation. *Geochemical Perspectives Letters*, pages 53–64, 2015.
- [184] Tatsuya Sakamaki, Eiji Ohtani, Hiroshi Fukui, Seiji Kamada, Suguru Takahashi, Takanori Sakairi, Akihiro Takahata, Takeshi Sakai, Satoshi Tsutsui, Daisuke Ishikawa, Rei Shiraishi, Yusuke Seto, Taku Tsuchiya, and Alfred Q. R. Baron. Constraints on Earth's inner core composition inferred from measurements of the sound velocity of hcp-iron in extreme conditions. *Science Advances*, 2(2):e1500802, February 2016.
- [185] C. Prescher, L. Dubrovinsky, E. Bykova, I. Kupenko, K. Glazyrin, A. Kantor, C. McCammon, M. Mookherjee, Y. Nakajima, N. Miyajima, R. Sinmyo, V. Cerantola, N. Dubrovinskaia, V. Prakapenka, R. Rüffer, A. Chumakov, and M. Hanfland. High Poisson's ratio of Earth's inner core explained by carbon alloying. *Nature Geoscience*, 8(3):220–223, March 2015.
- [186] Shigehiko Tateno, Kei Hirose, Yasuo Ohishi, and Yoshiyuki Tatsumi. The Structure of Iron in Earth's Inner Core. *Science*, 330(6002):359–361, October 2010.
- [187] L. Dubrovinsky, N. Dubrovinskaia, O. Narygina, I. Kantor, A. Kuznetzov, V. B. Prakapenka, L. Vitos, B. Johansson, A. S. Mikhaylushkin, S. I. Simak, and I. A. Abrikosov. Body-Centered Cubic Iron-Nickel Alloy in Earth9s Core. *Science*, 316(5833):1880–1883, June 2007.
- [188] George R. Helffrich and Bernard J. Wood. The Earth's mantle. *Nature*, 412(6846):501–507, August 2001.
- [189] A. E. Ringwood. A model for the upper mantle. *Journal of Geophysical Research*, 67(2):857–867, February 1962.
- [190] D. H. Green and A. E. Ringwood. Mineral assemblages in a model mantle composition. *Journal of Geophysical Research*, 68(3):937–945, February 1963.
- [191] Ian Jackson. *The Earth's Mantle: Composition, Structure, and Evolution.* Cambridge University Press, June 2000. Google-Books-ID: RlixwcPYF2AC.
- [192] W. F. McDonough and S. s. Sun. The composition of the Earth. *Chemical Geology*, 120(3):223–253, March 1995.
- [193] Adam M. Dziewonski and Don L. Anderson. Preliminary reference Earth model. *Physics of the Earth and Planetary Interiors*, 25(4):297–356, June 1981.

- [194] Angele Ricolleau, Yingwei Fei, Elizabeth Cottrell, Heather Watson, Liwei Deng, Li Zhang, Guillaume Fiquet, Anne-Line Auzende, Mathieu Roskosz, Guillaume Morard, and Vitali Prakapenka. Density profile of pyrolite under the lower mantle conditions. *Geophysical Research Letters*, 36(6):L06302, March 2009.
- [195] Tetsuo Irifune, Toru Shinmei, Catherine A. McCammon, Nobuyoshi Miyajima, David C. Rubie, and Daniel J. Frost. Iron Partitioning and Density Changes of Pyrolite in Earth's Lower Mantle. *Science*, 327(5962):193–195, January 2010.
- [196] Motohiko Murakami, Yasuo Ohishi, Naohisa Hirao, and Kei Hirose. A perovskitic lower mantle inferred from high-pressure, high-temperature sound velocity data. *Nature*, 485(7396):90–94, May 2012.
- [197] Xianlong Wang, Taku Tsuchiya, and Atsushi Hase. Computational support for a pyrolitic lower mantle containing ferric iron. *Nature Geoscience*, 8(7):556–559, July 2015.
- [198] Daniel J. Frost. The Upper Mantle and Transition Zone. *Elements*, 4(3):171–176, June 2008.
- [199] J. D. Bernal. Discussion. Observatory, 59:268, 1936.
- [200] A. E. Ringwood and A. Major. The system Mg2sio4Fe2sio4 at high pressures and temperatures. *Physics of the Earth and Planetary Interiors*, 3:89–108, January 1970.
- [201] Lin-Gun Liu. The post-spinel phase of forsterite. *Nature*, 262(5571):770–772, August 1976.
- [202] Eiji Ito and Eiichi Takahashi. Postspinel transformations in the system Mg2sio4-Fe2sio4 and some geophysical implications. *Journal of Geophysical Research: Solid Earth*, 94(B8):10637–10646, August 1989.
- [203] M. Akaogi and S. Akimoto. Pyroxene-garnet solid-solution equilibria in the systems Mg4si4o12Mg3al2si3o12 and Fe4si4o12Fe3al2si3o12 at high pressures and temperatures. *Physics of the Earth and Planetary Interiors*, 15(1):90–106, September 1977.
- [204] Bernard J. Wood. Phase transformations and partitioning relations in peridotite under lower mantle conditions. *Earth and Planetary Science Letters*, 174(3):341–354, January 2000.
- [205] Oliver Tschauner, Chi Ma, John R. Beckett, Clemens Prescher, Vitali B. Prakapenka, and George R. Rossman. Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite. *Science*, 346(6213):1100–1102, November 2014.
- [206] Wendy Mao, Jinfu Shu, Jingzhu Hu, Russell Hemley, and Ho-kwang Mao. Displacive transition in magnesiowüstite. *Journal of Physics: Condensed Matter*, 14(44):11349, 2002.

- [207] L. S. Dubrovinsky, N. A. Dubrovinskaia, S. K. Saxena, H. Annersten, E. Hålenius, H. Harryson, F. Tutti, S. Rekhi, and T. Le Bihan. Stability of Ferropericlase in the Lower Mantle. *Science*, 289(5478):430–432, July 2000.
- [208] Kazuhiko Otsuka, Micaela Longo, Catherine A. McCammon, and Shun-ichiro Karato. Ferric iron content of ferropericlase as a function of composition, oxygen fugacity, temperature and pressure: Implications for redox conditions during diamond formation in the lower mantle. *Earth and Planetary Science Letters*, 365:7–16, March 2013.
- [209] Nicola C. Richmond and John P. Brodholt. Calculated role of aluminum in the incorporation of ferric iron into magnesium silicate perovskite. *American Mineralogist*, 83(9-10):947–951, 2015.
- [210] D. Andrault, D.R. Neuville, A.-M. Flank, and Y. Wang. Cation sites in Al-rich MgSiO3 perovskites. *American Mineralogist*, 83(9-10):1045–1053, 2015.
- [211] Catherine McCammon. Perovskite as a possible sink for ferric iron in the lower mantle. *Nature*, 387(6634):694–696, June 1997.
- [212] Daniel J. Frost, Christian Liebske, Falko Langenhorst, Catherine A. McCammon, Reidar G. Trønnes, and David C. Rubie. Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature*, 428(6981):409–412, March 2004.
- [213] A. Kurnosov, H. Marquardt, D. J. Frost, T. Boffa Ballaran, and L. Ziberna. Evidence for a Fe3+-rich pyrolitic lower mantle from (Al,Fe)-bearing bridgmanite elasticity data. *Nature*, 543(7646):543–546, March 2017.
- [214] Sang-Heon Shim, Brent Grocholski, Yu Ye, E. Ercan Alp, Shenzhen Xu, Dane Morgan, Yue Meng, and Vitali B. Prakapenka. Stability of ferrous-iron-rich bridgmanite under reducing midmantle conditions. *Proceedings of the National Academy of Sciences*, 114(25):6468–6473, June 2017.
- [215] Roger G. Burns. *Mineralogical Applications of Crystal Field Theory*. Cambridge Topics in Mineral Physics and Chemistry. Cambridge University Press, 2 edition, 1993.
- [216] Jung-Fu Lin, Sergio Speziale, Zhu Mao, and Hauke Marquardt. Effects of the Electronic Spin Transitions of Iron in Lower Mantle Minerals: Implications for Deep Mantle Geophysics and Geochemistry. *Reviews of Geophysics*, 51(2):244–275, April 2013.
- [217] James Badro, Guillaume Fiquet, François Guyot, Jean-Pascal Rueff, Viktor V. Struzhkin, György Vankó, and Giulio Monaco. Iron Partitioning in Earth9s Mantle: Toward a Deep Lower Mantle Discontinuity. *Science*, 300(5620):789–791, May 2003.
- [218] Yingwei Fei, Li Zhang, Alexandre Corgne, Heather Watson, Angele Ricolleau, Yue Meng, and Vitali Prakapenka. Spin transition and equations of state of (Mg, Fe)O solid solutions. *Geophysical Research Letters*, 34(17):L17307, September 2007.

- [219] Tetsuya Komabayashi, Kei Hirose, Yukio Nagaya, Emiko Sugimura, and Yasuo Ohishi. High-temperature compression of ferropericlase and the effect of temperature on iron spin transition. *Earth and Planetary Science Letters*, 297(3):691–699, September 2010.
- [220] Jung-Fu Lin, Viktor V. Struzhkin, Steven D. Jacobsen, Michael Y. Hu, Paul Chow, Jennifer Kung, Haozhe Liu, Ho-kwang Mao, and Russell J. Hemley. Spin transition of iron in magnesiowüstite in the Earth's lower mantle. *Nature*, 436(7049):377–380, July 2005.
- [221] Anne-Line Auzende, James Badro, Frederick J. Ryerson, Peter K. Weber, Stewart J. Fallon, Ahmed Addad, Julien Siebert, and Guillaume Fiquet. Element partitioning between magnesium silicate perovskite and ferropericlase: New insights into bulk lower-mantle geochemistry. *Earth and Planetary Science Letters*, 269(1):164–174, May 2008.
- [222] Takeshi Sakai, Eiji Ohtani, Hidenori Terasaki, Naoki Sawada, Yusuke Kobayashi, Masaaki Miyahara, Masahiko Nishijima, Naohisa Hirao, Yasuo Ohishi, and Takumi Kikegawa. Fe-Mg partitioning between perovskite and ferropericlase in the lower mantle. *American Mineralogist*, 94(7):921–925, July 2009.
- [223] James Badro, Jean-Pascal Rueff, György Vankó, Giulio Monaco, Guillaume Fiquet, and François Guyot. Electronic Transitions in Perovskite: Possible Nonconvecting Layers in the Lower Mantle. *Science*, 305(5682):383–386, July 2004.
- [224] C. McCammon, I. Kantor, O. Narygina, J. Rouquette, U. Ponkratz, I. Sergueev, M. Mezouar, V. Prakapenka, and L. Dubrovinsky. Stable intermediate-spin ferrous iron in lower-mantle perovskite. *Nature Geoscience*, 1(10):684–687, October 2008.
- [225] Jung-Fu Lin, Heather Watson, György Vankó, Esen E. Alp, Vitali B. Prakapenka, Przemek Dera, Viktor V. Struzhkin, Atsushi Kubo, Jiyong Zhao, Catherine McCammon, and William J. Evans. Intermediate-spin ferrous iron in lowermost mantle post-perovskite and perovskite. *Nature Geoscience*, 1(10):688–691, October 2008.
- [226] Han Hsu, Peter Blaha, Matteo Cococcioni, and Renata M. Wentzcovitch. Spin-State Crossover and Hyperfine Interactions of Ferric Iron in \${\mathrm{MgSiO}}_{3}\$ Perovskite. *Physical Review Letters*, 106(11):118501, March 2011.
- [227] Krystle Catalli, Sang-Heon Shim, Vitali B. Prakapenka, Jiyong Zhao, Wolfgang Sturhahn, Paul Chow, Yuming Xiao, Haozhe Liu, Hyunchae Cynn, and William J. Evans. Spin state of ferric iron in MgSiO3 perovskite and its effect on elastic properties. *Earth and Planetary Science Letters*, 289(1):68–75, January 2010.
- [228] Ryosuke Sinmyo and Kei Hirose. Iron partitioning in pyrolitic lower mantle. *Physics and Chemistry of Minerals*, 40(2):107–113, February 2013.
- [229] Clemens Prescher, Falko Langenhorst, Leonid S. Dubrovinsky, Vitali B. Prakapenka, and Nobuyoshi Miyajima. The effect of Fe spin crossovers on its partitioning behavior and oxidation state in a pyrolitic Earth's lower mantle system. *Earth and Planetary Science Letters*, 399:86–91, August 2014.

