Insights into the core's structure, formation and evolution from first-principles calculations

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ABSTRACT

Understanding the formation, composition, and evolution of planetary cores is essential to unraveling the early history and internal dynamics of terrestrial planets. However, direct constraints on the physical and chemical properties of liquid metal under core-forming conditions remain limited due to the inaccessibility of the core and the challenges of reproducing its extreme pressures and temperatures in the laboratory. This thesis integrates first-principles molecular dynamics (FPMD) simulations with high-pressure experimental data to investigate the thermodynamics, chemical partitioning, and seismic implications of multicomponent metal liquids in the deep interiors of Earth and other differentiated bodies.

This thesis focuses on two fundamental properties of the core: its thermodynamic behavior and its chemical interaction with the silicate mantle during differentiation. The first part of the thesis develops a thermodynamic model for multicomponent metallic liquids-including Fe-Ni systems with light elements such as O, S, Si, C, and H-based on FPMD simulations and calibrated against experimental data. This model accurately reproduces pressure-volume-temperature relations and mixing behavior, and is consistent with both diamond anvil cell and shock wave measurements. The model forms the basis for a forward seismic modeling framework that allows direct comparison between core composition and observed density and velocity profiles in Earth's outer core. The second part of the thesis investigates the chemical partitioning of elements that record early planetary formation and evolution—specifically Sm, Nd, I, and Pu—between metal and silicate liquids at high temperatures. Two different approaches are employed to determine the partition coefficients: thermodynamic integration based on first-principles molecular dynamics for Sm and Nd, and two-phase FPMD simulations for I and Pu. With these partitioning behaviors quantified, the study further models core formation processes in differentiated planetesimals and Earth, providing new constraints on the extent of metal-silicate chemical exchange and fresh insights into the isotopic and volatile evolution of planetary mantles.

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 W.L designed the research, performed the FPMD calculations and interpreted the data, performed the multistage core formation modeling, collected and analyzed meteoritic xenon data, and wrote the initial manuscript.

TABLE OF CONTENTS

Acknowledgements	iii
Abstract	v
Published Content and Contributions	vi
Table of Contents	vi
List of Illustrations	ix
List of Tables	xii
Chapter I: Introduction	1
Chapter II: Thermodynamic properties of liquid metal using first-principles	
molecular dynamics	5
2.1 Introduction	5
2.2 Methods	8
2.3 Calibrating the pressure and energy correction to ab initio results for	
pure iron liquid	16
2.4 Thermodynamic model for pure iron liquid	18
2.5 Thermodynamic model for multicomponent metal compositions	23
2.6 Conclusion and future perspectives	29
Chapter III: Constraining the compositional and thermal state of the Earth's	
outer core using new thermodynamic model for multi-component metal	
liquids	36
3.1 Introduction	36
3.2 Methods	37
3.3 Summaries on seismic observations	40
3.4 Model/observation comparison approach	43
3.5 Comparison to PREM model	45
3.6 Comparison to ak135 model	50
3.7 Comparison to EPOC-V model	52
3.8 Comparison to ek137 model and more seismic models with no a	
priori Adams-Williamson constraint	54
3.9 Conclusions and future perspective	55
Chapter IV: The partition coefficients of Iodine and Plutonium between metal	
liquid and silicate melt	62
4.1 Introduction	62
4.2 Methods	64
4.3 Results on partitioning coefficient of I and Pu	73
4.4 I/Pu partitioning during core formation and mantle ¹²⁹ Xe*/ ¹³⁶ Xe* ^{Pu}	
observations	75
4.5 Homogeneous volatile accretion	75
4.6 Heterogeneous volatile accretion	83
4.7 Accretion model of differentiated planetesimal	86

Chapter V: THe partition coefficients of Samarium and Neodymium between					
silicate melt and metal liquid	98				
Appendix A: Supplementary Tables for Chapter II	99				
Appendix B: Supplementary Tables for Chapter III	.23				
Appendix C: Supplementary Tables for Chapter IV	.24				
Appendix D: Supplementary Tables for Chapter V	.34				

LIST OF ILLUSTRATIONS

Numbe	r I	Page					
2.1	Convergence tests on cutoff energy and self-consistent iteration ac-						
	curacy	9					
2.2	Tests on the relationship between Grüneisen parameter and tempera-						
	ture or volume	11					
2.3	Tests on the relationship between heat capacity and temperature or						
	volume	12					
2.4	Tests on the relationship between heat capacity and temperature or						
	volume	13					
2.5	Pressure correction as a function of density using thermodynamic						
	formalism.	17					
2.6	Comparison between thermodynamic model and experimental mea-						
	surements using an alternative set of correction parameters	18					
2.7	The corrected pressure and internal energy for pure iron liquid	20					
2.8	The uncorrected pressure and internal energy for pure iron liquid 21						
2.9	Comparison of new thermodynamic model with experiental shock						
	data for pure iron	22					
2.10	Equation of states for reference binaries	24					
2.11	Internal energies for reference binaries.	25					
2.12	Tests on mixing on pressures using $Fe_{90}Si_xO_{18-x}$	26					
2.13	Tests on mixing on internal energies using $Fe_{90}Si_xO_{18-x}$	27					
2.14	The comparison of different mixing models for Fe_xH_{108-x}	28					
2.15	Validation of the new ab initio thermodynamic model for multicom-						
	ponent metallic liquids against available shock wave data	29					
3.1	Comparison of thermodynamic model and seismic velocity models						
	across the outer core	42					
3.2	Distributions of model parameters for accepted samples of the MCMC						
	fit to the PREM model in the fiducial case.	47					
3.3	Comparison of the probability density functions for accepted MCMC						
	samples in the fiducial, H-free, and unshackled cases	48					
3.4	Distributions of model parameters for accepted samples of the MCMC						
	fit to the PREM model in the H-free case	49					

3.5	The magnitude of perturbation to temperature and light element con- centration to obtain an acceptable fit to the seismic velocity of the	
	ak135 model.	51
3.6	Comparison of the probability density functions of model parameters and outputs between 'fiducial' PREM model and 'fiducial' EPOV-C	
	model.	53
3.7	Comparison of the probability density functions of model parameters and outputs between 'H-free' PREM model and 'H-free' EPOV-C	
	model.	54
4.1	Snapshot of atomic configuration in the simulation cell.	66
4.2	Comparison of equilibrium constants from new FPMD simulations	
	with those from previous experiment and FPMD simulations	70
4.3	High-pressure metal-silicate equilibrium constants for iodine and plu-	
	tonium, as a function of temperature	74
4.4	Metal-silicate partition coefficients for iodine and plutonium as a	
	function of temperature at different $P - T - X_O^{metal}$ conditions	76
4.5	Metal-silicate partition coefficients for iodine and plutonium as a	
	function of pressure at different $P - T - X_{O}^{metal}$ conditions	77
4.6	Changes in I and Pu partitioning behaviors and their impact on the	
	I/Pu of Earth's reservoirs as a function of the mass accreted to the	
	Earth	78
4.7	Pressure and temperature sensitivity tests for homogeneous volatile	
	accretion scenarios.	79
4.8	Variations of the mantle I/Pu ratio as a function of the mass fraction	
	accreted to the Earth under homogeneous volatile accretion scenarios	
	for different fO_2 conditions and equilibrium T	80
4.9	Variations of I/Pu ratio with mass fraction accreted to the Earth	
	under homogeneous and heterogeneous accretion scenarios in an	
	equilibrium temperature that follows hot liquidus geotherm	81
4.10	Variations of I and Pu partitioning between silicate melt and metal	
	liquid as a function of the mass accreted to the Earth	82
4.11	Variations of I and Pu partitioning between silicate melt and metal	
	liquid as a function of the mass accreted to the Earth	83
4.12	Final MORB mantle's I/Pu ratio after normalized to the mantle I/Pu	
	at the end of Phase 1 as a function of the starting time of Phase 2 of	
	accretion	85

Х

4.13	Mantle's I/Pu ratio right after core formation processes after normal-	
	ized to the mantle I/Pu at the end of Phase 1 as a function of Phase 2	
	starting time	86
4.14	Schematic representation of the heterogeneous accretion history of	
	the Earth that is consistent with the more siderophile behavior of I	
	and Pu at high $P - T$ conditions	88
4.15	Variations of mantle Mg/Si ratio as a function of the mass fraction	
	accreted to the Earth	89

LIST OF TABLES

Numbe	r Page
2.1	Thermodynamic Model Parameters of Metallic Liquid
4.1	Results of first-principles molecular dynamics simulations on iodine
	partitioning
4.2	Results of first-principles molecular dynamics simulations on pluto-
	nium partitioning
A.1	DFT data of pure iron used for pressure correction based on DAC
	experiments (Kuwayama et al., 2020)
A.2	Ab initio simulation results for reference metals
A.3	Comparison of DFT pressure with model predictions
B.1	Correlation matrix among resulted model parameters
C.1	Xenon end-member compositions and meteoritic data used 125
C.2	Solutions for radiogenic ¹²⁹ Xe and plutonium-derived fissiogenic
	136 Xe of different meteorites using Phase-Q as the initial composition. 128
C.3	Solutions for radiogenic ¹²⁹ Xe and plutonium-derived fissiogenic
	¹³⁶ Xe of different meteorites using solar wind as the initial com-
	position

INTRODUCTION

The cores of terrestrial planets are central to their internal structure and long-term evolution. In the case of Earth, the core comprises approximately one-third of the planet's mass and is predominantly composed of an iron–nickel alloy. This metallic core resides beneath the silicate mantle, forming a dense central sphere that extends from the core–mantle boundary at approximately 2900 km depth down to the planetary center. Similar iron-dominated cores are thought to exist in other differentiated planetary bodies—including Mars, Mercury, Venus—as well as in smaller asteroidal bodies such as Vesta. Despite its fundamental importance, the core remains one of the most inaccessible regions of planetary interiors. Because it is buried deep beneath the mantle and cannot be sampled directly, our knowledge of the core relies almost entirely on indirect observations.

Understanding the core is of fundamental importance not only for deciphering the internal dynamics of Earth, but also for reconstructing its origin and evolutionary history. The core is a major internal heat source, supplying thermal energy that drives mantle convection and plate tectonics. It is also the engine of the geodynamo-the mechanism that generates Earth's magnetic field, which protects the planet's atmosphere and surface from solar wind and cosmic radiation. Furthermore, the core represents a chemically distinct reservoir, isolated to a large extent from the silicate mantle, yet possibly interacting with it in ways that remain poorly understood. Critically, if we can better constrain the structure and composition of the core, we can link it with the more accessible and better-sampled silicate mantle to form a comprehensive picture of Earth's bulk composition. Such knowledge offers a pathway to deciphering the conditions under which Earth formed, the materials it accreted from, and the differentiation events that shaped its interior. Ultimately, constraining the core's physical and chemical properties is essential to resolving long-standing questions about the origin of terrestrial planets, their thermal and magnetic evolution, and the diversity of planetary interiors within our solar system and beyond.