- [230] Sang-Heon Shim. The Postperovskite Transition. *Annual Review of Earth and Planetary Sciences*, 36(1):569–599, 2008.
- [231] Thorne Lay and Donald V. Helmberger. A lower mantle S-wave triplication and the shear velocity structure of D. *Geophysical Journal of the Royal Astronomical Society*, 75(3):799–837, December 1983.
- [232] Edward J. Garnero and Allen K. McNamara. Structure and Dynamics of Earth9s Lower Mantle. Science, 320(5876):626–628, May 2008.
- [233] Motohiko Murakami, Kei Hirose, Katsuyuki Kawamura, Nagayoshi Sata, and Yasuo Ohishi. Post-Perovskite Phase Transition in MgSiO₃. *Science*, 304(5672):855–858, May 2004.
- [234] Artem R. Oganov and Shigeaki Ono. Theoretical and experimental evidence for a postperovskite phase of MgSiO3 in Earth's D|[Prime]| layer. *Nature*, 430(6998):445–448, July 2004.
- [235] John W. Hernlund, Christine Thomas, and Paul J. Tackley. A doubling of the postperovskite phase boundary and structure of the Earth's lowermost mantle. *Nature*, 434(7035):882–886, April 2005.
- [236] Thorne Lay, John Hernlund, Edward J. Garnero, and Michael S. Thorne. A Post-Perovskite Lens and D99 Heat Flux Beneath the Central Pacific. Science, 314(5803):1272–1276, November 2006.
- [237] Edward J. Garnero, Allen K. McNamara, and Sang-Heon Shim. Continent-sized anomalous zones with low seismic velocity at the base of Earth's mantle. *Nature Geoscience*, 9(7):481–489, July 2016.
- [238] Jeannot Trampert, Frédéric Deschamps, Joseph Resovsky, and Dave Yuen. Probabilistic Tomography Maps Chemical Heterogeneities Throughout the Lower Mantle. *Science*, 306(5697):853–856, October 2004.
- [239] Miaki Ishii and Jeroen Tromp. Normal-Mode and Free-Air Gravity Constraints on Lateral Variations in Velocity and Density of Earth9s Mantle. *Science*, 285(5431):1231–1236, August 1999.
- [240] Allen K. McNamara and Shijie Zhong. Thermochemical structures beneath Africa and the Pacific Ocean. *Nature*, 437(7062):1136–1139, October 2005.
- [241] Paul J. Tackley. Mantle Convection and Plate Tectonics: Toward an Integrated Physical and Chemical Theory. *Science*, 288(5473):2002–2007, June 2000.
- [242] Michael S Thorne, Edward J Garnero, and Stephen P Grand. Geographic correlation between hot spots and deep mantle lateral shear-wave velocity gradients. *Physics of the Earth and Planetary Interiors*, 146(1):47–63, August 2004.

- [243] Scott W. French and Barbara Romanowicz. Broad plumes rooted at the base of the Earth's mantle beneath major hotspots. *Nature*, 525(7567):95–99, September 2015.
- [244] Li Zhang, Yue Meng, Wenge Yang, Lin Wang, Wendy L. Mao, Qiao-Shi Zeng, Jong Seok Jeong, Andrew J. Wagner, K. Andre Mkhoyan, Wenjun Liu, Ruqing Xu, and Ho-kwang Mao. Disproportionation of (Mg,Fe)SiO₃ perovskite in Earth's deep lower mantle. *Science*, 344(6186):877–882, May 2014.
- [245] Quentin Williams and Edward J. Garnero. Seismic Evidence for Partial Melt at the Base of Earth9s Mantle. *Science*, 273(5281):1528–1530, September 1996.
- [246] Allen K. McNamara, Edward J. Garnero, and Sebastian Rost. Tracking deep mantle reservoirs with ultra-low velocity zones. *Earth and Planetary Science Letters*, 299(1):1–9, October 2010.
- [247] Wendy L. Mao, Ho-kwang Mao, Wolfgang Sturhahn, Jiyong Zhao, Vitali B. Prakapenka, Yue Meng, Jinfu Shu, Yingwei Fei, and Russell J. Hemley. Iron-Rich Post-Perovskite and the Origin of Ultralow-Velocity Zones. *Science*, 312(5773):564–565, April 2006.
- [248] J. K. Wicks, J. M. Jackson, and W. Sturhahn. Very low sound velocities in iron-rich (Mg,Fe)O: Implications for the core-mantle boundary region. *Geophysical Research Letters*, 37(15):L15304, August 2010.
- [249] S. Labrosse, J. W. Hernlund, and N. Coltice. A crystallizing dense magma ocean at the base of the Earth's mantle. *Nature*, 450(7171):866–869, December 2007.
- [250] G. Fiquet, A. L. Auzende, J. Siebert, A. Corgne, H. Bureau, H. Ozawa, and G. Garbarino. Melting of Peridotite to 140 Gigapascals. *Science*, 329(5998):1516–1518, September 2010.
- [251] Denis Andrault, Sylvain Petitgirard, Giacomo Lo Nigro, Jean-Luc Devidal, Giulia Veronesi, Gaston Garbarino, and Mohamed Mezouar. Solid-liquid iron partitioning in Earth/'s deep mantle. *Nature*, 487(7407):354–357, July 2012.
- [252] Denis Andrault, Giacomo Pesce, Mohamed Ali Bouhifd, Nathalie Bolfan-Casanova, Jean-Marc Hénot, and Mohamed Mezouar. Melting of subducted basalt at the core-mantle boundary. *Science*, 344(6186):892–895, May 2014.
- [253] A. Jayaraman. Diamond anvil cell and high-pressure physical investigations. *Reviews of Modern Physics*, 55(1):65–108, January 1983.
- [254] D. Yamazaki, E. Ito, T. Yoshino, N. Tsujino, A. Yoneda, X. Guo, F. Xu, Y. Higo, and K. Funakoshi. Over 1mbar generation in the Kawai-type multianvil apparatus and its application to compression of (Mg0.92fe0.08)SiO3 perovskite and stishovite. *Physics of the Earth and Planetary Interiors*, 228:262–267, March 2014.
- [255] A. W. Lawson and TingYuan Tang. A Diamond Bomb for Obtaining Powder Pictures at High Pressures. *Review of Scientific Instruments*, 21(9):815–815, September 1950.

- [256] John C. Jamieson, A. W. Lawson, and N. D. Nachtrieb. New Device for Obtaining XRay Diffraction Patterns from Substances Exposed to High Pressure. *Review of Scientific Instruments*, 30(11):1016–1019, November 1959.
- [257] C. E. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting. Infrared studies in the 1-to 15-micron region to 30,000 atmospheres. *J. Res. Natl. Bur. Stand. A*, 63:55–62, 1959.
- [258] Arthur L. Ruoff, Hui Xia, Huan Luo, and Yogesh K. Vohra. Miniaturization techniques for obtaining static pressures comparable to the pressure at the center of the earth: Xray diffraction at 416 GPa. *Review of Scientific Instruments*, 61(12):3830–3833, December 1990.
- [259] Leonid Dubrovinsky, Natalia Dubrovinskaia, Vitali B. Prakapenka, and Artem M. Abakumov. Implementation of micro-ball nanodiamond anvils for high-pressure studies above 6 Mbar. *Nature Communications*, 3:ncomms2160, October 2012.
- [260] A. Van Valkenburg. Conference Internationale Sur-les-Hautes Pressions. *LeCreusot, Saone-et-Loire, France*, 1965.
- [261] Guoyin Shen and Ho Kwang Mao. High-pressure studies with x-rays using diamond anvil cells. *Reports on Progress in Physics*, 80(1):016101, 2017.
- [262] Richard A. Forman, Gasper J. Piermarini, J. Dean Barnett, and Stanley Block. Pressure Measurement Made by the Utilization of Ruby Sharp-Line Luminescence. *Science*, 176(4032):284–285, April 1972.
- [263] G. J. Piermarini and S. Block. Ultrahigh pressure diamondanvil cell and several semiconductor phase transition pressures in relation to the fixed point pressure scale. *Review of Scientific Instruments*, 46(8):973–979, August 1975.
- [264] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg. Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R1 fluorescence pressure gauge from 0.06 to 1 Mbar. *Journal of Applied Physics*, 49(6):3276–3283, June 1978.
- [265] H. K. Mao, J. Xu, and P. M. Bell. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *Journal of Geophysical Research: Solid Earth*, 91(B5):4673– 4676, April 1986.
- [266] Yingwei Fei, Angele Ricolleau, Mark Frank, Kenji Mibe, Guoyin Shen, and Vitali Prakapenka. Toward an internally consistent pressure scale. *Proceedings of the National Academy of Sciences*, 104(22):9182–9186, May 2007.
- [267] Rong Gao, Heping Li, and Jingtai Zhao. Dependence of R fluorescence lines of rubies on Cr³⁺ concentration at various temperatures, with implications for pressure calibrations in experimental apparatus. *American Mineralogist*, 100(7):1554–1561, July 2015.

- [268] Yuichi Akahama and Haruki Kawamura. High-pressure Raman spectroscopy of diamond anvils to 250gpa:Method for pressure determination in the multimegabar pressure range. *Journal of Applied Physics*, 96(7):3748–3751, September 2004.
- [269] M. Hanfland, K. Syassen, S. Fahy, Steven G. Louie, and Marvin L. Cohen. Pressure dependence of the first-order Raman mode in diamond. *Physical Review B*, 31(10):6896– 6899, May 1985.
- [270] Yuichi Akahama and Haruki Kawamura. Pressure calibration of diamond anvil Raman gauge to 410 GPa. *Journal of Physics: Conference Series*, 215(1):012195, 2010.
- [271] Natalia Dubrovinskaia and Leonid Dubrovinsky. Whole-cell heater for the diamond anvil cell. *Review of Scientific Instruments*, 74(7):3433–3437, June 2003.
- [272] Lichung Ming and William A. Bassett. Laser heating in the diamond anvil press up to 2000°C sustained and 3000°C pulsed at pressures up to 260 kilobars. *Review of Scientific Instruments*, 45(9):1115–1118, September 1974.
- [273] Laura Robin Benedetti and Paul Loubeyre. Temperature gradients, wavelengthdependent emissivity, and accuracy of high and very-high temperatures measured in the laser-heated diamond cell. *High Pressure Research*, 24(4):423–445, December 2004.
- [274] Dion L. Heinz, Jeffrey S. Sweeney, and Peter Miller. A laser heating system that stabilizes and controls the temperature: Diamond anvil cell applications. *Review of Scientific Instruments*, 62(6):1568–1575, June 1991.
- [275] Jie Deng, Zhixue Du, Laura Robin Benedetti, and Kanani K. M. Lee. The influence of wavelength-dependent absorption and temperature gradients on temperature determination in laser-heated diamond-anvil cells. *Journal of Applied Physics*, 121(2):025901, January 2017.
- [276] Sorin Bodea and Raymond Jeanloz. Model calculations of the temperature distribution in the laserheated diamond cell. *Journal of Applied Physics*, 65(12):4688–4692, June 1989.
- [277] R. Boehler, N. von Bargen, and A. Chopelas. Melting, thermal expansion, and phase transitions of iron at high pressures. *Journal of Geophysical Research: Solid Earth*, 95(B13):21731–21736, December 1990.
- [278] Andrew J. Campbell. Measurement of temperature distributions across laser heated samples by multispectral imaging radiometry. *Review of Scientific Instruments*, 79(1):015108, January 2008.
- [279] Zhixue Du, George Amulele, Laura Robin Benedetti, and Kanani K. M. Lee. Mapping temperatures and temperature gradients during flash heating in a diamond-anvil cell. *Review of Scientific Instruments*, 84(7):075111, July 2013.

- [280] Boris Kiefer and Thomas S. Duffy. Finite element simulations of the laser-heated diamond-anvil cell. *Journal of Applied Physics*, 97(11):114902, May 2005.
- [281] E. S. G. Rainey, J. W. Hernlund, and A. Kavner. Temperature distributions in the laserheated diamond anvil cell from 3-D numerical modeling. *Journal of Applied Physics*, 114(20):204905, November 2013.
- [282] Yue Meng, Rostislav Hrubiak, Eric Rod, Reinhard Boehler, and Guoyin Shen. New developments in laser-heated diamond anvil cell with in situ synchrotron x-ray diffraction at High Pressure Collaborative Access Team. *Review of Scientific Instruments*, 86(7):072201, July 2015.
- [283] N. Gomez-Perez, J. F. Rodriguez, and R. S. McWilliams. Finite element modeling of melting and fluid flow in the laser-heated diamond-anvil cell. *Journal of Applied Physics*, 121(14):145904, April 2017.
- [284] Dion L. Heinz. Thermal pressure in the laser-heated diamond anvil cell. *Geophysical Research Letters*, 17(8):1161–1164, July 1990.
- [285] Agnès Dewaele, Guillaume Fiquet, and Philippe Gillet. Temperature and pressure distribution in the laser-heated diamond–anvil cell. *Review of Scientific Instruments*, 69(6):2421–2426, June 1998.
- [286] C. E. Lesher and D. Walker. Thermal Diffusion in Petrology. In *Diffusion, Atomic Ordering, and Mass Transport*, Advances in Physical Geochemistry, pages 396–451. Springer, New York, NY, 1991. DOI: 10.1007/978-1-4613-9019-0_12.
- [287] Ryosuke Sinmyo and Kei Hirose. The Soret diffusion in laser-heated diamond-anvil cell. *Physics of the Earth and Planetary Interiors*, 180(3):172–178, June 2010.
- [288] Ryuichi Nomura, Haruka Ozawa, Shigehiko Tateno, Kei Hirose, John Hernlund, Shunsuke Muto, Hirofumi Ishii, and Nozomu Hiraoka. Spin crossover and iron-rich silicate melt in the Earth/'s deep mantle. *Nature*, 473(7346):199–202, May 2011.
- [289] Dion L. Heinz and Raymond Jeanloz. Measurement of the melting curve of Mg0.9fe0.1sio3 at lower mantle conditions and its geophysical implications. *Journal of Geophysical Research: Solid Earth*, 92(B11):11437–11444, October 1987.
- [290] Denis Andrault and Guillaume Fiquet. Synchrotron radiation and laser heating in a diamond anvil cell. *Review of Scientific Instruments*, 72(2):1283–1288, January 2001.
- [291] David B. Williams and C. Barry Carter. Transmission Electron Microscopy: A Textbook for Materials Science. Springer Science & Business Media, August 2009. Google-Books-ID: dXdrG39VtUoC.
- [292] R. Casting. *Application des sondes électroniques a une méthode d'analyse ponctuelle chimique et cristallographie.* PhD thesis, Thésis Univ. Paris, ONERA, Publ, 1951.

- [293] Marco Cantoni and Lorenz Holzer. Advances in 3d focused ion beam tomography. *MRS Bulletin*, 39(4):354–360, April 2014.
- [294] G. Cliff and G. W. Lorimer. The quantitative analysis of thin specimens. *Journal of Microscopy*, 103(2):203–207, March 1975.
- [295] J. Taftø and O. L. Krivanek. Site-Specific Valence Determination by Electron Energy-Loss Spectroscopy. *Physical Review Letters*, 48(8):560–563, February 1982.
- [296] P. Jenniskens, M. H. Shaddad, D. Numan, S. Elsir, A. M. Kudoda, M. E. Zolensky, L. Le, G. A. Robinson, J. M. Friedrich, D. Rumble, A. Steele, S. R. Chesley, A. Fitzsimmons, S. Duddy, H. H. Hsieh, G. Ramsay, P. G. Brown, W. N. Edwards, E. Tagliaferri, M. B. Boslough, R. E. Spalding, R. Dantowitz, M. Kozubal, P. Pravec, J. Borovicka, Z. Charvat, J. Vaubaillon, J. Kuiper, J. Albers, J. L. Bishop, R. L. Mancinelli, S. A. Sandford, S. N. Milam, M. Nuevo, and S. P. Worden. The impact and recovery of asteroid 2008 TC3. *Nature*, 458(7237):485–488, March 2009.
- [297] Addi Bischoff, Marian Horstmann, Andreas Pack, Matthias Laubenstein, and Siegfried Haberer. Asteroid 2008 TC3—Almahata Sitta: A spectacular breccia containing many different ureilitic and chondritic lithologies. *Meteoritics & Planetary Science*, 45(10-11):1638–1656, October 2010.
- [298] Jason S. Herrin, Michael E. Zolensky, Motoo Ito, Loan Le, David W. Mittlefehldt, Peter Jenniskens, Aidan J. Ross, and Muawia H. Shaddad. Thermal and fragmentation history of ureilitic asteroids: Insights from the Almahata Sitta fall. *Meteoritics & Planetary Science*, 45(10-11):1789–1803, October 2010.
- [299] Marian Horstmann and Addi Bischoff. The Almahata Sitta polymict breccia and the late accretion of asteroid 2008 TC3. *Chemie der Erde - Geochemistry*, 74(2):149–183, June 2014.
- [300] Yoshihiro Nakamuta and Shoichi Toh. Transformation of graphite to lonsdaleite and diamond in the Goalpara ureilite directly observed by TEM. *American Mineralogist*, 98(4):574–581, April 2013.
- [301] C. Hébert, P. Schattschneider, H. Franco, and B. Jouffrey. ELNES at magic angle conditions. *Ultramicroscopy*, 106(11):1139–1143, October 2006.
- [302] P. Schattschneider, C. Hébert, H. Franco, and B. Jouffrey. Anisotropic relativistic cross sections for inelastic electron scattering, and the magic angle. *Physical Review B*, 72(4):045142, July 2005.
- [303] Johanna Kraxner, Margit Schäfer, Otto Röschel, Gerald Kothleitner, Georg Haberfehlner, Manuel Paller, and Werner Grogger. Quantitative EDXS: Influence of geometry on a four detector system. *Ultramicroscopy*, 172:30–39, January 2017.

- [304] J. C. Walmsley and A. R. Lang. Transmission electron microscopic observations of deformation and microtwinning in a synthetic diamond compact. *Journal of materials science letters*, 2(12):785–788, 1983.
- [305] R. C. DeVries. Plastic deformation and "work-hardening" of diamond. *Materials Research Bulletin*, 10(11):1193–1199, November 1975.
- [306] G. Davies and T. Evans. Graphitization of diamond at zero pressure and at a high pressure. *Proc. R. Soc. Lond. A*, 328(1574):413–427, June 1972.
- [307] J. W. Harris and E. R. Vance. Induced graphitisation around crystalline inclusions in diamond. *Contributions to Mineralogy and Petrology*, 35(3):227–234, September 1972.
- [308] H. Chacham and Leonard Kleinman. Instabilities in Diamond under High Shear Stress. *Physical Review Letters*, 85(23):4904–4907, December 2000.
- [309] Hongliang He, T. Sekine, and T. Kobayashi. Direct transformation of cubic diamond to hexagonal diamond. *Applied Physics Letters*, 81(4):610–612, July 2002.
- [310] S. V. Zybin, M. L. Elert, and C. T. White. Orientation dependence of shock-induced chemistry in diamond. *Physical Review B*, 66(22):220102, December 2002.
- [311] C. Le Guillou, J. N. Rouzaud, L. Remusat, A. Jambon, and M. Bourot-Denise. Structures, origin and evolution of various carbon phases in the ureilite Northwest Africa 4742 compared with laboratory-shocked graphite. *Geochimica et Cosmochimica Acta*, 74(14):4167–4185, July 2010.
- [312] Péter Németh, Laurence A. J. Garvie, Toshihiro Aoki, Natalia Dubrovinskaia, Leonid Dubrovinsky, and Peter R. Buseck. Lonsdaleite is faulted and twinned cubic diamond and does not exist as a discrete material. *Nature Communications*, 5:ncomms6447, November 2014.
- [313] Hiroaki Ohfuji, Tetsuo Irifune, Konstantin D. Litasov, Tomoharu Yamashita, Futoshi Isobe, Valentin P. Afanasiev, and Nikolai P. Pokhilenko. Natural occurrence of pure nanopolycrystalline diamond from impact crater. *Scientific Reports*, 5:srep14702, October 2015.
- [314] Philippe Gillet and Ahmed El Goresy. Shock Events in the Solar System: The Message from Minerals in Terrestrial Planets and Asteroids. *Annual Review of Earth and Planetary Sciences*, 41(1):257–285, 2013.
- [315] Falko Langenhorst, George I. Shafranovsky, Victor L. Masaitis, and Marjatta Koivisto. Discovery of impact diamonds in a Fennoscandian crater and evidence for their genesis by solid-state transformation. *Geology*, 27(8):747–750, August 1999.
- [316] Ahmed El Goresy, Philippe Gillet, Ming Chen, Friedel Künstler, Günther Graup, and Volker Stähle. In situ discovery of shock-induced graphite-diamond phase transition in

gneisses from the Ries Crater, Germany. *American Mineralogist*, 86(5-6):611–621, May 2001.

- [317] Jean-Yves Raty and Giulia Galli. Ultradispersity of diamond at the nanoscale. *Nature Materials*, 2(12):792–795, December 2003.
- [318] Luca M. Ghiringhelli, Jan H. Los, Evert Jan Meijer, A. Fasolino, and Daan Frenkel. Modeling the Phase Diagram of Carbon. *Physical Review Letters*, 94(14):145701, April 2005.
- [319] F. P. Bundy, W. A. Bassett, M. S. Weathers, R. J. Hemley, H. U. Mao, and A. F. Goncharov. The pressure-temperature phase and transformation diagram for carbon; updated through 1994. *Carbon*, 34(2):141–153, January 1996.
- [320] M. J. Walter, S. C. Kohn, D. Araujo, G. P. Bulanova, C. B. Smith, E. Gaillou, J. Wang, A. Steele, and S. B. Shirey. Deep Mantle Cycling of Oceanic Crust: Evidence from Diamonds and Their Mineral Inclusions. *Science*, 334(6052):54–57, October 2011.
- [321] Evan M. Smith, Steven B. Shirey, Fabrizio Nestola, Emma S. Bullock, Jianhua Wang, Stephen H. Richardson, and Wuyi Wang. Large gem diamonds from metallic liquid in Earth's deep mantle. *Science*, 354(6318):1403–1405, December 2016.
- [322] Yingwei Fei, Constance M. Bertka, and Larry W. Finger. High-Pressure Iron-Sulfur Compound, Fe3s2, and Melting Relations in the Fe-FeS System. *Science*, 275(5306):1621– 1623, March 1997.
- [323] Yingwei Fei, Jie Li, Constance M. Bertka, and Charles T. Prewitt. Structure type and bulk modulus of Fe3s, a new iron-sulfur compound. *American Mineralogist*, 85(11-12):1830– 1833, November 2000.
- [324] A. J. Stewart and M. W. Schmidt. Sulfur and phosphorus in the Earth's core: The Fe-P-S system at 23 GPa. *Geophysical Research Letters*, 34(13):L13201, July 2007.
- [325] Tingting Gu, Yingwei Fei, Xiang Wu, and Shan Qin. Phase stabilities and spin transitions of Fe3(S1xPx) at high pressure and its implications in meteorites. *American Mineralogist*, 101(1):205–210, January 2016.
- [326] Christopher T. Seagle, Andrew J. Campbell, Dion L. Heinz, Guoyin Shen, and Vitali B. Prakapenka. Thermal equation of state of Fe3s and implications for sulfur in Earth's core. *Journal of Geophysical Research: Solid Earth*, 111(B6):B06209, June 2006.
- [327] Satoru Urakawa, Ryosuke Matsubara, Tomoo Katsura, Tohru Watanabe, and Takumi Kikegawa. Stability and bulk modulus of Ni3s, a new nickel sulfur compound, and the melting relations of the system Ni-NiS up to 10 GPa. *American Mineralogist*, 96(4):558– 565, April 2011.
- [328] Ming Chen, Jinfu Shu, Ho-kwang Mao, Xiande Xie, and Russell J. Hemley. Natural occurrence and synthesis of two new postspinel polymorphs of chromite. *Proceedings of the National Academy of Sciences*, 100(25):14651–14654, December 2003.