Two major challenges currently hinder our understanding of the core. First, the extreme pressure and temperature conditions of the present-day core, as well as

those during its formation, are difficult to reproduce in laboratory settings. As a result, our knowledge of the physical properties of metal liquids, and of the chemical equilibria between metallic and silicate phases, remains limited. Second, even when such properties can be inferred, translating them into geophysical, geochemical, and cosmochemical observables is nontrivial. Bridging this gap requires robust models that link fundamental physical and chemical behavior of core materials to measurable planetary signatures. Only then can we construct self-consistent interpretations of planetary interiors and reconstruct the formation and evolution of terrestrial planets.

To address the first challenge, first-principles calculations have emerged as a powerful tool for investigating the behavior of metal liquids under core-forming conditions. When combined with the limited but crucial high-pressure, high-temperature experimental data available, this approach enables mutual validation: simulations can be used to extrapolate material behavior beyond the experimental regime, while experimental results help constrain and calibrate the computational predictions. Together, they offer a robust framework for determining the thermodynamic and chemical properties of core-forming materials under extreme conditions that are otherwise inaccessible to direct observation.

To address the second challenge, it is essential to develop internally consistent and physically grounded mathematical models. These models must integrate thermodynamic behavior, chemical partitioning, and isotopic evolution to connect atomicscale interactions with seismic, geochemical, and cosmochemical signatures. When built upon first-principles calculations and constrained by experimental or observational data, such models provide a quantitative framework for interpreting seismic velocity and density profiles, modeling elemental partitioning during metal–silicate equilibration, and reconstructing the thermal and chemical evolution of planetary interiors.

This thesis comprises four components of research:

Chapter II in this thesis is about the development of a new thermodynamic model for multicomponent metallic liquids under conditions relevant to the Earth's outer core. Using first-principles molecular dynamics simulations, calibrated with experimental data through a physically grounded pressure correction scheme, the model captures the equation of state and thermodynamic properties of Fe–Ni liquids with light elements (O, S, Si, C, H). The approach integrates non-ideal mixing behavior, allowing accurate interpolation across composition space. Crucially, the model reproduces experimental observations from both diamond anvil cell (DAC) and

shock wave studies over a wide range of pressures and temperatures. This level of agreement demonstrates the model's robustness and generality, making it a powerful tool for interpreting the physical behavior of liquid metals.

Chapter III in this thesis is establishing a forward modeling framework that links first-principles calculations with seismic observations. By embedding the model in the self-gravitating Adams–Williamson equation and solving for radial profiles of velocity and density, this approach allows simultaneous fitting of seismic models using a Bayesian MCMC inversion. The results show that commonly used seismic models such as PREM and EPOC-V can be matched with plausible core compositions, while others (e.g., ak135) require non-adiabatic or compositionally layered cores.

Chapter IV in this thesis is the metal–silicate partitioning behavior of iodine and plutonium under high-pressure, high-temperature conditions using two-phase first-principles molecular dynamics simulations. These elements are the radioactive parents of xenon isotopes used to trace early Earth accretion. The simulations reveal that both I and Pu partially partition into metal liquid during core formation processes, and this differential partitioning is insufficient to explain the observed mantle heterogeneities in I/Pu. Instead, the results support a heterogeneous accretion history, whereby Earth primarily accreted from volatile-poor differentiated planetesimals. This finding provides a new geochemical constraint on Earth's building blocks and volatile delivery, and helps reconcile Xe isotope systematics in mantle reservoirs with early accretion processes.

Chapter V in this thesis is the partitioning behavior of samarium and neodymium during metal–silicate differentiation under high-temperature conditions relevant to early planetary evolution. A thermodynamic integration approach based on first-principles molecular dynamics was used to compute the equilibrium constants and partition coefficients of Sm and Nd between liquid metal and silicate melt. The results suggested that, under plausible early solar system conditions, differential partitioning of Sm and Nd may lead to measurable variations in the Sm/Nd ratio of the residual mantle. This process offers a potential explanation for the elevated μ^{142} Nd values observed in early-formed differentiated bodies such as Vesta and the angrite parent body, providing new insight into the origin of Earth's μ^{142} Nd excess. The results suggest that rare earth elements (REEs) may have partitioned into the core in subtly different proportions during differentiation, potentially challenging conventional assumptions about the formation and evolution of the primitive mantle.

This thesis provides new insights into the structure and chemical evolution of planetary interiors by integrating first-principles molecular dynamics with geochemical and geophysical constraints. A robust thermodynamic model for multicomponent metallic liquids is established, accurately reproducing all available high-pressure, high-temperature experimental data, including results from both diamond anvil cell and shock wave experiments. Embedding this model into forward geophysical calculations reveals that multiple seismic models of Earth's outer core are consistent with plausible, thermodynamically constrained compositions. On the geochemical side, metal–silicate partitioning simulations show that previous lithophile elements (iodine, plutonium, samarium, and neodymium) display measurable partitioning behavior at early solar system conditions. These results suggest that early core formation played a more chemically selective role than previously recognized, leaving lasting isotopic signatures in planetary mantles and providing new constraints on the origin and differentiation history of Earth and its building blocks.

Chapter 2

THERMODYNAMIC PROPERTIES OF LIQUID METAL USING FIRST-PRINCIPLES MOLECULAR DYNAMICS

2.1 Introduction

The combination of cosmochemical, geochemical, and geophysical constraints show that the Earth's outer core primarily consists of Fe-Ni metallic liquid alloy, with minor quantities of light elements such as Si, S, O, and C (Allègre et al., 2001; Badro et al., 2015; Fischer et al., 2017; McDonough and Sun, 1995; Rubie et al., 2011; Rubie et al., 2015). Recent research suggests that the highly volatile element hydrogen (H) also likely entered the Earth's core in significant amounts during core formation (Y. Li et al., 2020; Young et al., 2023) and may facilitate the generation of the magnetic field in the Earth's core (He et al., 2022), making H an additional plausible candidate for a light element in the core (Oka et al., 2022; Umemoto and Hirose, 2015). Accurate knowledge of the relative contents of these light elements plays a crucial role in unraveling the mysteries of Earth's formation and evolution, the mechanisms driving the geodynamo, and the bulk composition of the Earth. But this remains an open question, in part because density and sound speed do not yield enough constraints to uniquely determine the answer. However, an additional constraint can be obtained from the geophysically well-constrained velocity profile of the Earth's outer core, if the thermodynamic properties (the relationships among velocity-density-pressure-temperature-internal energy) of candidate liquid metals are known well enough at core conditions and are used to construct a self-consistent model of the whole outer core.

Previous work has attempted to derive the equation of state (EOS) for liquid metal alloys appropriate to the core, starting from the EOS of pure iron. Shock compression experiments (Al'tshuler et al., 1958; Al'tshuler et al., 1981; Brown et al., 2000; Brown and McQueen, 1986; Marsh and Los Alamos Scientific Laboratory, 1980) give relations among velocity-pressure-density-internal energy ($V_P - P - \rho - U$) along the Hugoniot curve, reaching more than 400 GPa (the outer core extends from the core mantle boundary (CMB) at ~135 GPa to the inner core boundary (ICB) at ~330 GPa, and the solid inner core from ~330 to 360 GPa (Dziewonski and D. L. Anderson, 1981)). However, the Hugoniot has a very different trajectory through

pressure-temperature space than the actual outer core geotherm, so the shock wave data must be corrected from the Hugoniot to core conditions. Since the temperature cannot be directly measured to high precision in shock compression experiments on opaque materials, the magnitude of this correction remains uncertain even when the (composition-dependent) Grüneisen parameter and heat capacity are well-known. More recently, diamond-anvil cell (DAC) experiments have allowed measurement of the EOS of pure iron liquid (i.e., $P - \rho - T$ relation) at conditions approaching those of the outer core, but presently the maximum P - T conditions achieved are 4350 K and 116 GPa (Kuwayama et al., 2020), so extrapolation is still required to reach outer core conditions. Moreover, shock-wave based parameterizations of thermodynamic parameters (W. W. Anderson and Ahrens, 1994; Brown and Mc-Queen, 1986; Yoo et al., 1993) have been interpreted to show a notable discrepancy between extrapolations of DAC experiments and results from shock compression experiments. In shock compression experiments, melting is complete at P = 260 GPa and $\rho = 12.5 \text{ Mg/m}^3$ (Nguyen and Holmes, 2004), which also represents the melting point at this pressure. Conventional methods of predicting the temperature on the Hugoniot at this pressure and density yield ~6000 K (Brown and McQueen, 1986; Yoo et al., 1993), approximately 1500 K higher than the temperature obtained by extrapolating the DAC EOS to this condition (Kuwayama et al., 2020), and also exceeding by about 1000 K the melting point of pure iron measured in a DAC at 260 GPa (Sinmyo et al., 2019). Although more recent interpretations of shock wave data (Nguyen and Holmes, 2004) indicate lower melting temperatures than the earliest studies (Williams et al., 1987; Yoo et al., 1993), there remains an impression of inconsistent constraints on the EOS of liquid Fe.

The experimental situation is considerably worse when considering the multicomponent metal alloy liquids that must make up the actual outer core, given the wellresolved mismatch between the geophysical properties of the core and those of pure Fe. Shock wave experiments are available for only a handful of highly simplified multicomponent Fe-rich liquids (Huang et al., 2018; Huang et al., 2011; Zhang et al., 2016), and DAC experiments have not yet probed the EOS of core-relevant multicomponent liquids at any conditions approaching those of the core.

First-principles or ab initio molecular dynamics (FPMD) simulations offer an alternative approach to deriving the EOS and thermodynamic properties of multicomponent metal liquid compositions under outer core conditions. Numerous studies have focused on the density and velocity of liquid pure iron (Alfè et al., 2002; Ichikawa et al., 2014; Q. Li et al., 2022; Wagle and Steinle-Neumann, 2019) using various levels of theory and computational strategies. However, raw ab initio results from these pure iron studies tend to systematically underestimate experimental pressures (Brown and McQueen, 1986; Kuwayama et al., 2020) at density conditions suitable for the core. Therefore, a pressure and energy correction must be applied to bring ab initio results into alignment with experimental data before any accurate comparison with the core can be attempted. Previous studies have tackled this issue by applying a simple pressure shift based on data from shock compression experiments (Badro et al., 2014; Umemoto et al., 2014; Umemoto and Hirose, 2020). There are at least three significant limitations to this approach. First, the temperatures of the states probed by the shock experiments are not measured and must be inferred from the thermodynamic model, making it challenging to compare computed and experimental pressures at equal density and temperature. Second, the data all lie on the Hugoniot and cannot address possible tradeoffs between temperature and density errors that might be resolved with better coverage of the conditions along the core adiabat. Third, a constant pressure shift cannot be correct over wide ranges of density, as it yields nonphysical behavior at high and low limits of volume (French and Mattsson, 2014). That is, an EOS with a constant non-zero pressure shift will not approach the Thomas-Fermi limit at zero volume, nor will it approach zero pressure in the limit of infinite volume. We are in a position to solve all three of these issues by adding constraints from recent DAC experiments (Kuwayama et al., 2020), in which temperature was accurately measured, and by adopting an improved formulation for the pressure shift that obeys all relevant limiting behaviors.

The multicomponent nature of the problem introduces additional difficulties in application of ab initio methods to interpreting the composition and state of the core. It is impractical to compute all possible compositions in multicomponent space, and so an interpolation scheme is necessary to describe the EOS as a function of composition based on a limited number of computed compositions. The most common interpolation scheme, adopted by most previous authors, is ideal mixing of volumes at equal pressure and temperature (Badro et al., 2014; Umemoto and Hirose, 2020). However, this scheme lacks physical justification and is rarely tested on ternaries and more complicated metal system. If it does not apply, some better interpolation rule must be developed and potential errors due to interpolation rigorously estimated.

In this chapter, we present a comprehensive set of first-principles molecular dynam-

ics simulations of liquids in the Fe-Ni-S-Si-O-C-H system. We use these simulations to develop an accurate compositional interpolation rule, an internally consistent formulation of the pressure shift, and a thermal equation of state that defines the properties of multicomponent liquid alloys at P - T conditions spanning the whole outer core.

2.2 Methods

First-principles molecular dynamics simulations details

Calculations were carried out in the ab initio molecular dynamics program VASP (Kresse and Furthmüller, 1996). The projector-augmented wave potentials (Blöchl, 1994; Kresse and Joubert, 1999) were used together with the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential (Perdew et al., 1996), in which 8 valence electrons were considered for Fe $(3d^{7}4s^{1})$, 10 for Ni $(3d^{8}4s^{2})$, 4 for C $(2s^{2}2p^{2})$, 6 for O $(2s^{2}2p^{4})$, 6 for S $(3s^{2}3p^{4})$, 4 for Si $(3s^23p^2)$, and 1 for H $(1s^1)$. The plane-wave basis set cutoff was 300 eV and the accuracy for electronic self-consistent iteration was 10^{-4} eV (convergence tests are presented in Fig 2.1). The Brillouin zone sampling was performed only at the gamma point and Fermi-Dirac smearing was used to incorporate the temperature effect on the electron distribution. Molecular dynamics simulations were performed on cubic cells containing 108 atoms in the N - V - T canonical ensemble (i.e., number of atoms, volume, and temperature remain constant during simulation). The number of atoms is the same as in Badro et al. (2014). The volume range considered yields pressures spanning \sim 90-450 GPa. The temperature was controlled at 4,000 K, 4,500 K, 5,000 K, 5,500 K, and 6,000 K using a Nosé-Hoover thermostat (Hoover, 1985; Nosé, 1984). Fe₁₀₈ was used to compare with high P - T experimental data and determine the thermodynamic model of pure iron. Fe₇₆O₃₂ (also Fe₉₀O₁₈), $Fe_{90}Si_{18}$, $Fe_{90}S_{18}$, $Fe_{90}Ni_{18}$, $Fe_{90}Ni_{18}$, and $Fe_{76}H_{32}$ were chosen to study the effects of these elements on the thermal properties of metallic liquid. Other selected binary and ternary compositions were computed to study mixing effects, test ideal mixing approximations, and develop an accurate compositional interpolation scheme. The time step was set to be 1 femtosecond. We first performed FPMD at 10,000 K for 5,000 steps to obtain a liquid structure. Then, 1,000 steps were used to allow the liquid structure to reach equilibrium at each target volume and temperature; we confirmed that statistically steady properties were reached by the end of this equilibration. Finally, another 4,000 steps or more were used to calculate the pressure and internal energy (U) by taking their averages over time. All calculations

were performed without considering spin polarization due to its high computational cost. Previous ab initio studies have demonstrated that spin polarization can significantly influence computational results for metal alloys at low pressures such as those relevant to Mercury's core (~40 GPa), but the magnetic moments of metal alloys decrease progressively with increasing pressure and their equation of state becomes consistent with non-spin-polarized ab initio results at P - T conditions of the Earth's CMB (Edgington et al., 2019).



Figure 2.1: Coverage tests that were performed to determine the optimal cutoff energy and electronic self-consistent iteration accuracy (EDIFF) based on (a, b) pressure and (c, d) internal energy (U) for liquid pure iron. We finally select the plane-wave basis set cutoff to be 300 eV and EDIFF to be 10^{-4} eV. (a,c) The calculations varied cut-off energy but set EDIFF to be 10^{-4} (b,d) The calculations varied EDIFF but set cut-off energy to be 300 eV.

Pressure and energy correction scheme

In order to correct the mismatch of ab initio pressure, we used the temperatureindependent correction method of French and Mattsson (2014), following the recommendation of Wagle and Steinle-Neumann (2019). In this method, the corrections added to the ab initio internal energy (ΔU) and pressure (ΔP) are written as:

$$\Delta U(V) = \frac{\Delta P_0 V_{0c}}{\chi + 1} \left\{ 1 - exp\left[\frac{\chi + 1}{\chi} \left(1 - \left(\frac{V_{0c}}{V}\right)^{\chi}\right)\right] \right\},\tag{2.1}$$

$$\Delta P = \Delta P_0 \left(\frac{V_{0c}}{V}\right)^{\chi+1} exp\left[\frac{\chi+1}{\chi}\left(1 - \left(\frac{V_{0c}}{V}\right)^{\chi}\right)\right],\tag{2.2}$$

where V is the volume (of the simulation box containing 108 atoms) and ΔP_0 , V_{0c} and χ are constants. We note that ΔP_0 and V_{0c} are the maximum value of the pressure correction and the volume at which this maximum occurs. V_{0c} should not be confused with the reference volume V_0 in the EOS. V_{0c} is obtained from:

$$V_{0c} = V_r \left(1 - \frac{\Delta K_r}{\Delta P_r(\chi + 1)} \right)^{\frac{1}{\chi}},\tag{2.3}$$

where *r* denotes a reference state at volume V_r where the differences in pressure and isothermal bulk modulus between an experimental measurement and an ab initio calculation are ΔP_r and ΔK_r , respectively.

Thermodynamic model of metallic liquid

The thermodynamic model for a reference composition is constructed from the isothermal EOS and a single reference internal energy U_0 to obtain expressions for the pressure (*P*) and internal energy (*U*, of 108 atoms) as a function of volume (*V*, of 108 atoms) and temperature (*T*):

$$P(V,T) = P(V,T_0) + \int_{T_0}^T \left(\frac{\partial P}{\partial T}\right)_V dT = P(V,T_0) + \int_{T_0}^T \frac{\gamma C_V}{V} dT, \qquad (2.4)$$

$$U(V,T) = U_0 + \int_{S_0(V_0,T_0)}^{S(V,T)} T dS - \int_{V_0}^V P dV$$

= $U_0 + \int_{T_0}^T T \left(\frac{\partial S}{\partial T}\right)_V dT - \int_{V_0}^V \left(P - T \left(\frac{\partial S}{\partial V}\right)_T\right) dV$ (2.5)
= $U_0 + \int_{T_0}^T C_V dT - \int_{V_0}^V \left(P - T \frac{\gamma C_V}{V}\right) dV,$

where C_V is the heat capacity (of 108 atoms) at constant volume and γ is the Grüneisen parameter, both of which are naturally functions of volume and temperature. As illustrated in Figures 2.2 and 2.3, the functional dependence of these two parameters on V and T can be directly obtained from FPMD data, and we find that γ exhibits a linear relation with V and can be expressed to high accuracy with no dependence on T. We also find that C_V can be considered as a constant (Dulong-Petit law, Petit and Dulong (1819)), independent of both temperature and volume, over the P - T range of our simulations. Thus:

$$\gamma \equiv V \left(\frac{\partial P(V,T)}{\partial U(V,T)} \right)_V = a_\gamma V + b_\gamma, \qquad (2.6)$$

$$C_V \equiv \left(\frac{dU(V,T)}{dT}\right) = c_{C_V},\tag{2.7}$$



Figure 2.2: For pure iron liquid and each of the calculated reference binary alloy liquids, the top panels show the relationship between the product of pressure and volume (*PV*) and internal energy (*U*) as temperature changes at constant *V* (each value of V is indicated by color). Given the definition of Grüneisen parameter $\gamma = \left(\frac{V\partial P}{\partial U}\right)_V$, a linear relation in PV - U at constant *V* implies that γ is independent of temperature and given by the slope of the line, which is confirmed by the data. The bottom panels then show the relationship between $\gamma(V)$ and *V*. In the $\gamma - V$ relation, γ exhibits a linear relation with *V*. All the data for each composition can be well fit by a line (shown in black) radiating from the limiting value of 2/3 at V = 0, with one free parameter a_{γ} . The uncertainties in γ are derived from MC simulations for 100,000 steps; error bars are shown as 1σ .

where a_{γ} and c_{C_V} are parameters independent of *T* and *V*. Considering the Thomas-Fermi infinite pressure limit $\gamma(V \rightarrow 0) = 2/3$ (Stacey, 2000), we set b_{γ} to be 2/3 for all compositions. Meanwhile, our new FPMD data indicate that the isothermal pressure-volume EOS for all the compositions studied can be fit well by the thirdorder Birch-Murnaghan (third-order BM) form (Umemoto and Hirose, 2020), which therefore has been chosen as the form for the isothermal EOS. We note that the



Figure 2.3: For pure iron liquid and each of the calculated reference binary alloy liquids, the top panels show the relationship between U and temperature (T) at constant V (each value of V is indicated by color). The slope of this relationship is heat capacity $C_V = \left(\frac{\partial E}{\partial T}\right)_V$. The perfect linear relationships at each volumes show that C_V is independent of temperature. The bottom panels then show the relationship between $C_V(V)$ and V. Within uncertainty, each composition can be fit by a single constant value of C_V , indicated by the horizontal black lines. The uncertainties in C_V are derived from MC simulations for 100,000 steps and are shown as 1σ .

isothermal Vinet EOS (Ichikawa et al., 2014; Vinet et al., 1987) and the isothermal Murnaghan EOS (Murnaghan, 1951; Ricard et al., 2022) also fit well for pure iron data, with differences from the third-order Birch-Murnaghan EOS within 0.6 GPa (Fig. 2.4). Putting the third-order BM equation and equations (2.6-2.7) into equations (2.4-2.5), we obtain the closed-form expressions for P and U at any volume and temperature as:

$$P(V,T) = 3K_0 f (1+2f)^{\frac{5}{2}} \left(1 + \frac{3}{2}(K'_0 - 4)f\right) + C_V (a_\gamma + \frac{b_\gamma}{V})(T - T_0), \qquad (2.8)$$

$$U(V,T) = U_0 + C_V(T - T_0) + \frac{9V_0K_0}{2}f^2\{1 + f(K'_0 - 4)\} + C_VT_0\Big(a_\gamma(V - V_0) + b_\gamma ln(\frac{V}{V_0})\Big),$$
(2.9)

where *f* is the Eulerian finite strain:

$$f = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right], \tag{2.10}$$

and U_0 , T_0 , V_0 , K_0 , and K'_0 are the reference energy, temperature, volume, isothermal bulk modulus and isothermal pressure derivative of the isothermal bulk modulus. We set T_0 to be 4,000 K. The parameters a_γ , c_{C_V} , U_0 , V_0 , K_0 , and K'_0 can be derived by fitting the FPMD results in pressure and internal energy (after application of the correction from eq. 2.1-2.3).