- [329] Ming Chen, Jinfu Shu, Xiande Xie, and Ho-kwang Mao. Natural CaTi2o4-structured FeCr2o4 polymorph in the Suizhou meteorite and its significance in mantle mineralogy. *Geochimica et Cosmochimica Acta*, 67(20):3937–3942, October 2003.
- [330] Takayuki Ishii, Hiroshi Kojitani, Shoichi Tsukamoto, Kiyoshi Fujino, Daisuke Mori, Yoshiyuki Inaguma, Noriyoshi Tsujino, Takashi Yoshino, Daisuke Yamazaki, Yuji Higo, Kenichi Funakoshi, and Masaki Akaogi. High-pressure phase transitions in FeCr2o4 and structure analysis of new post-spinel FeCr2o4 and Fe2cr2o5 phases with meteoritical and petrological implications. *American Mineralogist*, 99(8-9):1788–1797, August 2014.
- [331] Cyrena Anne Goodrich, George E. Harlow, James A. Van Orman, Stephen R. Sutton, Michael J. Jercinovic, and Takashi Mikouchi. Petrology of chromite in ureilites: Deconvolution of primary oxidation states and secondary reduction processes. *Geochimica et Cosmochimica Acta*, 135:126–169, June 2014.
- [332] Joseph S. Boesenberg, Jeremy S. Delaney, and Roger H. Hewins. A petrological and chemical reexamination of Main Group pallasite formation. *Geochimica et Cosmochimica Acta*, 89:134–158, July 2012.
- [333] John T. Wasson, David E. Lange, Carl A. Francis, and Finn Ulff-Møller. Massive chromite in the Brenham pallasite and the fractionation of Cr during the crystallization of asteroidal cores. *Geochimica et Cosmochimica Acta*, 63(7):1219–1232, April 1999.
- [334] Alexander N. Krot, Nina I. Zaslavskay, Michail I. Petaev, Natalya N. Kononkova, Gennady M. Kolesov, and Lydia D. Barsukova. The Sychevka IIIAB iron meteorite: A new find from Russia. *Meteoritics*, 27(4):465–466, September 1992.
- [335] Karl Thomas Fehr and Alain Carion. Unusual large chromite crystals in the Saint Aubin iron meteorite. *Meteoritics & Planetary Science*, 39(S8):A139–A141, August 2004.
- [336] F. Ulff-Møller. Solubility of chromium and oxygen in metallic liquids and the cocrystallization of chromite and metal in iron meteorite parent bodies. In *Lunar and Planetary Science Conference*, volume 29, 1998.
- [337] Edward J. Olsen, Alfred Kracher, Andrew M. Davis, Ian M. Steele, Ian D. Hutcheon, and T. E. Bunch. The phosphates of IIIAB iron meteorites. *Meteoritics & Planetary Science*, 34(2):285–300, March 1999.
- [338] O. T. Lord, M. J. Walter, R. Dasgupta, D. Walker, and S. M. Clark. Melting in the Fe–C system to 70 GPa. *Earth and Planetary Science Letters*, 284(1):157–167, June 2009.
- [339] Liwei Deng, Yingwei Fei, Xi Liu, Zizheng Gong, and Anat Shahar. Effect of carbon, sulfur and silicon on iron melting at high pressure: Implications for composition and evolution of the planetary terrestrial cores. *Geochimica et Cosmochimica Acta*, 114:220–233, August 2013.

- [340] Alexandre Corgne, Bernard J. Wood, and Yingwei Fei. C- and S-rich molten alloy immiscibility and core formation of planetesimals. *Geochimica et Cosmochimica Acta*, 72(9):2409–2416, May 2008.
- [341] Rajdeep Dasgupta, Antonio Buono, Geoff Whelan, and David Walker. High-pressure melting relations in Fe–C–S systems: Implications for formation, evolution, and structure of metallic cores in planetary bodies. *Geochimica et Cosmochimica Acta*, 73(21):6678–6691, November 2009.
- [342] Kyusei Tsuno and Rajdeep Dasgupta. Fe–Ni–Cu–C–S phase relations at high pressures and temperatures The role of sulfur in carbon storage and diamond stability at mid-to deep-upper mantle. *Earth and Planetary Science Letters*, 412:132–142, February 2015.
- [343] Julien Siebert, François Guyot, and Valérie Malavergne. Diamond formation in metal–carbonate interactions. *Earth and Planetary Science Letters*, 229(3):205–216, January 2005.
- [344] A. Morbidelli, M. Lambrechts, S. Jacobson, and B. Bitsch. The great dichotomy of the Solar System: Small terrestrial embryos and massive giant planet cores. *Icarus*, 258:418–429, September 2015.
- [345] S. A. Jacobson and A. Morbidelli. Lunar and terrestrial planet formation in the Grand Tack scenario. *Phil. Trans. R. Soc. A*, 372(2024):20130174, September 2014.
- [346] W. Brian Tonks and H. Jay Melosh. Magma ocean formation due to giant impacts. *Journal of Geophysical Research: Planets*, 98(E3):5319–5333, March 1993.
- [347] Sebastian Rost, Edward J. Garnero, Quentin Williams, and Michael Manga. Seismological constraints on a possible plume root at the core–mantle boundary. *Nature*, 435(7042):666–669, June 2005.
- [348] Denis Andrault, Nathalie Bolfan-Casanova, Giacomo Lo Nigro, Mohamed A. Bouhifd, Gaston Garbarino, and Mohamed Mezouar. Solidus and liquidus profiles of chondritic mantle: Implication for melting of the Earth across its history. *Earth and Planetary Science Letters*, 304(1):251–259, April 2011.
- [349] Reinhard Boehler. MELTING TEMPERATURE OF THE EARTH'S MANTLE AND CORE: Earth's Thermal Structure. *Annual Review of Earth and Planetary Sciences*, 24(1):15–40, 1996.
- [350] S. Anzellini, A. Dewaele, M. Mezouar, P. Loubeyre, and G. Morard. Melting of Iron at Earth's Inner Core Boundary Based on Fast X-ray Diffraction. *Science*, 340(6131):464–466, April 2013.
- [351] Gopal K. Pradhan, Guillaume Fiquet, Julien Siebert, Anne-Line Auzende, Guillaume Morard, Daniele Antonangeli, and Gaston Garbarino. Melting of MORB at core–mantle boundary. *Earth and Planetary Science Letters*, 431:247–255, December 2015.

- [352] Ryuichi Nomura, Kei Hirose, Kentaro Uesugi, Yasuo Ohishi, Akira Tsuchiyama, Akira Miyake, and Yuichiro Ueno. Low Core-Mantle Boundary Temperature Inferred from the Solidus of Pyrolite. *Science*, 343(6170):522–525, January 2014.
- [353] Lars Stixrude, Nico de Koker, Ni Sun, Mainak Mookherjee, and Bijaya B. Karki. Thermodynamics of silicate liquids in the deep Earth. *Earth and Planetary Science Letters*, 278(3):226–232, February 2009.
- [354] Jed L. Mosenfelder, Paul D. Asimow, and Thomas J. Ahrens. Thermodynamic properties of Mg2sio4 liquid at ultra-high pressures from shock measurements to 200 GPa on forsterite and wadsleyite. *Journal of Geophysical Research: Solid Earth*, 112(B6):B06208, June 2007.
- [355] Lars Stixrude and Bijaya Karki. Structure and Freezing of MgSiO₃ Liquid in Earth9s Lower Mantle. *Science*, 310(5746):297–299, October 2005.
- [356] Sylvain Petitgirard, Wim J. Malfait, Ryosuke Sinmyo, Ilya Kupenko, Louis Hennet, Dennis Harries, Thomas Dane, Manfred Burghammer, and Dave C. Rubie. Fate of MgSiO3 melts at core–mantle boundary conditions. *Proceedings of the National Academy of Sciences*, 112(46):14186–14190, November 2015.
- [357] Shigehiko Tateno, Kei Hirose, and Yasuo Ohishi. Melting experiments on peridotite to lowermost mantle conditions. *Journal of Geophysical Research: Solid Earth*, 119(6):2013JB010616, June 2014.
- [358] C.-E. Boukaré, Y. Ricard, and G. Fiquet. Thermodynamics of the MgO-FeO-SiO2 system up to 140 GPa: Application to the crystallization of Earth's magma ocean. *Journal of Geophysical Research: Solid Earth*, 120(9):2015JB011929, September 2015.
- [359] P. A. van Aken and B. Liebscher. Quantification of ferrous/ferric ratios in minerals: new evaluation schemes of Fe L23 electron energy-loss near-edge spectra. *Physics and Chemistry of Minerals*, 29(3):188–200, April 2002.
- [360] Asmaa Boujibar, Nathalie Bolfan-Casanova, Denis Andrault, M. Ali Bouhifd, and Nicolas Trcera. Incorporation of Fe²⁺ and Fe³⁺ in bridgmanite during magma ocean crystallization. *American Mineralogist*, 101(7):1560–1570, July 2016.
- [361] D. Andrault, N. Bolfan-Casanova, M. A. Bouhifd, A. Boujibar, G. Garbarino, G. Manthilake, M. Mezouar, J. Monteux, P. Parisiades, and G. Pesce. Toward a coherent model for the melting behavior of the deep Earth's mantle. *Physics of the Earth and Planetary Interiors*, 265:67–81, April 2017.
- [362] J. P. Poirier, J. Peyronneau, M. Madon, F. Guyot, and A. Revcolevschi. Eutectoid phase transformation of olivine and spinel into perovskite and rock salt structures. *Nature*, 321(6070):603–605, June 1986.
- [363] Ryosuke Sinmyo, Kei Hirose, Daisuke Nishio-Hamane, Yusuke Seto, Kiyoshi Fujino, Nagayoshi Sata, and Yasuo Ohishi. Partitioning of iron between perovskite/postperovskite and ferropericlase in the lower mantle. *Journal of Geophysical Research: Solid Earth*, 113(B11):B11204, November 2008.
- [364] E Ito, A Kubo, T Katsura, and M. J Walter. Melting experiments of mantle materials under lower mantle conditions with implications for magma ocean differentiation. *Physics of the Earth and Planetary Interiors*, 143:397–406, June 2004.
- [365] Eiji Ohtani, Koji Moriwaki, Takumi Kato, and Kosuke Onuma. Melting and crystal–liquid partitioning in the system Mg2sio4–Fe2sio4 to 25 GPa. *Physics of the Earth and Planetary Interiors*, 107(1):75–82, April 1998.
- [366] Satoka Ohnishi, Yasuhiro Kuwayama, and Toru Inoue. Melting relations in the MgO–MgSiO3 system up to 70 GPa. *Physics and Chemistry of Minerals*, 44(6):445–453, June 2017.
- [367] Li Zhang and Yingwei Fei. Melting behavior of (Mg,Fe)O solid solutions at high pressure. *Geophysical Research Letters*, 35(13):L13302, July 2008.
- [368] Yingwei Fei, Daniel J. Frost, Ho-Kwang Mao, Charles T. Prewitt, and Daniel Haeusermann. In situ structure determination of the high-pressure phase of Fe₃ O₄. American Mineralogist, 84(1-2):203–206, February 1999.
- [369] Camilla Haavik, Svein Stølen, Helmer Fjellvåg, Michael Hanfland, and Daniel Häusermann. Equation of state of magnetite and its high-pressure modification: Thermodynamics of the Fe-O system at high pressure. *American Mineralogist*, 85(3-4):514–523, March 2000.
- [370] D. Andrault and N. Bolfan-Casanova. High-pressure phase transformations in the MgFe2o4 and Fe2o3–MgSiO3 systems. *Physics and Chemistry of Minerals*, 28(3):211–217, April 2001.
- [371] Lars Stixrude and Carolina Lithgow-Bertelloni. Thermodynamics of mantle minerals I. Physical properties. *Geophysical Journal International*, 162(2):610–632, August 2005.
- [372] Rebecca A. Fischer, Andrew J. Campbell, Gregory A. Shofner, Oliver T. Lord, Przemysław Dera, and Vitali B. Prakapenka. Equation of state and phase diagram of FeO. *Earth and Planetary Science Letters*, 304(3):496–502, April 2011.
- [373] Nico de Koker, Bijaya B. Karki, and Lars Stixrude. Thermodynamics of the MgO–SiO2 liquid system in Earth's lowermost mantle from first principles. *Earth and Planetary Science Letters*, 361:58–63, January 2013.
- [374] Francis Dominic Murnaghan. *Finite Deformation of an Elastic Solid*. John Wiley & Sons, 1951. Google-Books-ID: LvRQAAAAMAAJ.