Figure 2.4: Results of fitting pure iron data using different choices of isothermal EOS. (a) Vinet EOS (Ichikawa et al., 2014; Vinet et al., 1987) with fitting parameters $K_0 = 0.164$ GPa, V_0 (for 108 atoms) = 3.97×10^3 Å³, and $K'_0 = 10.7$ for reference temperature 4,000 K. Colored error bars represent the corrected ab initio molecular dynamics data, and the corresponding colored curves show the fitted thermodynamic model isotherms at the indicated temperatures. The uncertainties of the ab initio data are reported as 1σ . All fitted isotherms fall entirely within the 1σ uncertainty range of the ab initio data. (b) Murnaghan EOS (Murnaghan, 1951; Ricard et al., 2022) with fitting parameters $K_0 = 55.6$ GPa, V_0 (for 108 atoms) = 1.72×10^3 Å³, n = 3.77 for reference temperature 4,000 K. (c) Comparison of the Vinet EOS, Murnaghan EOS, and third-order Birch-Murnaghan (BM) EOS at T = 4000 K.

With these expressions for pressure and internal energy, any thermodynamic property of the system can be derived as a function of V and T. For instance, by taking the partial derivative of pressure with respect to V at constant T, we obtain the isothermal bulk modulus (K_T) :

$$K_T(V,T) = -V\left(\frac{dP}{dV}\right)_T$$

= $\frac{K_0}{2}(1+2f)^{\frac{5}{2}}(2+(6K'_0-10)f+27(K'_0-4)f^2) + \frac{C_V b_{\gamma}}{V}(T-T_0).$
(2.11)

Then, the adiabatic bulk modulus can be obtained via:

$$K_S(V,T) = (1 + \alpha \gamma T) K_T$$

= $K_T(V,T) + \frac{C_V T}{V} (a_\gamma V + b_\gamma)^2.$ (2.12)

where α is the isobaric coefficient thermal expansivity, given by $\alpha = \frac{1}{V} (\partial V / \partial T)_P = \frac{C_V \gamma}{K_T V}$. Finally, the seismic parameter (Φ) and velocity (V_P) of compressional waves in the liquid are given by:

$$\Phi(V,T) = \frac{K_S(V,T)}{\rho},\tag{2.13}$$

$$V_P(V,T) = \sqrt{\Phi(V,T)}, \qquad (2.14)$$

where ρ denotes the density, which can be written as:

$$\rho = \frac{m}{V} \tag{2.15}$$

and *m* is the mass of 108 atoms of the selected composition.

Meanwhile, given the state of an unshocked system $(U_{us}, P_{us}, V_{us}, \text{ and } T_{us})$, the series of states along the Hugoniot curve can be derived by solving for the temperature T_h following the Rankine-Hugoniot relations:

$$U_h(V_h, T_h) - U_{us} = -\frac{1}{2}(P_h(V_h, T_h) + P_{us})(V_h - V_{us}), \qquad (2.16)$$

where V_h , U_h , and P_h are the volume per atom, internal energy per atom, and pressure along the Hugoniot curve.

Mixing model of metallic liquid

The mixing model is constructed to estimate the thermodynamic parameters for multicomponent metal compositions on the basis of the constructed thermodynamic models for a set of reference compositions including pure iron and several binary mixtures. Computed ternary mixtures are not used to construct the model but are available to test its power for interpolation into multicomponent space. Previous studies assumed ideal mixing of volume at equal pressure and temperature (i.e., $V(P,T) = \sum n_i V_i(P,T)$, where n_i is the mole fraction of each end member) among a set of computed liquid compositions (Badro et al., 2014; Umemoto and Hirose, 2020). Here, inspired by Henry's law, we propose (and calibrate, and demonstrate the superior accuracy of) a different thermodynamically self-consistent non-ideal mixing model for pressure and internal energy (of 108 atoms) at equal volume (of 108 atoms) and temperature which is expressed as:

$$P(\mathbf{n}, V, T) = \sum_{i} n_i \Gamma_i P_i(V, T), \qquad (2.17)$$

$$U(\mathbf{n}, V, T) - U(\mathbf{n}, V_0, T_0) = \sum_i n_i \Gamma_i (U_i(V, T) - U_i(V_0, T_0)), \qquad (2.18)$$

where *i* indexes the series of elements considered (including Fe, Ni, O, H, S, Si, and C), n_i is its mole fraction, Γ_i is the activity coefficient, and P_i and U_i are the pressure and internal energy of the pure endmember (i.e., a virtual metal liquid containing only element *i* with $n_i = 1$). Plugging equations 2.17 and 2.18 into the definitions of C_V , γ , and K_T , we obtain the mixing model of these thermodynamic parameters:

$$C_V(\mathbf{n}, V, T) = \left(\frac{dU(\mathbf{n}, V, T)}{dT}\right)_V = \sum_i n_i \Gamma_i C_V^i(V, T), \qquad (2.19)$$

$$\gamma(\mathbf{n}, V, T) = V \left(\frac{\partial P(\mathbf{n}, V, T)}{\partial U(\mathbf{n}, V, T)} \right)_{V} = \frac{\sum_{i} n_{i} \Gamma_{i} C_{V}^{i}(V, T) \gamma_{i}(V, T)}{\sum_{i} n_{i} \Gamma_{i} C_{V}^{i}(V, T)},$$
(2.20)

$$K_T(\mathbf{n}, V, T) = -V \left(\frac{dP(\mathbf{n}, V, T)}{dV}\right)_T = \sum_i n_i \Gamma_i K_T^i(V, T), \qquad (2.21)$$

where C_V^i , γ_i , and K_T^i are the heat capacity at constant volume, Grüneisen parameter, and isothermal bulk modulus of the pure endmember of element *i*. Once these three thermodynamic parameters are obtained, the velocity for any composition **n** can be derived through equations (2.12-2.14). Furthermore, we assume that the activity coefficients Γ_i are expressed as:

$$\Gamma_{i}(n_{i}) = d_{\Gamma}^{i} + (1 - d_{\Gamma}^{i})n_{i}, \qquad (2.22)$$

where d_{Γ}^{i} is a constant independent of concentration, temperature, and volume. We note that the solution is ideal with respect to volume and temperature in the case of $d_{\Gamma}^{i} = 1$, and that this form approaches Raoultian ideality for all components $(\Gamma_{i}(1) = 1)$. The d_{Γ}^{i} are obtained by regressing the ab initio pressure data of pure iron liquid and binaries with various compositions at equal volume and temperature. Once d_{Γ}^{i} is determined, the thermodynamic parameters (i.e. $P_{i}, C_{V}^{i}, \gamma_{i}$, and K_{T}^{i}) of the virtual pure endmember i can be obtained at any volume and temperature from the thermodynamic model of the reference binaries. Subsequently, these parameters for the pure endmember can be employed to compute desired properties for any multicomponent metal composition.

2.3 Calibrating the pressure and energy correction to ab initio results for pure iron liquid

As explained above, we adopt the correction scheme proposed by French and Mattsson (2014) to correct ab initio results due to its thermodynamically valid behavior in the limits of high and low densities. Within this scheme, three parameters (ΔP_0 , V_{0c} , and χ) need to be determined, requiring at least two reference states for their derivation. These reference states can be any condition for which there exists experimental data on pressure and/or bulk modulus.

In this work, we select the ambient pressure melting point of iron as the first reference point, following Wagle and Steinle-Neumann (2019). At $T_r = 1805$ K (Cezairliyan and McClure, 1974) and $\rho_r = 7.04$ Mg/m³ (Assael et al., 2006), the pressure is 10^{-5} GPa and $K_T = 88$ GPa (Wagle and Steinle-Neumann, 2018; Wagle and Steinle-Neumann, 2019; Williams, 2009). By contrast, at this temperature and volume, the uncorrected *ab initio* simulation results in P = -20.9 GPa and $K_T = 64.0$ GPa, giving $\Delta P_r = 20.9$ GPa and $\Delta K_r = 24.0$ GPa in Eq. (2.3). We note that other experiments suggest $K_T = 70$ GPa (i.e., $\Delta K_r = 6.0$ GPa) at the ambient-pressure melting point of pure iron liquid (Assael et al., 2006).

We still require a second reference state to determine the correction parameters. Previous work used shock wave data for pressure correction (Badro et al., 2014; Umemoto and Hirose, 2020). However, the temperature of the shock wave experiments on iron is not directly measured (because Fe is opaque and its temperature can only be observed at an interface) but rather deduced from a thermodynamic model. Another natural approach is to use the critical point in the iron system (Wagle and Steinle-Neumann, 2019) as the second reference point, but there is a large uncertainty in the pressure, density, and temperature of the critical point of iron and it is far from the conditions of the Earth's core. Therefore, here we adopt results from a recent DAC study of the EOS of iron liquid spanning P = 21 - 116 GPa and T = 2600 - 4350 K (Kuwayama et al., 2020). We carried out FPMD simulations at the same set of densities and temperatures as the DAC experiments, and the results are shown in Table A.1. By minimizing the mismatch between the DAC



Figure 2.5: Correction for pressure as a function of density or volume (per 108 atoms) using the formalism of (French and Mattsson, 2014). The black filled square is the pressure offset of the original ab initio data with respect to ambient pressure. The gray open diamonds are the pressure offset between the ab initio calculation and DAC experiments (Kuwayama et al., 2020), with the error bar reporting the fitting mismatch between the DAC pressure measurement and the EOS from Kuwayama et al. (2020). The choice of K_T at ambient condition significantly affects the correction parameter χ . The red solid curve represents the correction we adopted, based on $K_T = 88$ GPa (implying $\Delta K_r = 24.0$ GPa compared to ab initio calculation) with $\chi = 2.7$. The blue dashed curve shows an alternative case for $K_T = 70$ GPa ($\Delta K_r = 6.0$ GPa) with $\chi = 1$, which does not retrieve the mismatch between DAC and ab initio data as effectively as the red curve.

and ab-initio data using a least squares metric, we obtained $\chi = 2.7$, $\Delta P_0 = 22.9$ GPa, and $V_{0c} = 1231.0$ Å³ for the case where $\Delta K_r = 24.0$ GPa (red solid line in Fig. 2.5), and $\chi = 1.0$, $\Delta P_0 = 21.4$ GPa, and $V_{0c} = 1210.3$ Å³ for the case of $\Delta K_r = 6.0$ GPa (blue dashed line in Fig. 2.5). However, the latter case yields a much higher mismatch between the DAC data and the ab initio data. Hence, we will use $\chi = 2.7$, $\Delta P_0 = 22.9$ GPa, and $V_{0c} = 1231.0$ Å³ as our correction parameters for pure Fe. In fact, we will see below that this set of parameters appears sufficiently general to match available experimental data on all multicomponent compositions in our composition range, while using the other set of parameters leads to significant deviations from the experimental data for pure iron (Fig. 2.6).



Figure 2.6: The corrected ab initio results using the parameter set $\Delta K_r = 6.0$ GPa, $\chi = 1.0, \Delta P_0 = 21.4$ GPa, and $V_{0c} = 1210.3$ Å⁻³. The fitted thermodynamic parameters are $V_0 = 1590 \text{ Å}^3$, $K_0 = 72.4 \text{ GPa}$, $K'_0 = 4.73$, $C_V = 7.28 \times 10^{-21} \text{ J/K}$, $a_{\gamma} = 8.05 \times 10^{-4} \text{ Å}^3$, $b_{\gamma} = 2/3$. (a) The corrected pressure for pure iron liquid under the Earth's outer core. Colored error bars show the corrected ab initio molecular dynamics data and matching colored curves show the fitted thermodynamic model isotherms at the temperatures indicated. The two black open circles with error bars are EOS experimental data near the outer core conditions (Kuwayama et al., 2020) at $P = 106.3 \pm 3.5$ GPa, $\rho = 10.01 \pm 0.11$ Mg m⁻³, $T = 4250 \pm 425$ K and $P = 116.1 \pm 3.9$ GPa, $\rho = 10.10 \pm 0.14$ Mg m⁻³, $T = 4350 \pm 435$ K. The black dashed line is the 4,000 K isotherm extrapolated from DAC data (Kuwayama et al., 2020). The extrapolated pressures from DAC experimental measurements at low P-T conditions are notably smaller than the corrected ab initio results at equal volume. Comparison of the theoretical Hugoniot for liquid iron with experimental shock data in (b) pressure vs. density and (c) sound velocity vs. density. The Hugoniot curve (red, with 1σ uncertainty indicated by light red bands) is computed from our new ab initio thermodynamic model with Eq. (2.16), with the unshocked condition: $P_{us} = 0$ GPa, $V_{us} = 1276$ Å³ (per 108 atoms, corresponding to density of 7.85 Mg m⁻³) and $U_{us} = -870$ eV (per 108 atoms). In (b) the blue circles with 1σ error bars are propagated from shock compression measurements (Al'tshuler et al., 1958; Al'tshuler et al., 1981; Brown et al., 2000; Marsh and Los Alamos Scientific Laboratory, 1980) of particle velocity and shock velocity.). In (c) the blue circles with 1σ error bars are recalculated from rarefaction overtake measurements (Brown and McQueen, 1986; Nguyen and Holmes, 2004) using our new pressuredensity relation. The thermodynamic model underestimates the velocity by 0.3 km/s compared to the shock experiments. This exercise reinforces the choice of correction parameter set $\chi = 2.7$, $\Delta P_0 = 22.9$ GPa, and $V_{0c} = 1231.0$ Å³

2.4 Thermodynamic model for pure iron liquid

With the calibrated pressure and energy correction function and our new FPMD data for pure iron liquid spanning the range of outer core conditions, we can now construct a new thermodynamic model for pure iron liquid and validate it against

available static and dynamic compression experiments.

The original and corrected ab initio results for pure iron at plausible conditions spanning the whole outer core are listed in Table A.2. We fit the full set of corrected ab initio U(V,T) and P(V,T) points with an unweighted least squares metric to obtain the thermodynamic parameters a_{γ} , C_V , V_0 , K_0 , and K'_0 (Table 2.1). Figures 2.7a and 2.7b illustrate the result, showing that the model agrees with every computed ab initio point to better than the 1σ uncertainty of the ab initio data. The small fitting errors suggest that the thermodynamic model described in the section 2.2 is an appropriate description of the properties of Fe liquid across the P - T range of the Earth's outer core.

Compositi	ion	Thermodynamic parameters (each 108 atoms)					Activity coefficient	
Element	Reference	V_0	K_0	$K' C_V$	C_V	Grüneisen param	eter	dr
		(10^3 Å^3)	(GPa)	m ₀	$(10^{-21} J/K)$	$a_{\gamma} (10^{-4} \text{ \AA}^{-3})$	b_{γ}	u
Fe	Fe ₁₀₈	2.69	1.20	18.7	7.28	8.05	2/3	0.382
0	Fe ₇₆ O ₃₂	2.57	0.41	37.4	5.83	9.32	2/3	1
Si	Fe90Si18	2.98	0.73	20.6	6.96	8.05	2/3	1
S	Fe90S18	3.17	0.26	40.9	6.85	9.60	2/3	1
С	Fe90C18	2.40	0.59	39.4	6.50	9.56	2/3	1
Ni	Fe90Ni18	2.85	0.48	33.8	7.13	8.11	2/3	1
Н	Fe ₇₆ H ₃₂	1.10	110	4.50	6.03	9.19	2/3	-2.42

Table 2.1: Thermodynamic Model Parameters of Metallic Liquid

Now, we compare our newly derived thermodynamic model with DAC (Kuwayama et al., 2020) and shock compression (Al'tshuler et al., 1981; Al'tshuler et al., 1958; Brown et al., 2000; Brown and McQueen, 1986; Nguyen and Holmes, 2004; Marsh and Los Alamos Scientific Laboratory, 1980) experiments. While the original FPMD data significantly underestimate pressure compared with DAC measurements near CMB conditions (by 22 GPa at $\rho = 10.01 \pm 0.11$ Mg/m³ and $T = 4250 \pm 425$ K, and by 27 GPa at $\rho = 10.10 \pm 0.14 \text{ Mg/m}^3$ and $T = 4350 \pm 435 \text{ K}$; Figs. 2.5 and 2.8a), our corrected data reduces these disparities to 4 and 9 GPa, respectively. Similarly, when extrapolating the EOS constructed from low P-T DAC data (Kuwayama et al., 2020) to 4,000 K and outer core pressure conditions (black dashed line in Fig. 2.7a), the extrapolated pressures are ~ 5 GPa higher than the ab initio data at equal volume. Although this discrepancy exceeds the pressure uncertainty of the FPMD data (~ 3 GPa), it falls within the pressure uncertainty of the DAC results at the given temperature and density (7.0 GPa, estimated as $\sqrt{\sigma_P^2 + \sigma_T^2 * \left(\frac{\partial P}{\partial T}\right)_o^2 + \sigma_\rho^2 * \left(\frac{\partial P}{\partial \rho}\right)_T^2}$ where σ is the uncertainty on each type of measurement). Consequently, our new EOS constructed from ab initio data and a consistent pressure correction scheme recovers the EOS constraints for pure Fe liquid from DAC experiments, within their



Figure 2.7: The corrected (a) Pressure and (b) Internal energy for pure iron liquid under the Earth's outer core conditions. Corrections are made using parameter set $\chi = 2.7$, $\Delta P_0 = 22.9$ GPa, and $V_{0c} = 1231.0$ Å³. Colored error bars show the corrected ab initio molecular dynamics data and matching colored curves show the fitted thermodynamic model isotherms at the temperatures indicated. The two black open circles with error bars in (a) are EOS experimental data near the outer core conditions (Kuwayama et al., 2020) at $P = 106.3 \pm 3.5$ GPa, $\rho = 10.01 \pm 0.11$ Mg m⁻³, $T = 4250 \pm 425$ K and $P = 116.1 \pm 3.9$ GPa, $\rho = 10.10 \pm 0.14$ Mg m⁻³, $T = 4350 \pm 435$ K. The black dashed line is the 4,000 K isotherm extrapolated from DAC data (Kuwayama et al., 2020). The uncertainties of both ab initio and experimental data are reported as 1σ .

stated uncertainties.

Meanwhile, we calculate the shock Hugoniot using the Rankine-Hugoniot relations (eq. 2.16) and our new corrected ab initio thermodynamic model for pure iron in the liquid region. The results are shown in Fig. 2.9. In shock experiments, by measuring sound velocity, Brown and McQueen (1986) suggested that pure iron begins to melt, transitioning from a solid state (γ -iron) to partial melting at 243 GPa, and becomes fully molten at 260 GPa. However, γ -iron has subsequently been shown to be unstable at these conditions. Through more refined measurements near the melting point, Nguyen and Holmes (2004) indicated that melting starts at 225 GPa (from ϵ -iron) and is complete at 260 GPa. Although some early shock compression data near 260 GPa (as indicated by a vertical black dotted line on Figures 2.9a and 2.9b) show values higher than those predicted by our new thermodynamic model, the new



Figure 2.8: Same as Figure 2.7 for the uncorrected (a) pressure and (b) internal energy. The discrepancy with the DAC data in part (a) is evident.

theoretical Hugoniot agrees well with recent shock compression measurements of $P - \rho$ relations and $\rho - V_P$ relations in the liquid region at higher P and ρ .