- [375] Rebecca A. Fischer and Andrew J. Campbell. High-pressure melting of wüstite. *American Mineralogist*, 95(10):1473–1477, October 2010.
- [376] Claire W. Thomas, Qiong Liu, Carl B. Agee, Paul D. Asimow, and Rebecca A. Lange. Multi-technique equation of state for Fe2sio4melt and the density of Fe-bearing silicate melts from 0 to 161 GPa. *Journal of Geophysical Research: Solid Earth*, 117(B10):B10206, October 2012.
- [377] Y. Fei, J. Van Orman, J. Li, W. van Westrenen, C. Sanloup, W. Minarik, K. Hirose, T. Komabayashi, M. Walter, and K. Funakoshi. Experimentally determined postspinel transformation boundary in Mg2sio4 using MgO as an internal pressure standard and its geophysical implications. *Journal of Geophysical Research: Solid Earth*, 109(B2):B02305, February 2004.
- [378] Christian Liebske and Daniel J. Frost. Melting phase relations in the MgO–MgSiO3 system between 16 and 26gpa: Implications for melting in Earth's deep interior. *Earth and Planetary Science Letters*, 345:159–170, September 2012.
- [379] Michel Fialin, Gilles Catillon, and Denis Andrault. Disproportionation of Fe2+ in Al-free silicate perovskite in the laser heated diamond anvil cell as recorded by electron probe microanalysis of oxygen. *Physics and Chemistry of Minerals*, 36(4):183–191, April 2009.
- [380] Hélène Piet, James Badro, Farhang Nabiei, Teresa Dennenwaldt, Sang-Heon Shim, Marco Cantoni, Cécile Hébert, and Philippe Gillet. Spin and valence dependence of iron partitioning in Earth's deep mantle. *Proceedings of the National Academy of Sciences*, 113(40):11127–11130, October 2016.
- [381] Kei Hirose, Ryosuke Sinmyo, Nagayoshi Sata, and Yasuo Ohishi. Determination of postperovskite phase transition boundary in MgSiO3 using Au and MgO pressure standards. *Geophysical Research Letters*, 33(1):L01310, January 2006.
- [382] Krystle Catalli, Sang-Heon Shim, and Vitali Prakapenka. Thickness and Clapeyron slope of the post-perovskite boundary. *Nature*, 462(7274):782–U101, December 2009. WOS:000272559900037.
- [383] Brent Grocholski, Krystle Catalli, Sang-Heon Shim, and Vitali Prakapenka. Mineralogical effects on the detectability of the postperovskite boundary. *Proceedings of the National Academy of Sciences*, 109(7):2275–2279, February 2012.
- [384] Adam M. Dziewonski, Vedran Lekic, and Barbara A. Romanowicz. Mantle Anchor Structure: An argument for bottom up tectonics. *Earth and Planetary Science Letters*, 299(1):69–79, October 2010.
- [385] François Guyot, Michel Madon, Jean Peyronneau, and Jean Paul Poirier. X-ray microanalysis of high-pressure/high-temperature phases synthesized from natural olivine in a diamond-anvil cell. *Earth and Planetary Science Letters*, 90(1):52–64, September 1988.

- [386] Isabelle Martinez, Yanbin Wang, Francois Guyot, Robert C. Liebermann, and Jean-Claude Doukhan. Microstructures and iron partitioning in (Mg,Fe)SiO3 perovskite-(Mg,Fe)O magnesiowüstite assemblages: An analytical transmission electron microscopy study. *Journal of Geophysical Research: Solid Earth*, 102(B3):5265–5280, March 1997.
- [387] Ho-kwang Mao, Guoyin Shen, and Russell J. Hemley. Multivariable Dependence of Fe-Mg Partitioning in the Lower Mantle. *Science*, 278(5346):2098–2100, December 1997.
- [388] Denis Andrault. Evaluation of (Mg,Fe) partitioning between silicate perovskite and magnesiowustite up to 120 GPa and 2300 K. *Journal of Geophysical Research: Solid Earth*, 106(B2):2079–2087, February 2001.
- [389] S. E Kesson, J. D Fitz Gerald, H. St. C O'Neill, and J. M. G Shelley. Partitioning of iron between magnesian silicate perovskite and magnesiowüstite at about 1 Mbar. *Physics of the Earth and Planetary Interiors*, 131(3):295–310, August 2002.
- [390] Daniel J. Frost and Falko Langenhorst. The effect of Al2o3 on Fe–Mg partitioning between magnesiowüstite and magnesium silicate perovskite. *Earth and Planetary Science Letters*, 199(1):227–241, May 2002.
- [391] Motohiko Murakami, Kei Hirose, Nagayoshi Sata, and Yasuo Ohishi. Post-perovskite phase transition and mineral chemistry in the pyrolitic lowermost mantle. *Geophysical Research Letters*, 32(3):L03304, February 2005.
- [392] Yusuke Kobayashi, Tadashi Kondo, Eiji Ohtani, Naohisa Hirao, Nobuyoshi Miyajima, Takehiko Yagi, Toshiro Nagase, and Takumi Kikegawa. Fe-Mg partitioning between (Mg, Fe)SiO3 post-perovskite, perovskite, and magnesiowüstite in the Earth's lower mantle. *Geophysical Research Letters*, 32(19):L19301, October 2005.
- [393] Takeshi Sakai, Eiji Ohtani, Hidenori Terasaki, Masaaki Miyahara, Masahiko Nishijima, Naohisa Hirao, Yasuo Ohishi, and Nagayoshi Sata. Fe–Mg partitioning between postperovskite and ferropericlase in the lowermost mantle. *Physics and Chemistry of Minerals*, 37(7):487–496, July 2010.
- [394] T. J. Shankland and J. M. Brown. Homogeneity and temperatures in the lower mantle. *Physics of the Earth and Planetary Interiors*, 38(1):51–58, March 1985.
- [395] Ryosuke Sinmyo, Kei Hirose, Hugh St. C. O'Neill, and Eiji Okunishi. Ferric iron in Al-bearing post-perovskite. *Geophysical Research Letters*, 33(12):L12S13, June 2006.
- [396] John P. Brodholt. Pressure-induced changes in the compression mechanism of aluminous perovskite in the Earth's mantle. *Nature*, 407(6804):620–622, October 2000.
- [397] James Badro. Spin Transitions in Mantle Minerals. *Annual Review of Earth and Planetary Sciences*, 42(1):231–248, May 2014.

- [398] Yousheng Xu, Catherine McCammon, and Brent T. Poe. The Effect of Alumina on the Electrical Conductivity of Silicate Perovskite. *Science*, 282(5390):922–924, October 1998.
- [399] Alexander F. Goncharov, Pierre Beck, Viktor V. Struzhkin, Benjamin D. Haugen, and Steven D. Jacobsen. Thermal conductivity of lower-mantle minerals. *Physics of the Earth and Planetary Interiors*, 174(1):24–32, May 2009.
- [400] M. W. Ammann, J. P. Brodholt, J. Wookey, and D. P. Dobson. First-principles constraints on diffusion in lower-mantle minerals and a weak D layer. *Nature*, 465(7297):462–465, May 2010.
- [401] Jennifer Girard, George Amulele, Robert Farla, Anwar Mohiuddin, and Shun-ichiro Karato. Shear deformation of bridgmanite and magnesiowüstite aggregates at lower mantle conditions. *Science*, 351(6269):144–147, January 2016.
- [402] Yong-Hong Zhao, Mark E. Zimmerman, and David L. Kohlstedt. Effect of iron content on the creep behavior of olivine: 1. Anhydrous conditions. *Earth and Planetary Science Letters*, 287(1):229–240, September 2009.
- [403] Alessandro M. Forte and Jerry X. Mitrovica. Deep-mantle high-viscosity flow and thermochemical structure inferred from seismic and geodynamic data. *Nature*, 410(6832):1049– 1056, April 2001.
- [404] J. F. Justo, G. Morra, and D. A. Yuen. Viscosity undulations in the lower mantle: The dynamical role of iron spin transition. *Earth and Planetary Science Letters*, 421:20–26, July 2015.
- [405] Maxwell L. Rudolph, Vedran Lekić, and Carolina Lithgow-Bertelloni. Viscosity jump in Earth's mid-mantle. *Science*, 350(6266):1349–1352, December 2015.
- [406] Hauke Marquardt and Lowell Miyagi. Slab stagnation in the shallow lower mantle linked to an increase in mantle viscosity. *Nature Geoscience*, 8(4):311–314, April 2015.
- [407] Chuan Huang, Wei Leng, and Zhongqing Wu. Iron-spin transition controls structure and stability of LLSVPs in the lower mantle. *Earth and Planetary Science Letters*, 423:173–181, August 2015.
- [408] Louis Hennet, Irina Pozdnyakova, Aleksei Bytchkov, Viviana Cristiglio, Pierre Palleau, Henry E. Fischer, Gabriel J. Cuello, Mark Johnson, Philippe Melin, Didier Zanghi, Séverine Brassamin, Jean-François Brun, David L. Price, and Marie-Louise Saboungi. Levitation apparatus for neutron diffraction investigations on high temperature liquids. *Review of Scientific Instruments*, 77(5):053903, May 2006.
- [409] Yuichi Akahama and Haruki Kawamura. Pressure calibration of diamond anvil Raman gauge to 310gpa. *Journal of Applied Physics*, 100(4):043516, August 2006.

- [410] Ryosuke Sinmyo, Kei Hirose, Shunsuke Muto, Yasuo Ohishi, and Akira Yasuhara. The valence state and partitioning of iron in the Earth's lowermost mantle. *Journal of Geophysical Research: Solid Earth*, 116(B7):B07205, July 2011.
- [411] Caterina E. Tommaseo, Jim Devine, Sébastien Merkel, Sergio Speziale, and Hans-Rudolf Wenk. Texture development and elastic stresses in magnesiowűstite at high pressure. *Physics and Chemistry of Minerals*, 33(2):84–97, April 2006.
- [412] Wendy L. Mao, Guoyin Shen, Vitali B. Prakapenka, Yue Meng, Andrew J. Campbell, Dion L. Heinz, Jinfu Shu, Russell J. Hemley, and Ho-kwang Mao. Ferromagnesian postperovskite silicates in the D layer of the Earth. *Proceedings of the National Academy* of Sciences of the United States of America, 101(45):15867–15869, November 2004.
- [413] S. M. Dorfman and T. S. Duffy. Effect of Fe-enrichment on seismic properties of perovskite and post-perovskite in the deep lower mantle. *Geophysical Journal International*, 197(2):910–919, May 2014.
- [414] David P. Dobson and John P. Brodholt. Subducted banded iron formations as a source of ultralow-velocity zones at the core–mantle boundary. *Nature*, 434(7031):371–374, March 2005.
- [415] Yingwei Fei. Solid solutions and element partitioning at high pressures and temperatures. *Reviews in mineralogy*, 37:343–367, 1998.
- [416] Tomoo Katsura and Eiji Ito. Determination of Fe-Mg partitioning between perovskite and magnesiowüstite. *Geophysical Research Letters*, 23(16):2005–2008, August 1996.
- [417] Ho-kwang Mao, Guoyin Shen, and Russell J. Hemley. Multivariable Dependence of Fe-Mg Partitioning in the Lower Mantle. *Science*, 278(5346):2098–2100, December 1997.
- [418] Yoichi Nakajima, Daniel J. Frost, and David C. Rubie. Ferrous iron partitioning between magnesium silicate perovskite and ferropericlase and the composition of perovskite in the Earth's lower mantle. *Journal of Geophysical Research: Solid Earth*, 117(B8):B08201, August 2012.
- [419] Joshua M. R. Muir and John P. Brodholt. Ferrous iron partitioning in the lower mantle. *Physics of the Earth and Planetary Interiors*, 257:12–17, August 2016.
- [420] Yoshinori Tange, Eiichi Takahashi, Yu Nishihara, Ken-ichi Funakoshi, and Nagayoshi Sata. Phase relations in the system MgO-FeO-SiO2 to 50 GPa and 2000°C: An application of experimental techniques using multianvil apparatus with sintered diamond anvils. *Journal of Geophysical Research: Solid Earth*, 114(B2):B02214, February 2009.
- [421] Susannah M. Dorfman, Yue Meng, Vitali B. Prakapenka, and Thomas S. Duffy. Effects of Fe-enrichment on the equation of state and stability of (Mg,Fe)SiO3 perovskite. *Earth* and Planetary Science Letters, 361:249–257, January 2013.