In this work, we suggest that the discrepancy between the $P - \rho - T$ relations extrapolated using DAC experiment at lower P - T than the Earth's outer core conditions and those extrapolated from shock compression experiments using previous parameterized thermodynamic models (W. W. Anderson and Ahrens, 1994; Brown and McQueen, 1986; Yoo et al., 1993) are not in fact the result of errors in either source for equation of state data. Rather, they stem from inaccuracy in the models used to estimate unmeasured properties (e.g., T in shock experiments), to infer the location of phase transitions (Brown and McQueen, 1986; Nguyen and Holmes, 2004), or to correct the data to common conditions. Within the partial melting region (225–260 GPa), the temperature along the equilibrium Hugoniot curve coincides with the melting curve. However, due to the lack of knowledge regarding the entropy change associated with the phase transition, the precise temperature variation in this region cannot be calculated until complete melting occurs. Our new theoretical model suggests a temperature of 5280 K at the complete melting point, where the melting curve meets the liquid segment of the principal Hugoniot (Fig. 2.9c). This new theoretical estimate aligns well with the iron melting point of 5000 ± 250 K at 257 ± 13 GPa directly measured under static compression by DAC experiment (Sinmyo et al., 2019), though previous extrapolated results based on DAC measurements at lower pressures (< ~200 GPa) have suggested either higher or lower melting temperatures (Anzellini et al., 2013; Boehler, 1993). Overall, our new ab initio thermodynamic



Figure 2.9: Comparison of the theoretical Hugoniot for liquid iron based on the new ab initio thermodynamic model with experimental shock data for pure Fe in (a) pressure vs. density, (b) sound velocity vs. density, and (c) temperature vs. density. The Hugoinot curves are calculated same as Figs. 2.6b and 2.6c with $U_{us} = -850$ eV (per 108 atoms). On the Hugoniot curve, pure iron is fully molten at and above P = 260 GPa and $\rho = 12.5$ Mg m⁻³. In (a) the blue dashed line is the experimental Hugoniot fit from W. W. Anderson and Ahrens (1994). In (b) the blue circles with 1σ error bars are recalculated from rarefaction overtake measurements (Brown and McQueen, 1986; Nguyen and Holmes, 2004) using our new pressure-density relation. In (c) the green dash-dotted line is the original theoretical Hugoniot curve of (Brown and McQueen, 1986) constructed for the solid state, which lacked data constraints on the heat capacity. The gray points and corresponding dashed line are direct measurements of the melting point of pure iron at different pressures in the DAC (Sinmyo et al., 2019), while the purple Anzellini et al., 2013 and blue (Boehler, 1993) dashed lines are previous extrapolated results from low pressures. The Hugoniot temperatures should plot on the melting curve of pure iron from 225 – 260 GPa (Nguyen and Holmes, 2004), where partial melting is observed in shock experiments. Our new theoretical Hugoniot in the liquid state predicts shock temperature 5280 K at 260 GPa (compared to 6100 K from Brown and McQueen (1986) that ignored the change of entropy for solid-liquid transition), consistent with the DAC melting point (5000 \pm 250 K at 257 \pm 13 GPa). In comparison, Brown and McQueen (1986) predicted a temperature of 5700 K at the onset of melting (green point, 243 GPa), which is significantly higher than the DAC melting point $(4660 \pm 230 \text{ K} \text{ at } 244 \pm 12 \text{ GPa})$. Even considering subsequent study Nguyen and Holmes (2004) that revised the onset of melting pressure to 225 GPa, the predicted temperature (5100 K) remains notably higher than the DAC melting point (4440 \pm 220 K at 216 ± 11 GPa).

model of pure iron liquid is consistent with both DAC experiments at low pressures and shock compression experiments at high pressures along the Hugoniot.

2.5 Thermodynamic model for multicomponent metal compositions

We then aim to establish a thermodynamic model for multicomponent metal compositions spanning all reasonable candidate compositions for the Earth's outer core. This model will consider the individual or combined influences of Ni, Si, O, C, S, and H on iron-rich liquids. To achieve this, we conducted 108 atom FPMD simulations on selected binary and ternary compositions. After applying the same pressure and energy correction (as a function of volume) calibrated for pure Fe liquid, we assess the accuracy of the model compared to experiments. Due to the near absence of DAC data on the EOS of multicomponent metal liquids at high P - T, we validate the model against shock compression experiments.

Although ab initio molecular dynamics theoretically enables the determination of thermodynamic properties for any composition, the associated computational costs make direct computation of numerous arbitrary multicomponent compositions infeasible. To obtain a dataset that enables practical searching over the range of plausible outer core compositions, we computed ab initio properties at specific binary compositions as reference points, followed by the construction of a mixing model to infer the thermodynamic properties of arbitrary plausible compositions spanned by the computed components. We used a selected set of additional binary and ternary compositions to verify that our interpolation rules are valid.

First, we derive the thermodynamic model of reference binaries. The reference binary compositions selected for this study are $Fe_{76}O_{32}$, $Fe_{90}Si_{18}$, $Fe_{90}S_{18}$, $Fe_{90}C_{18}$, $Fe_{90}Ni_{18}$, and $Fe_{76}H_{32}$. These compositions are close to the general geophysical estimates of the concentrations needed to describe the Earth's core if it contains only one light element, and to a cosmochemically reasonable Ni fraction. We conducted ab initio simulations on these reference binaries across a range of temperature and volume entirely spanning the Earth's outer core, and we apply the pressure and energy correction (as a function of volume per 108 atoms) calibrated on pure Fe liquid to these binary results (and additional ab initio results later in this section). The corrected ab initio data are reported in Table A.2 and the parameters and uncertainties of fitting each composition to our EOS formalism are listed in Table 2.1 and illustrated in Fig. 2.10 and Fig. 2.11. The fitting errors of the EOS for all state points along all reference binaries fall almost entirely within the 1 σ uncertainty of the ab initio data.

Next, we refine the value of the activity parameters d_{Γ}^{Fe} , d_{Γ}^{Si} and d_{Γ}^{O} , for the non-ideal mixing model (detailed in the section 2.2) by adding to the above results the corrected



Figure 2.10: The corrected pressure for binaries of (a) Fe₇₆O₃₂, (b) Fe₉₀Si₁₈, (c) Fe₉₀S₁₈, (d) Fe₉₀C₁₈, (e) Fe₉₀Ni₁₈, and (f) Fe₇₆H₃₂ under the Earth's outer core conditions, given as the difference from the pressure in pure Fe at 4,000 K and equal density $(P_{Binary}(T, \rho) - P_{Fe}(4000 \text{ K}, \rho))$. Colored points with 1 σ error bars show the corrected ab initio data and colored curves show the isotherms of the fitted thermodynamic model. The change of $P_{Binary}(T, \rho) - P_{Fe}(4000 \text{ K}, \rho)$ with temperature at constant density reflects the thermal pressure for each binary. Since the presence of light elements (O, Si, S, C, and H) in metal alloys results in a higher bulk modulus than pure iron at outer core P - T conditions, the pressure difference relative to pure iron increases with density as $\Delta K_T = \rho \frac{\partial \Delta P}{\partial \rho}$.

ab initio pressure and internal energy data (Table A.3) for the additional compositions $Fe_{90}O_{18}$ (47 state points), $Fe_{99}Si_9$ (24 points), $Fe_{90}O_6Si_{12}$ (37 points), $Fe_{90}O_9Si_9$ (37 points), and $Fe_{90}O_{12}Si_6$ (37 points) at various volumes and temperatures. Given the exceptionally close agreement of ab initio pressures and internal energies for ternary compositions $Fe_{90}Si_xO_{18-x}$ with prediction of ideal mixing between $Fe_{90}O_{18}$ and $Fe_{90}Si_{18}$ (Figs. 2.12 and 2.13), the parameters d_{Γ}^{Si} and d_{Γ}^{O} are set to be 1. This amounts to ideal mixing of pressures between Si and O at the same molar Fe concentration and volume. Then, based on the thermodynamic model of the reference binaries $Fe_{76}O_{32}$ and $Fe_{90}Si_{18}$, we fit the ab initio pressure for both $Fe_{90}O_{18}$ and $Fe_{99}Si_9$ by least squares and obtain $d_{\Gamma}^{Fe} = 0.382$ (Table 2.1). This single parameter allows us to fit both the Fe-O and Fe-Si binaries and all examined ternary compositions in the Fe-Si-O system within the range spanned by Fe_{108} , $Fe_{90}Si_{18}$, and $Fe_{76}O_{32}$. (i.e. 0 - 9.1 wt% Si and 0 - 10.8 wt% O).

Finally, we refine the values d_{Γ}^{H} , d_{Γ}^{C} , d_{Γ}^{S} , and d_{Γ}^{Ni} . For the element H, additional


Figure 2.11: The corrected internal energy (of 108 atoms) for binaries of (a) $Fe_{76}O_{32}$, (b) $Fe_{90}Si_{18}$, (c) $Fe_{90}S_{18}$, (d) $Fe_{90}C_{18}$, (e) $Fe_{90}Ni_{18}$, and (f) $Fe_{76}H_{32}$ under the Earth's outer core conditions. Colored points with 1σ error bars show the corrected ab initio data and colored curves show the isotherms of the fitted thermodynamic model.

ab initio calculations were performed on Fe₉₉H₉, Fe₉₀H₁₈, Fe₈₁H₂₇, Fe₇₂H₃₆ and Fe₆₃H₄₅, at volume 753.571 Å³ and temperature 4,000 K (Table A.3). Keeping the activity parameter d_{Γ}^{Fe} obtained above in the second step fixed, we fit all Fe_xH_{108-x} results by least squares and obtained $d_{\Gamma}^{H} = -2.42$ (Table 2.1, Fig. 2.14). For the latter three elements, ab initio calculations on Fe₉₉S₉ and Fe₉₉Ni₉ at volume 912.673 Å³ and temperature 4,000 K, and on Fe₉₉C₉ at volume 857.375 Å³ and temperature 4,000 K (Table A.3) could be fit within the 1 σ uncertainty of the ab initio quantities with the ideal model $d_{\Gamma}^{i} = 1$ (for i = C, S or Ni). Therefore, we set d_{Γ}^{C} , d_{Γ}^{S} and d_{Γ}^{Ni} to be 1 (Table 2.1).

Here, we compare our new non-ideal mixing model with two previously published ideal mixing models: (1) ideal mixing of volume among the reference compositions (including pure iron calculated in the last section and reference binaries in this section) at equal temperature and volume ("Vegard's law", hereafter named 'ideal mixing model I'), as adopted by Badro et al. (2014) and Umemoto and Hirose (2020); and (2) ideal mixing of pressure at equal temperature and pressure ("Amagat's law", hereafter named 'ideal mixing model II'). To validate the accuracy of these thermodynamic models in predicting the pressures of multicomponent metallic liquids, we conducted single ab initio simulations on 19 additional compositions: $Fe_{90}O_6C_{12}$, $Fe_{90}O_9C_9$, $Fe_{90}O_{12}C_6$, $Fe_{90}Si_6C_{12}$, $Fe_{90}Si_9C_9$, $Fe_{90}Si_{12}C_6$, $Fe_{90}S_6C_{12}$, $Fe_{90}S_9C_9$,



Figure 2.12: The pressures for $Fe_{90}Si_{18}$, $Fe_{90}O_6Si_{12}$, $Fe_{90}O_9Si_9$, $Fe_{90}O_{12}Si_6$, and $Fe_{90}O_{18}$ at different temperatures and volumes. The red points with error bars are calculation results from ab initio simulations. The blue lines are calculated assuming ideal mixing of pressure at equal volume and temperature between the reference compositions $Fe_{90}Si_{18}$ and $Fe_{90}O_{18}$. Along this particular compositional join, no deviation from ideal mixing can be resolved at any pressure. All error bars are plotted as 1σ .