- [422] Yingwei Fei, Yanbin Wang, and Larry W. Finger. Maximum solubility of FeO in (Mg, Fe)SiO3-perovskite as a function of temperature at 26 GPa: Implication for FeO content in the lower mantle. *Journal of Geophysical Research: Solid Earth*, 101(B5):11525–11530, May 1996.
- [423] Shigehiko Tateno, Kei Hirose, Nagayoshi Sata, and Yasuo Ohishi. Solubility of FeO in (Mg,Fe)SiO3 perovskite and the post-perovskite phase transition. *Physics of the Earth and Planetary Interiors*, 160(3):319–325, March 2007.
- [424] Han Hsu, Koichiro Umemoto, Peter Blaha, and Renata M. Wentzcovitch. Spin states and hyperfine interactions of iron in (Mg,Fe)SiO3 perovskite under pressure. *Earth and Planetary Science Letters*, 294(1):19–26, May 2010.
- [425] Zhu Mao, Fan Wang, Jung-Fu Lin, Suyu Fu, Jing Yang, Xiang Wu, Takuo Okuchi, Naotaka Tomioka, Vitali B. Prakapenka, Yuming Xiao, and Paul Chow. Equation of state and hyperfine parameters of high-spin bridgmanite in the Earth's lower mantle by synchrotron X-ray diffraction and Mössbauer spectroscopy. *American Mineralogist*, 102(2):357–368, February 2017.
- [426] Susannah M. Dorfman, James Badro, Jean-Pascal Rueff, Paul Chow, Yuming Xiao, and Philippe Gillet. Composition dependence of spin transition in (Mg,Fe)SiO3 bridgmanite. *American Mineralogist*, 100(10):2246–2253, October 2015.
- [427] Wendy L. Mao, Yue Meng, Guoyin Shen, Vitali B. Prakapenka, Andrew J. Campbell, Dion L. Heinz, Jinfu Shu, Razvan Caracas, Ronald E. Cohen, Yingwei Fei, Russell J. Hemley, and Ho-kwang Mao. Iron-rich silicates in the Earth's D layer. *Proceedings of the National Academy of Sciences of the United States of America*, 102(28):9751–9753, July 2005.
- [428] Kei Hirose, Naoto Takafuji, Kiyoshi Fujino, Sean R. Shieh, and Thomas S. Duffy. Iron partitioning between perovskite and post-perovskite: A transmission electron microscope study. *American Mineralogist*, 93(10):1678–1681, October 2008.
- [429] Masaaki Miyahara, Takeshi Sakai, Eiji Ohtani, Yusuke Kobayashi, Seiji Kamada, Tadashi Kondo, Toshiro Nagase, Jung Ho Yoo, Masahiko Nishijima, and Zahra Vashaei. Application of FIB system to ultra-high-pressure Earth science. *Journal of Mineralogical and Petrological Sciences*, 103(2):88–93, 2008.
- [430] Richard Wirth. Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale. *Chemical Geology*, 261(3):217–229, April 2009.
- [431] S. M. Dorfman, V. B. Prakapenka, Y. Meng, and T. S. Duffy. Intercomparison of pressure standards (Au, Pt, Mo, MgO, NaCl and Ne) to 2.5 Mbar. *Journal of Geophysical Research: Solid Earth*, 117(B8):B08210, August 2012.

- [432] V. B. Prakapenka, A. Kubo, A. Kuznetsov, A. Laskin, O. Shkurikhin, P. Dera, M. L. Rivers, and S. R. Sutton. Advanced flat top laser heating system for high pressure research at GSECARS: application to the melting behavior of germanium. *High Pressure Research*, 28(3):225–235, September 2008.
- [433] Guoyin Shen, Mark L. Rivers, Yanbin Wang, and Stephen R. Sutton. Laser heated diamond cell system at the Advanced Photon Source for in situ x-ray measurements at high pressure and temperature. *Review of Scientific Instruments*, 72(2):1273–1282, January 2001.
- [434] P. Carrez, H. Leroux, P. Cordier, and F. Guyot. Electron-irradiation-induced phase transformation and fractional volatilization in (Mg, Fe)2sio4 olivine thin films. *Philosophical Magazine A*, 81(12):2823–2840, December 2001.
- [435] Tadashi Kondo, Eiji Ohtani, Naohisa Hirao, Takehiko Yagi, and Takumi Kikegawa. Phase transitions of (Mg,Fe)O at megabar pressures. *Physics of the Earth and Planetary Interiors*, 143:201–213, June 2004.
- [436] S. Lundin, K. Catalli, J. Santillán, S. H. Shim, V. B. Prakapenka, M. Kunz, and Y. Meng. Effect of Fe on the equation of state of mantle silicate perovskite over 1mbar. *Physics of the Earth and Planetary Interiors*, 168(1):97–102, May 2008.
- [437] H. K. Mao, R. J. Hemley, Y. Fei, J. F. Shu, L. C. Chen, A. P. Jephcoat, Y. Wu, and W. A. Bassett. Effect of pressure, temperature, and composition on lattice parameters and density of (Fe,Mg)SiO3-perovskites to 30 GPa. *Journal of Geophysical Research: Solid Earth*, 96(B5):8069–8079, May 1991.
- [438] Natalia V. Solomatova, Jennifer M. Jackson, Wolfgang Sturhahn, June K. Wicks, Jiyong Zhao, Thomas S. Toellner, Bora Kalkan, and William M. Steinhardt. Equation of state and spin crossover of (Mg,Fe)O at high pressure, with implications for explaining topographic relief at the core-mantle boundary. *American Mineralogist*, 101(5):1084–1093, May 2016.
- [439] S. Speziale, A. Milner, V. E. Lee, S. M. Clark, M. P. Pasternak, and R. Jeanloz. Iron spin transition in Earth's mantle. *Proceedings of the National Academy of Sciences of the United States of America*, 102(50):17918–17922, December 2005.
- [440] Li Zhang, Yue Meng, and Wendy L. Mao. Effect of pressure and composition on lattice parameters and unit-cell volume of (Fe,Mg)SiO3 post-perovskite. *Earth and Planetary Science Letters*, 317:120–125, February 2012.
- [441] R. J. Angel. Equations of State. *Reviews in Mineralogy and Geochemistry*, 41(1):35–59, January 2000.
- [442] June K. Wicks, Jennifer M. Jackson, Wolfgang Sturhahn, and Dongzhou Zhang. Sound velocity and density of magnesiowüstites: Implications for ultralow-velocity zone topography. *Geophysical Research Letters*, 44(5):2016GL071225, March 2017.

- [443] James Badro, Viktor V. Struzhkin, Jinfu Shu, Russell J. Hemley, Ho-kwang Mao, Chi-chang Kao, Jean-Pascal Rueff, and Guoyin Shen. Magnetism in FeO at Megabar Pressures from X-Ray Emission Spectroscopy. *Physical Review Letters*, 83(20):4101–4104, November 1999.
- [444] Haruka Ozawa, Kei Hirose, Kenji Ohta, Hirofumi Ishii, Nozomu Hiraoka, Yasuo Ohishi, and Yusuke Seto. Spin crossover, structural change, and metallization in NiAs-type FeO at high pressure. *Physical Review B*, 84(13):134417, October 2011.
- [445] M. P. Pasternak, R. D. Taylor, R. Jeanloz, X. Li, J. H. Nguyen, and C. A. McCammon. High Pressure Collapse of Magnetism in F\${\mathrm{e}}_{0.94}\$O: M\"ossbauer Spectroscopy Beyond 100 GPa. *Physical Review Letters*, 79(25):5046–5049, December 1997.
- [446] S. M. Dorfman, V. Potapkin, I. Kupenko, A. I. Chumakov, F. Nabiei, A. Magrez, L. S. Dubrovinsky, C. A. McCammon, and P. Gillet. Complex Effects of Alumina/Silica on Ferric/Ferrous Iron in Earth's Lower Mantle. In AGU Fall Meeting Abstracts, 2014.
- [447] Amelia Bengtson, Kristin Persson, and Dane Morgan. Ab initio study of the composition dependence of the pressure-induced spin crossover in perovskite (Mg1x,Fex)SiO3. *Earth and Planetary Science Letters*, 265(3):535–545, January 2008.
- [448] Razvan Caracas, Haruka Ozawa, Kei Hirose, Hirofumi Ishii, Nozomu Hiraoka, Yasuo Ohishi, and Naohisa Hirao. Identifying the spin transition in Fe2+-rich MgSiO3 perovskite from X-ray diffraction and vibrational spectroscopy. *American Mineralogist*, 99(7):1270–1276, July 2014.
- [449] Koichiro Umemoto, Renata M. Wentzcovitch, Yonggang G. Yu, and Ryan Requist. Spin transition in (Mg,Fe)SiO3 perovskite under pressure. *Earth and Planetary Science Letters*, 276(1):198–206, November 2008.
- [450] Sergio Speziale, Chang-Sheng Zha, Thomas S. Duffy, Russell J. Hemley, and Ho-kwang Mao. Quasi-hydrostatic compression of magnesium oxide to 52 GPa: Implications for the pressure-volume-temperature equation of state. *Journal of Geophysical Research: Solid Earth*, 106(B1):515–528, January 2001.
- [451] Francis Birch. Finite Elastic Strain of Cubic Crystals. *Physical Review*, 71(11):809–824, June 1947.
- [452] Nicolas Guignot, Denis Andrault, Guillaume Morard, Nathalie Bolfan-Casanova, and Mohamed Mezouar. Thermoelastic properties of post-perovskite phase MgSiO3 determined experimentally at core–mantle boundary P–T conditions. *Earth and Planetary Science Letters*, 256(1):162–168, April 2007.
- [453] Daisuke Nishio-Hamane and Takehiko Yagi. Equations of state for postperovskite phases in the MgSiO3–FeSiO3–FeAlO3 system. *Physics of the Earth and Planetary Interiors*, 175(3):145–150, July 2009.

- [454] Bin Chen, Jennifer M. Jackson, Wolfgang Sturhahn, Dongzhou Zhang, Jiyong Zhao, June K. Wicks, and Caitlin A. Murphy. Spin crossover equation of state and sound velocities of (Mg0.65fe0.35)O ferropericlase to 140 GPa. *Journal of Geophysical Research: Solid Earth*, 117(B8):B08208, August 2012.
- [455] Zhu Mao, Jung-Fu Lin, Jin Liu, and Vitali B. Prakapenka. Thermal equation of state of lower-mantle ferropericlase across the spin crossover. *Geophysical Research Letters*, 38(23):L23308, December 2011.
- [456] Hauke Marquardt, Sergio Speziale, Hans J. Reichmann, Daniel J. Frost, Frank R. Schilling, and Edward J. Garnero. Elastic Shear Anisotropy of Ferropericlase in Earth's Lower Mantle. *Science*, 324(5924):224–226, April 2009.
- [457] Pascal Richet, Ho-Kwang Mao, and Peter M. Bell. Bulk moduli of magnesiowüstites from static compression measurements. *Journal of Geophysical Research: Solid Earth*, 94(B3):3037–3045, March 1989.
- [458] Yoshinori Tange, Yu Nishihara, and Taku Tsuchiya. Unified analyses for P-V-T equation of state of MgO: A solution for pressure-scale problems in high P-T experiments. *Journal of Geophysical Research: Solid Earth*, 114(B3):B03208, March 2009.
- [459] Kirill K. Zhuravlev, J. M. Jackson, A. S. Wolf, J. K. Wicks, J. Yan, and S. M. Clark. Isothermal compression behavior of (Mg,Fe)O using neon as a pressure medium. *Physics and Chemistry of Minerals*, 37(7):465–474, July 2010.
- [460] R. M. Wentzcovitch, J. F. Justo, Z. Wu, C. R. S. da Silva, D. A. Yuen, and D. Kohlstedt. Anomalous compressibility of ferropericlase throughout the iron spin cross-over. *Proceedings of the National Academy of Sciences*, 106(21):8447–8452, May 2009.
- [461] S. Speziale, V. E. Lee, S. M. Clark, J. F. Lin, M. P. Pasternak, and R. Jeanloz. Effects of Fe spin transition on the elasticity of (Mg, Fe)O magnesiowüstites and implications for the seismological properties of the Earth's lower mantle. *Journal of Geophysical Research: Solid Earth*, 112(B10):B10212, October 2007.
- [462] Frédéric Deschamps, Laura Cobden, and Paul J. Tackley. The primitive nature of large low shear-wave velocity provinces. *Earth and Planetary Science Letters*, 349:198–208, October 2012.
- [463] Rajdeep Dasgupta and Marc M. Hirschmann. The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters*, 298(1):1–13, September 2010.
- [464] Peter B. Kelemen and Craig E. Manning. Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences*, 112(30):E3997–E4006, July 2015.

- [465] Frank E. Brenker, Christian Vollmer, Laszlo Vincze, Bart Vekemans, Anja Szymanski, Koen Janssens, Imre Szaloki, Lutz Nasdala, Werner Joswig, and Felix Kaminsky. Carbonates from the lower part of transition zone or even the lower mantle. *Earth and Planetary Science Letters*, 260(1):1–9, August 2007.
- [466] Andrey V. Korsakov and Jörg Hermann. Silicate and carbonate melt inclusions associated with diamonds in deeply subducted carbonate rocks. *Earth and Planetary Science Letters*, 241(1):104–118, January 2006.
- [467] Alian Wang, Jill D. Pasteris, Henry O. A. Meyer, and Marie L. Dele-Duboi. Magnesitebearing inclusion assemblage in natural diamond. *Earth and Planetary Science Letters*, 141(1):293–306, June 1996.
- [468] Andrew R. Thomson, Michael J. Walter, Simon C. Kohn, and Richard A. Brooker. Slab melting as a barrier to deep carbon subduction. *Nature*, 529(7584):76–79, January 2016.
- [469] N. S. Martirosyan, T. Yoshino, A. Shatskiy, A. D. Chanyshev, and K. D. Litasov. The CaCO3–Fe interaction: Kinetic approach for carbonate subduction to the deep Earth's mantle. *Physics of the Earth and Planetary Interiors*, 259:1–9, October 2016.
- [470] Daniel J. Frost and Catherine A. McCammon. The Redox State of Earth's Mantle. *Annual Review of Earth and Planetary Sciences*, 36(1):389–420, 2008.
- [471] I. D. Ryabchikov and F. V. Kaminsky. Oxygen potential of diamond formation in the lower mantle. *Geology of Ore Deposits*, 55(1):1–12, February 2013.
- [472] Felix Kaminsky. Mineralogy of the lower mantle: A review of 'super-deep' mineral inclusions in diamond. *Earth-Science Reviews*, 110(1):127–147, January 2012.
- [473] Arno Rohrbach and Max W. Schmidt. Redox freezing and melting in the Earth/'s deep mantle resulting from carbon-iron redox coupling. *Nature*, 472(7342):209–212, April 2011.
- [474] B. Harte. Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones. *Mineralogical Magazine*, 74(2):189–215, April 2010.
- [475] Ralf Tappert, Thomas Stachel, Jeff W. Harris, Karlis Muehlenbachs, Thomas Ludwig, and Gerhard P. Brey. Subducting oceanic crust: The source of deep diamonds. *Geology*, 33(7):565–568, July 2005.
- [476] V. Stagno, Y. Tange, N. Miyajima, C. A. McCammon, T. Irifune, and D. J. Frost. The stability of magnesite in the transition zone and the lower mantle as function of oxygen fugacity. *Geophysical Research Letters*, 38(19):L19309, October 2011.
- [477] Yuri N. Pal'yanov, Alexander G. Sokol, Yuri M. Borzdov, Alexander F. Khokhryakov, and Nikolay V. Sobolev. Diamond formation through carbonate-silicate interaction. *American Mineralogist*, 87(7):1009–1013, July 2002.

- [478] V. Stagno, D. J. Frost, C. A. McCammon, H. Mohseni, and Y. Fei. The oxygen fugacity at which graphite or diamond forms from carbonate-bearing melts in eclogitic rocks. *Contributions to Mineralogy and Petrology*, 169(2):16, February 2015.
- [479] Vincenzo Stagno, Dickson O. Ojwang, Catherine A. McCammon, and Daniel J. Frost. The oxidation state of the mantle and the extraction of carbon from Earth/'s interior. *Nature*, 493(7430):84–88, January 2013.
- [480] Makoto Arima, Yusuke Kozai, and Minoru Akaishi. Diamond nucleation and growth by reduction of carbonate melts under high-pressure and high-temperature conditions. *Geology*, 30(8):691–694, August 2002.
- [481] Yuri N. Palyanov, Yuliya V. Bataleva, Alexander G. Sokol, Yuri M. Borzdov, Igor N. Kupriyanov, Vadim N. Reutsky, and Nikolai V. Sobolev. Mantle–slab interaction and redox mechanism of diamond formation. *Proceedings of the National Academy of Sciences*, 110(51):20408–20413, December 2013.
- [482] J. Rouquette, D. Dolejš, I. Yu. Kantor, C. A. McCammon, D. J. Frost, V. B. Prakapenka, and L. S. Dubrovinsky. Iron-carbon interactions at high temperatures and pressures. *Applied Physics Letters*, 92(12):121912, March 2008.
- [483] Maiko Isshiki, Tetsuo Irifune, Kei Hirose, Shigeaki Ono, Yasuo Ohishi, Tetsu Watanuki, Eiji Nishibori, Masaki Takata, and Makoto Sakata. Stability of magnesite and its highpressure form in the lowermost mantle. *Nature*, 427(6969):60–63, January 2004.
- [484] T. Katsura and E. Ito. Melting and subsolidus phase relations in the MgSiO3mgco3 system at high pressures: implications to evolution of the Earth's atmosphere. *Earth and Planetary Science Letters*, 99(1):110–117, July 1990.
- [485] Isabelle Martinez, Eva Maria Chamorro Peréz, Jan Matas, Philippe Gillet, and Gérard Vidal. Experimental investigation of silicate-carbonate system at high pressure and high temperature. *Journal of Geophysical Research: Solid Earth*, 103(B3):5143–5163, March 1998.
- [486] N. A. Solopova, L. Dubrovinsky, A. V. Spivak, Yu A. Litvin, and N. Dubrovinskaia. Melting and decomposition of MgCO3 at pressures up to 84 GPa. *Physics and Chemistry of Minerals*, 42(1):73–81, January 2015.
- [487] A. V. Spivak, L. S. Dubrovinskii, and Yu A. Litvin. Congruent melting of calcium carbonate in a static experiment at 3500 K and 10–22 GPa: Its role in the genesis of ultradeep diamonds. *Doklady Earth Sciences*, 439(2):1171, August 2011.
- [488] Renbiao Tao, Yingwei Fei, and Lifei Zhang. Experimental determination of siderite stability at high pressure. *American Mineralogist*, 98(8-9):1565–1572, August 2013.
- [489] Sujoy Ghosh, Eiji Ohtani, Konstantin D. Litasov, and Hidenori Terasaki. Solidus of carbonated peridotite from 10 to 20 GPa and origin of magnesiocarbonatite melt in the Earth's deep mantle. *Chemical Geology*, 262(1):17–28, May 2009.

- [490] Felix V. Kaminsky, Igor D. Ryabchikov, and Richard Wirth. A primary natrocarbonatitic association in the Deep Earth. *Mineralogy and Petrology*, 110(2-3):387–398, April 2016.
- [491] D. Phillips and J. W. Harris. Geothermobarometry of diamond inclusions from the De Beers pool mines, Kimberley, South Africa. In Sixth International Kimberlite Conference, Novosibirsk, Extended Abstracts, pages 441–443, 1995.
- [492] Henry O. A. Meyer and Malcolm E. McCallum. Mineral Inclusions in Diamonds from the Sloan Kimberlites, Colorado. *The Journal of Geology*, 94(4):600–612, July 1986.
- [493] Claudine Biellmann, Philippe Gillet, Franç,ois Guyot, Jean Peyronneau, and Bruno Reynard. Experimental evidence for carbonate stability in the Earth's lower mantle. *Earth and Planetary Science Letters*, 118(1):31–41, July 1993.
- [494] Yusuke Seto, Daisuke Hamane, Takaya Nagai, and Kiyoshi Fujino. Fate of carbonates within oceanic plates subducted to the lower mantle, and a possible mechanism of diamond formation. *Physics and Chemistry of Minerals*, 35(4):223–229, May 2008.
- [495] Jung-Fu Lin, Jin Liu, Caleb Jacobs, and Vitali B. Prakapenka. Vibrational and elastic properties of ferromagnesite across the electronic spin-pairing transition of iron. *American Mineralogist*, 97(4):583–591, April 2012.
- [496] Jin Liu, Jung-Fu Lin, and Vitali B. Prakapenka. High-Pressure Orthorhombic Ferromagnesite as a Potential Deep-Mantle Carbon Carrier. *Scientific Reports*, 5:srep07640, January 2015.
- [497] E. Boulard, N. Menguy, A. L. Auzende, K. Benzerara, H. Bureau, D. Antonangeli, A. Corgne, G. Morard, J. Siebert, J. P. Perrillat, F. Guyot, and G. Fiquet. Experimental investigation of the stability of Fe-rich carbonates in the lower mantle. *Journal of Geophysical Research: Solid Earth*, 117(B2):B02208, February 2012.
- [498] Artem R. Oganov, Shigeaki Ono, Yanming Ma, Colin W. Glass, and Alberto Garcia. Novel high-pressure structures of MgCO3, CaCO3 and CO2 and their role in Earth's lower mantle. *Earth and Planetary Science Letters*, 273(1):38–47, August 2008.
- [499] Chris J. Pickard and Richard J. Needs. Structures and stability of calcium and magnesium carbonates at mantle pressures. *Physical Review B*, 91(10):104101, March 2015.
- [500] Eglantine Boulard, Alexandre Gloter, Alexandre Corgne, Daniele Antonangeli, Anne-Line Auzende, Jean-Philippe Perrillat, François Guyot, and Guillaume Fiquet. New host for carbon in the deep Earth. *Proceedings of the National Academy of Sciences*, 108(13):5184–5187, March 2011.
- [501] Shigeaki Ono, Takumi Kikegawa, and Yasuo Ohishi. High-pressure transition of CaCO3. *American Mineralogist*, 92(7):1246–1249, July 2007.