Fe₉₀S₁₂C₆, Fe₉₀O₆S₁₂, Fe₉₀O₉S₉, Fe₉₀O₁₂S₆, Fe₉₀Si₆S₁₂, Fe₉₀Si₉S₉, Fe₉₀Si₁₂S₆, Fe₁₀₀O₄Si₄, Fe₇₈O₂₄Si₆, Fe₈₀O₁₆Si₄S₄C₄, and Fe₈₀O₅Si₄S₅C₄ (Table A.3). All the ab initio results in Table A.3–total of 210 state points–are compared with predictions generated by the three mixing models. Our new non-ideal model effectively decreases the misfit, expressed as reduced χ^2 using the uncertainties of the ab initio data, to 0.2, compared to 0.7 and 2.9 for ideal mixing models I and II, respectively. The most notable failures of the ideal mixing models are for H-bearing compositions; the two ideal mixing models yield misfits of 7.5 and 17.0 times the ab initio uncertainty, respectively, for Fe₆₃H₄₅. Such significant deviations indicate that neither



Figure 2.13: The internal energies for $Fe_{90}Si_{18}$, $Fe_{90}O_6Si_{12}$, $Fe_{90}O_9Si_9$, $Fe_{90}O_{12}Si_6$, and $Fe_{90}O_{18}$ at different temperatures and volumes compared to the ideal mixing model as in Figure S8. Along this particular compositional join, no deviation from ideal mixing can be resolved at any pressure. All error bars are plotted as 1σ .

ideal mixing model is suitable for systems containing hydrogen in concentrations necessary for H to be a major light element in the core. In contrast, our new mixing model reduce this misfit to 0.7 times the ab initio uncertainty (Figure 2.14). For all 210 ab initio data, the new model maintains the misfit within a maximum of 1.2 times the ab initio uncertainty, illustrating the appropriateness of our new mixing model for the set of elements considered across the full P - T range of the Earth's outer core.

Our final validation step for the complete derived multicomponent EOS model—including the functional form of the EOS, the assumption that the pressure shift estimated for Fe applies to all our compositions, and the form of our non-ideal mixing model—is to compare predictions of this model to available shock compression experiments



Figure 2.14: The comparison of different mixing models for Fe_xH_{108-x} . The blue points with 1 σ error bars are ab initio pressures for several binary compositions at volume of 753.571 Å³ and temperature 4,000 K. Each mixing model is fixed at the reference compositions Fe_{108} and $Fe_{76}H_{32}$, marked by open grey triangles. The red line is calculated using our new non-ideal mixing model with activity parameters $d_{\Gamma}^{H} = -2.42$ and $d_{\Gamma}^{Fe} = 0.382$. The yellow dotted line is based on ideal mixing model I, linear mixing of volume at equal temperature and pressure as in Badro et al. (2014) and Umemoto and Hirose (2020). The purple dashed line is based on ideal mixing model II, linear mixing of pressure at equal temperature and volume.

on multicomponent Fe-rich liquids. Shock velocity data are available only for Fe_{87.6}S_{20.4} (equivalent to Fe_{88.2}S_{11.8} in wt%) from Huang et al. (2018), Fe_{91.3}O_{7.6}S_{9.1} (Fe_{92.5}O_{2.2}S_{5.3} in wt%) from Huang et al. (2011) and Fe_{79.9}Si_{19.6}Ni_{8.5} (Fe₈₁Si₁₀Ni₉ in wt%) from Zhang et al. (2016). The calculated theoretical Hugoniots agree to better than 1σ (reported experimental uncertainties) with all the shock compression measurements in both $\rho - P$ and $\rho - V_P$ terms (Fig. 2.15). The consistency between the measurements and the theoretical Hugoniot for Fe_{87.6}S_{20.4}, which is close to the reference binary composition Fe₉₀S₁₈, underscores the reliability of applying the pressure and internal energy correction calibrated on pure Fe liquid to all metal

compositions. The consistency for the other two compositions further demonstrates the effectiveness of our new non-ideal mixing model for multicomponent metal compositions in Fe-O-S-Si-Ni.



Figure 2.15: Validation of the new ab initio thermodynamic model for multicomponent metallic liquids against available shock wave data. The red curves (with 1σ uncertainty shown by pink bands) show the calculated theoretical Hugoniot in (a-c) the Hugoniot pressure (d-f) the Hugoniot sound velocity. (a,d) The Hugoniot for Fe_{87.6}S_{20.4} (equivalent to Fe_{88.2}S_{11.8} in wt%). Blue squares with 1σ error bars are from Huang et al. (2018). The Hugoniot curve is calculated from the unshocked condition $P_{us} = 0$ GPa, $V_{us} = 1.417 \times 10^3$ Å³ per 108 atoms ($\rho_{us} = 6.5$ Mg/m³) and $U_{us} = -773$ eV (per 108 atoms). (b,e) The Hugoniot for Fe_{91.3}O_{7.6}S_{9.1} (Fe_{92.5}O_{2.2}S_{5.3} in wt%). The blue circles with 1σ error bars are from Huang et al. (2011). The unshocked state is assumed to be $P_{us} = 0$ GPa, $V_{us} = 1.346 \times 10^3$ Å³ per 108 atoms ($\rho_{us} = 6.5$ Mg/m³) and $U_{us} = -758$ eV (per 108 atoms). (c,f) The Hugoniot for Fe_{79.9}Si_{19.6}Ni_{8.5} (Fe₈₁Si₁₀Ni₉ in wt%). Blue triangles with 1σ error bars are from Zhang et al. (2016). Calculation assumes $P_{us} = 0$ GPa, $V_{us} = 1.335 \times 10^3$ Å³ per 108 atoms ($\rho_{us} = 6.85$ Mg/m³) and $U_{us} = -829$ eV (per 108 atoms).

2.6 Conclusion and future perspectives

In this chapter, we carried out ab initio molecular dynamics calculations of a large set of simplified liquid compositions that includes Fe, Ni, and most of the proposed light elements (Si, S, C, O, H). We adopted a self-consistent form of the pressure and energy correction that reconciles static and shock data on the EOS of Fe liquid and show that this correction appears to apply equally well to multicomponent liquids, at least in the Fe-S-O and Fe-Ni-Si systems where shock compression data are available for validation. We examined the nature of compositional mixing in the metallic liquid system under core conditions and showed that Fe and H require nonzero activity coefficients. We developed a thermodynamic model based on our new data, which is well-aligned with existing shock wave experimental results. However, we note that there are presently no applicable experimental EOS data on Fe-H liquids at high P - T (the lack of a stable Fe-hydride at ambient conditions, the reactivity of H₂ gas, and the low X-ray scattering power of H combine to make such experiments very challenging (Tagawa et al., 2022)) so validation of our new thermodynamic model for H-bearing systems awaits the results of future experiments.

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Chapter 3

CONSTRAINING THE COMPOSITIONAL AND THERMAL STATE OF THE EARTH'S OUTER CORE USING NEW THERMODYNAMIC MODEL FOR MULTI-COMPONENT METAL LIQUIDS

3.1 Introduction

The sound velocity and density of any selected composition in the Fe-Ni-S-C-Si-O-H system at given temperature and pressure can be obtained from the thermodynamic model we have built from our ab initio results in Chapter 2. Meanwhile, seismic observations have been translated into models of the best-fitting radial distributions (that is, 1-D spherically symmetric models) of seismic velocity and density at each depth within the Earth's interior. Once the relationship of P and T with radius is established, we can compare the seismic velocity and density obtained from the thermodynamic model with a radial seismic model to determine whether a certain composition is consistent with the seismic observations of the Earth, at least for a liquid layer where the shear velocity is zero. As such, we have the ingredients to constrain the thermal and compositional state of the Earth's outer core, including the contents of Fe, Ni, S, C, Si, O, and H and the temperature, pressure, and mass distributions as functions of radius.

This exercise, however, brings up two additional difficulties. The first is that the temperature of the outer core is poorly constrained, even though we can be confident that the solid inner core and liquid outer core are in equilibrium at the inner core boundary (ICB). This does not yield a unique temperature constraint because the magnitude of freezing point depression caused by various light elements in Fe-Ni metal has rarely been measured at ICB conditions. Consequently, Badro et al. (2014) compared their thermodynamic model with seismic density and velocity exclusively at the CMB and ICB by varying temperatures over reasonable ranges, and Umemoto and Hirose (2020) compared the whole outer core based on temperature profiles which required an arbitrarily preset ICB temperature. The second difficulty is that the pressure-density profile and the pressure-sound speed profile are often fitted independently, whereas for a homogeneous and adiabatic convecting layer these profiles are strictly coupled through the Adams-Williamson equation for hydrostatic

equilibrium in a self-gravitating liquid medium. As such, no existing model matches the outer core's sound speed and density profiles.

Both these issues can be addressed by computing a posterior distribution of core compositions and thermal states by Bayesian inference using the Markov chain Monte Carlo (MCMC) approach, applied simultaneously to density and sound speed using the Adams-Williamson constraint. This statistical approach has been successfully used in inversion problems in geophysical and geochemical studies (Dauphas et al., 2024; Deng et al., 2023; Irving et al., 2018; Kipp and Tissot, 2022) to explore the posterior distributions of variables and their potential intercorrelations. An acceptable fit to a seismic model yields a range of compositions and thermal states that are geophysically consistent. By contrast, an absence of any acceptable fit implies a failure either of the data or the model assumptions; for example, the outer core may not in fact be a homogeneous, adiabatic liquid layer.

In this chapter, combined with different types of radial seismic models for the average 1-D structure of the Earth's outer core, the new thermodynamic model leads to a posterior distribution of parameters constraining the possible compositional and thermal states of the Earth's outer core, including P and T at the ICB, the mass of the inner core, and the concentrations of Fe, Ni, S, C, Si, O, and H. The results confirm that some seismic models based only on body wave travel times imply a velocity structure for the outer core that is incompatible with the equation of state of any plausible liquid, leading us to concur with a number of previous assessments (Gubbins et al., 2008; Helffrich and Kaneshima, 2010; Helffrich and Kaneshima, 2013; Hernlund and Mcnamara, 2015; Kennett, 2020; Kennett et al., 1995) that the outer core is inhomogeneous or highly non-adiabatic (or both), or that there are unresolved issues with these seismic models.