- [502] Elise Knittle and Raymond Jeanloz. Simulating the core-mantle boundary: An experimental study of high-pressure reactions between silicates and liquid iron. *Geophysical Research Letters*, 16(7):609–612, July 1989.
- [503] Kazuhiko Otsuka and Shun-ichiro Karato. Deep penetration of molten iron into the mantle caused by a morphological instability. *Nature*, 492(7428):243–246, December 2012.
- [504] Shigeaki Ono, Takumi Kikegawa, Yasuo Ohishi, and Jun Tsuchiya. Post-aragonite phase transformation in CaCO3 at 40 GPa. *American Mineralogist*, 90(4):667–671, April 2005.
- [505] Andrew R. Thomson, Michael J. Walter, Oliver T. Lord, and Simon C. Kohn. Experimental determination of melting in the systems enstatite-magnesite and magnesite-calcite from 15 to 80 GPa. *American Mineralogist*, 99(8-9):1544–1554, August 2014.
- [506] H. K. Mao, Y. Wu, L. C. Chen, J. F. Shu, and Andrew P. Jephcoat. Static compression of iron to 300 GPa and Fe0.8ni0.2 alloy to 260 GPa: Implications for composition of the core. *Journal of Geophysical Research: Solid Earth*, 95(B13):21737–21742, December 1990.
- [507] K. Sato and T. Katsura. Experimental investigation on dolomite dissociation into aragonite+magnesite up to 8.5 GPa. *Earth and Planetary Science Letters*, 184(2):529–534, January 2001.
- [508] Miki Shirasaka, Eiichi Takahashi, Yu Nishihara, Kyoko Matsukage, and Takumi Kikegawa. In situ X-ray observation of the reaction dolomite = aragonite + magnesite at 900–1300 K. American Mineralogist, 87(7):922–930, July 2002.
- [509] Lkhamsuren Bayarjargal, Tatyana G. Shumilova, Alexandra Friedrich, and Björn Winkler. Diamond formation from CaCO3 at high pressure and temperature. *European Journal of Mineralogy*, 22(1):29–34, January 2010.
- [510] J. M. Brown and T. J. Shankland. Thermodynamic parameters in the Earth as determined from seismic profiles. *Geophysical Journal International*, 66(3):579–596, September 1981.
- [511] Yu N. Pal'yanov, A. G. Sokol, Yu M. Borzdov, A. F. Khokhryakov, and N. V. Sobolev. Diamond formation from mantle carbonate fluids. *Nature*, 400(6743):417–418, July 1999.
- [512] Henry P. Scott, Quentin Williams, and Elise Knittle. Stability and equation of state of Fe3c to 73 GPa: Implications for carbon in the Earth's core. *Geophysical Research Letters*, 28(9):1875–1878, May 2001.
- [513] M. Iizuka, H. Ikawa, and O. Fukunaga. Nucleation and growth of diamond using NiTi, NiNb and FeB alloy as solvents. *Diamond and Related Materials*, 5(1):38–42, January 1996.

- [514] Arno Rohrbach, Chris Ballhaus, Ute Golla–Schindler, Peter Ulmer, Vadim S. Kamenetsky, and Dmitry V. Kuzmin. Metal saturation in the upper mantle. *Nature*, 449(7161):456–458, September 2007.
- [515] Audrey M. Martin and Tahar Hammouda. Role of iron and reducing conditions on the stability of dolomite + coesite between 4.25 and 6 GPa – a potential mechanism for diamond formation during subduction. *European Journal of Mineralogy*, 23(1):5–16, January 2011.
- [516] Naira S. Martirosyan, Konstantin D. Litasov, Anton Shatskiy, and Eiji Ohtani. The reactions between iron and magnesite at 6 GPa and 1273–1873 K: Implication to reduction of subducted carbonate in the deep mantle. *Journal of Mineralogical and Petrological Sciences*, 110(2):49–59, 2015.
- [517] N. S. Martirosyan, K. D. Litasov, A. F. Shatskiy, and E. Ohtani. Reactions of iron with calcium carbonate at 6 GPa and 1273–1873 K: implications for carbonate reduction in the deep mantle. *Russian Geology and Geophysics*, 56(9):1322–1331, September 2015.
- [518] Zhou Zhang, Susannah M. Dorfman, Jabrane Labidi, Shuai Zhang, Mingming Li, Michael Manga, Lars Stixrude, William F. McDonough, and Quentin Williams. Primordial metallic melt in the deep mantle. *Geophysical Research Letters*, 43(8):2016GL068560, April 2016.
- [519] Elizabeth Cottrell and Katherine A. Kelley. Redox Heterogeneity in Mid-Ocean Ridge Basalts as a Function of Mantle Source. *Science*, 340(6138):1314–1317, June 2013.
- [520] William M. White. Oceanic Island Basalts and Mantle Plumes: The Geochemical Perspective. *Annual Review of Earth and Planetary Sciences*, 38(1):133–160, 2010.

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Academic Background

• PhD in Materials Science and Engineering École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland	June 2013 to present
• M. Sc. in Materials Science and Engineering École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland	Sept. 2011 to June 2013
• B. Sc. in Material Science and Engineering Sharif University of Technology, Tehran, Iran	Sept. 2007 to July. 2011
• Diploma in Mathematics and Physics Shahid Madani High School, National Organization for Development of Ex Tabriz, Iran	Sept. 2003 to June. 2007 receptional Talents (NODET),
Work Experiences	
• Doctoral assistantship Earth and Planetary Science Laboratory (EPSL), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland	June. 2013 to present
• Teaching Assistantship, Electron Microscopy: Advanced Methodes Interdisciplinary Centre Electron Microscopy (CIME), École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland	Feb. 2013 to present
• Internship HTceramix, Yverdon-les-Bains, Switzerland Investigation of fuel cell anode and its pollution mainly by electron microsco	<i>Sept. 2012 to Dec. 2012</i> py tools.
• Assistantship	June. 2010 to June. 2011
Structural characterization Lab., Sharif University of Technology I experienced the transmission electron microscopy(TEM), X-ray diffractic cence(XRF).	on(XRD) and X-ray fluores-
• Teaching Assistantship , Physical Metallurgy 2 Department of Material Science and Engineering, Sharif University of Techn	Sept. 2010 to June. 2011 pology
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• Internship	Jun. 2010 to Sep. 2010

 Internship
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 Sina Mashin Co., Tehran, Iran
 Materials selection industrial fans as well as different welding and machining precesses during the internship.

ACADEMIC RESEARCH EXPERIENCES

- Characterization of inclusions in extraterrestrial diamonds June. 2013 to present PhD thesis, Earth and Planetary Science Laboratory (EPSL), EPFL Interdisciplinary Centre for Electron Microscopy (CIME), EPFL Ureilite samples were studied with the transmission electron microscopy and spectroscopy techniques.
- **3D** electron microscopy characterization of materials synthesized at lower mantle conditions June. 2013 to present PhD thesis, Earth and Planetary Science Laboratory (EPSL), EPFL

Interdisciplinary Centre for Electron Microscopy (CIME), EPFL Sample molten in the laser heated diamond anvil cell at lower mantle pressures are studied with 3D FIB-EDX tomography as well as with the transmission electron microscopy and Spectroscopy.

• Transmission electron microscopy microtructural characterisation of doped alumina ceramics for transparent ceramic applications Master thesis, Interdisciplinary Centre for Electron Microscopy (CIME), EPFL

The aim of this project is to study codoped Alumina to relate concentration of different dopant to different orientations of grain boundaries by transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (XEDS) techniques.

- Investigation of oxide particles in ODS steel Feb. 2012 to June. 2012 Semester project, Interdisciplinary Centre for Electron Microscopy (CIME), EPFL The aim of this project was to investigate the spatial distribution of the particles dispersion by transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (XEDS) techniques.
- Influence of precipitation on formation of deformation twins Sept. 2010 to June. 2011 B. Sc. thesis, Sharif University of Technology Formation of deformation twins is investigated in AEREX 350 superalloys which undergone to different heat treatment cycles. Samples are studied by simple pressure test and electron microscopy.

PUBLICATIONS

• Diamonds from a lost planet

F.Nabiei, J. Badro, T. Dennenwaldt, E. Oveisi, M. Cantoni, C. Hebert, A. El Goresy, J. A. Barrat, P. Gillet, submitted to Nature Communications (under revision)

- Carbonate stability in the reduced lower mantle S. M. Dorfman, J. Badro, F. Nabiei, V. B. Prakapenka, M. Cantoni and P. Gillet, submitted to Earth and Planetary Science Letters (under review)
- Composition and pressure effects on partitioning of ferrous iron in iron-rich lower mantle heterogeneities

S. M. Dorfman, F. Nabiei, V. B. Prakapenka, M. Cantoni, J. Badro and P. Gillet, submitted to Physics of Earth and Planetary Interiors (under review)

- Spin and valence dependence of iron partitioning in Earths deep mantle H. Piet, J. Badro, F. Nabiei, T. Dennenwaldt, S.-H. Shim, M. Cantoni, C. Hbert and P. Gillet, Proceeding of National Academy of Science, Volume 113, Number 40, Pages 11127-11130, 2016
- Towards knowledge based grain boundary engineering of transparent polycrystalline alumina combining advanced TEM and atomistic modelling A. Tewari, F. Nabiei, S. Parker, M. Cantoni, M. Stuer, P. Bowen and C. Hebert, Journal of the American Ceramic Society, Volume 98, Issue 6, Pages 1959-1964, 2015
- Segregation of anion (Cl-) impurities at transparent polycrystalline alumina interfaces A. Tewari, F. Nabiei, M. Cantoni, P. Bowen and C. Hebert, Journal of European Ceramics Society, Volume 34, Issue 12, Pages 3037-3045, 2014

Conference presentations

- Characterization of inclusions in extraterrestrial diamonds (oral presentation by F. Nabiei) F. Nabiei, J. Badro, T. Dennenwaldt, E. Oveisi, M. Cantoni, C. Hebert, A. El Goresy and P. Gillet, Microscopy Conference, Luasanne, Switzerland, 2017
- From extraterrestrial diamond inclusions to a lost planet (poster presentation by F. Nabiei) F. Nabiei, J. Badro, T. Dennenwaldt, E. Oveisi, M. Cantoni, C. Hebert, A. El Goresy, J. A. Barrat and P. Gillet, Accretion and Early Differentiation of the Earth and Terrestrial Planets, Nice, France, 2017
- 3D analytical investigation of melting at lower mantle conditions in laser-heated diamond anvil cell (oral presentation by F. Nabiei)
 F. Nabiei, M. Cantoni, J. Badro, S. Dorfman, R. Gaal, H. Piet and P. Gillet, European Microscopy Congress, Lyon, France, 2016
- 3D analytical investigation of melting at lower mantle conditions in laser-heated diamond anvil cell (oral presentation by F. Nabiei) F. Nabiei, M. Cantoni, J. Badro, S. Dorfman, R. Gaal, H. Piet and P. Gillet, European Microscopy Congress, Lyon, France, 2016
- 3D analytical investigation of melting at lower mantle conditions in laser-heated diamond anvil cell (poster presentation by F. Nabiei)
 F. Nabiei, M. Cantoni, J. Badro, S. Dorfman, R. Gaal, H. Piet and P. Gillet, AGU Fall Meeting, San Francisco, USA, 2015
- 3D mapping of chemical distribution from melting at lower mantle conditions in the laserheated diamond anvil cell (oral presentation by S. Dorfman) F. Nabiei, M. Cantoni, J. Badro, S. Dorfman, R. Gaal and P. Gillet, AGU Fall Meeting, San Francisco, USA, 2014
- 3D imaging of chemical distribution from melting in laser heated diamond anvil cell (oral presentation by S. Dorfman)

F. Nabiei, M. Cantoni, S. M. Dorfman, R. Gaal, J. Badro and P. Gillet, European High Pressure Research Group International Meeting, Lyon, France, 2014

- Transmission electron microscopy investigation of transparent alumina (oral presentation by F.Nabiei) F.Nabiei, A. Tewari, M. Cantoni, P. Bowen and C. Hebert, International Microscopy Congress, Prague,
- Czech Republic, 2014
 3D imaging of chemical distribution from melting in laser heated diamond anvil cell (poster presentation by F. Nabiei)

F. Nabiei, M. Cantoni, J. Badro, S. M. Dorfman, R. Gaal and P. Gillet, International Microscopy Congress, Prague, Czech Republic, 2014

Skills

- Languages: Persian (Native), Azeri (Native), English (Fluent), Turkish (Fluent), French(Beginner)
- **Professional Software and Programming Languages**: Mathematica, MATLAB, DigitalMicrograph, Python, ImageJ, AutoIt, AutoCAD, Pascal
- Typesetting and Office Software: LATEX 2ε , Microsoft Office Suite, LibreOffice
- Operating Systems: GNU/Linux Ubuntu, Microsoft Windows