3.2 Methods

Self-gravitating Adams-Williamson equation

The Adams-Williamson equation is used to map the thermodynamic equation of state into internally consistent functions of radius (r), assuming that the Earth's outer core is homogeneous and adiabatic, in which case the density profile of the liquid outer core follows from hydrostatic equilibrium and the definition of the isentropic bulk modulus:

$$\frac{d\rho(r)}{dr} = -\frac{\rho(r)g(r)}{\Phi(r)},\tag{3.1}$$

where Φ , ρ , and g are seismic parameter, density, and acceleration due to gravity. Based on eq. (2.13), seismic parameter is a function of volume and temperature. $\rho(r)$ and V(r) are related by eq. (2.15) and T(r) for the adiabatic case follows from γ by:

$$d\ln T(r) = \gamma d\ln \rho(r). \tag{3.2}$$

Combining eqs. (2.6), (2.15), and (3.2) and integrating the expression, the temperature at radius r can be written as:

$$T(r) = T(r_c) \left(\frac{\rho(r)}{\rho(r_c)}\right)^{b_{\gamma}} \exp\left(a_{\gamma} \left(\frac{m}{\rho(r_c)} - \frac{m}{\rho(r)}\right)\right),\tag{3.3}$$

where r_c represents the radius of a reference location within the Earth's outer core, at which temperature and density are $T(r_c)$ and $\rho(r_c)$, respectively. Therefore, plugging eq. (2.15) and eq. (3.3) into eq. (2.13), the seismic parameter can be expressed formally as a function of a single variable $\rho(r)$ as:

$$\Phi(\rho(r)) = \frac{K_s(V(\rho(r)), T(\rho(r)))}{\rho(r)}.$$
(3.4)

Meanwhile, $\rho(r)$ and g(r) are related to the mass of the core inside radius r(M(r)) by:

$$\rho(r) = \frac{1}{4\pi r^2} \frac{dM(r)}{dr}$$
(3.5)

and

$$g(r) = \frac{GM(r)}{r^2},\tag{3.6}$$

where G is the universal gravitational constant. Plugging eq. (3.4)-(3.6) into eq. (3.1), the second derivative of M(r) with respect to r can be written as a closed-form second-order ordinary differential equation:

$$\frac{d^2 M(r)}{dr^2} = f(M(r), M'(r), r) = \frac{2M'(r)}{r} - \frac{GM(r)M'(r)}{r^2 \Phi(4\pi M'(r))},$$
(3.7)

where M'(r) is the first order derivative of M(r). After specifying the boundary conditions (e.g., $M(r_c)$, $T(r_c)$, and $P(r_c)$), this equation can be solved numerically to obtain M(r), $\rho(r)$, T(r), and $\Phi(r)$ using the fourth order Runge–Kutta method. Consequently, the variation of velocity with radius follows from Equation 2.14. We leave r_c unspecified at this point because it is unclear a priori whether the most model-independent result follows from integrating downwards from the CMB or upwards from the ICB.

Markov chain Monte Carlo (MCMC) framework

Constructing a core velocity (and density) variation using the Adams-Williamson equation and our non-ideal multi-component liquid equation of state necessitates the input of a set of model parameters, for example: the temperature and pressure at the ICB, the mass of the inner core, and the composition of the Earth's outer core including the contents of Fe, Ni, S, C, Si, O, and H. To determine the posterior probability distributions of the model parameters that result in velocity (and density) profiles matching an observed seismic model, we apply Bayesian inference using the Metropolis-Hastings MCMC approach (Hastings, 1970; Metropolis et al., 1953). Conceptually, in a probabilistic framework with predefined prior distributions over model parameters, the MCMC scheme is employed to generate samples from a posterior distribution of model parameters given the observed value, in which the Markov chain is constructed with the Metropolis-Hastings algorithm. In detail, the simulation commences with a set of model parameters, and the algorithm iteratively generates new sets and decides whether to accept the new set (x_j) or retain the old set (x_i) based on the acceptance probability ($P_{acc}(x_i \rightarrow x_j)$), which is given by:

$$P_{acc}(\mathbf{x_i} \to \mathbf{x_j}) = min(1, \frac{P(\mathbf{x_j})g(\mathbf{x_i}|\mathbf{x_j})f(\mathbf{d}|\mathbf{x_j})}{P(\mathbf{x_i})g(\mathbf{x_j}|\mathbf{x_i})f(\mathbf{d}|\mathbf{x_i})}),$$
(3.8)

where P is the prior distribution of model parameter vector \mathbf{x} , $g(\mathbf{x_i}|\mathbf{x_i})$ is the proposal probability of generating a set of model parameters \mathbf{x}_i from \mathbf{x}_i , and f is the likelihood function that defines the probability of obtaining a set of observables **d** when the set of model parameters \mathbf{x} is used. Here, we assume a uniform prior distribution of all the model parameters within a geochemically and geophysically reasonable range. The proposal probability g suggests a candidate for a next sample given the previous sample value. In this work, we set the random walk of each scalar member y in the model parameter vector **x** independent of each other (i.e. $g(\mathbf{x}_i | \mathbf{x}_j) = \prod g(y_i | y_j)$) within the range $[y_{min}, y_{max}]$, and define the proposal probability $g(y_i|y_i)$ to be a uniform distribution spanning from $max(y_{min}, y_j - k(y_{max} - y_{min}))$ to $min(y_{max}, y_j +$ $k(y_{max} - y_{min}))$, where k is a damping factor regulating the maximum value change for a single random walk step. In most cases, $g(y_i|y_i) = g(y_i|y_i)$, except when y_i and/or y_i are in close proximity to the boundary of the model parameter range for y. We note that the choice of prior distribution and proposal probability functions only affects the convergence rates of MCMC simulation but not the target posterior distribution. The likelihood function takes the form:

$$f(\mathbf{d}|\mathbf{x}) = \exp(-E(\mathbf{x})), \tag{3.9}$$

where $E(\mathbf{x})$ is defined as:

$$E(\mathbf{x}) = \sum_{r}^{outer \ core} \frac{(V_{\mathbf{x}}^r - V_{\mathbf{d}}^r)^2}{(\sigma^r)^2},$$
(3.10)

where $V_{\mathbf{x}}^r$ is the value at radius *r* predicted by our model with the set of model parameters \mathbf{x} , and $V_{\mathbf{d}}^r$ is the value reported by a radial seismic model at radius *r*. The σ^r factor should be the uncertainty of the profile at radius *r* derived from the thermodynamic model, rather than the uncertainty of the seismic radial model, to ensure that the expression conforms to the definition of the likelihood function $f(\mathbf{d}|\mathbf{x})$.

In this study, we conducted 500,000 iterations for each MCMC calculation. The initial 100,000 steps of the chain are designated as the burn-in period and consequently discarded. The subsequent 400,000 steps are considered a good representation of the posterior distribution of the model parameters $P(\mathbf{x}|\mathbf{d})$.

3.3 Summaries on seismic observations

As the criteria for identifying the thermal and compositional state of the Earth's outer core, the methods and assumptions underlying the derivation of radial seismic models must be considered first.

Several radial core velocity models (i.e., $V_P(r)$, where r is radius from the Earth's center) have been proposed on the basis of the period and attenuation of free oscillations (normal modes) and/or the travel times of body waves. The selection of different combinations of seismic phases and subsets of normal modes results in small differences, about 1%, among Earth models (Souriau and Calvet, 2015). In the following discussion, we will thus focus on the two most commonly used global models, PREM (Dziewonski and Anderson, 1981) and ak135 (Kennett et al., 1995), and on two newly proposed models that emphasize the outer core, EPOC-V (Irving et al., 2018) and ek137 (Kennett, 2020). The PREM model was constructed using data from both the body waves and normal modes, with an assumption of a homogeneous and adiabatic outer core (i.e., satisfying the Adams-Williamson equation) imposed as a prior constraint. By contrast, ak135 was constructed solely from the travel times of body waves without any additional constraint. As more seismic phases traveling through the Earth's core were included, ak135 is generally considered to be a better description of P-wave velocity in the core (Souriau and Calvet, 2015). As shown in Figure 3.1a, in comparison to PREM, ak135 exhibits lower velocities at the CMB and ICB (by 0.11 km s⁻¹ and 0.07 km s⁻¹, respectively),

but is slightly faster in the middle of the outer core (by $0.02 \ km \ s^{-1}$). Recently, the EPOC-V model was constructed by directly optimizing the parameters of the isentropic Vinet EOS for the outer core to achieve the best fit for a dataset consisting solely of normal mode frequencies, which incorporates 79 normal modes that were not included in the PREM model (Irving et al., 2018). Compared to PREM, EPOC-V has lower velocities at the CMB by 0.07 km s⁻¹, but the velocities in the lower part of the outer core are close to PREM, with a difference of less than 0.017 km s⁻¹ (Figure 3.1a). Using EPOC-V as the starting outer core model for travel time inversion, ek137 was constructed without considering normal modes or imposing the adiabatic core constraint assumed by PREM and EPOC-V (Kennett, 2020). The velocity in the lower part of the outer core of ek137 is nearly identical to that of ak135, while in the upper part of the outer core, it is consistently ~ 0.07 km s⁻¹ faster than EPOC-V (Figure 3.1a).

In addition to the radial velocity structure, radial models of density such as PREM and ak135-f (Montagner and Kennett, 1996) have been constructed by incorporating normal mode observations and the constraints of the Earth's total mass and moment of inertia. However, at the same radial resolution (100 km for PREM, 50 km for ak135 and ek137), the velocity models derived from the travel times of body waves exhibit significantly smaller uncertainties compared to the related density models from normal modes (Masters and Gubbins, 2003). The limited number of normal modes with significant energy in the core region yields density models with an uncertainty level of 10%, which is an order of magnitude higher than the that of velocity models (Kennett, 2020; Kennett et al., 1995). Even velocity model based solely on normal modes have smaller uncertainties compared to the corresponding density model. Recently, the EPOC-V density model was constructed, with refinements confined to Earth's outer core and maintaining the PREM model for the rest of the Earth (Irving et al., 2018). The EPOC-V density model has a relative uncertainty ~5 times larger than that of the EPOC-V velocity model. Meanwhile, the EPOC-V density model has been found to be sensitive to changes in mantle density structure and fails to meet the constraints of Earth's total mass and moment of inertia (Irving et al., 2018). Hence, our subsequent discussion, while ensuring that we maintain acceptable fits to the density profile, will prioritize comparison to velocity profile models to constrain the thermal and compositional state of the Earth's outer core.



Figure 3.1: Comparison of seismic velocity models and thermodynamic model fits to the uncertainties and differences among the seismic models across the outer core. (a) The blue solid line, dark cyan dotted line and dark green dashed line mark the difference between the PREM model and ak135 model, between the PREM model and ek137 model, and between the PREM model and EPOC-V model, respectively. The red shaded area represents the 1σ uncertainty on the velocity profile for pure iron liquid calculated from our new thermodynamic model, assuming $T_{ICB} = 5500$ K (the estimated melting point of pure iron). (b) The grey shaded area marks the 1σ uncertainties on the PREM velocity model, estimated using Bayesian inference (Wit et al., 2013). The yellow solid line represents the velocity difference between the PREM model and our optimal fit in the fiducial case. The pink dashed line shows the difference between the PREM model and the optimal "H-free" fit. (c) The purple shaded area marks the bound range of models around the ak135 model that fit the seismic travel time data well. The orange solid line shows the velocity difference between the ak135 model and the optimal "unshackled" fit. (e) The cyan shaded area marks the 1σ uncertainties on the EPOC-V velocity model. The blue solid line represents the velocity difference between the PREM model and our optimal "fiducial" fit, with uncertainties of 0.020, 0.022 and 0.035 km s⁻¹ at ICB, 2,600 km, and CMB, respectively. The dark red dashed line shows the difference between the EPOC-V model and the optimal "H-free" fit. (f) The green shaded area marks the 1σ uncertainties on the ek137 velocity model. The dark pink solid line shows the velocity difference between the ek137 model and the optimal "unshackled" fit, with uncertainties of 0.023, 0.020 and 0.032 km s⁻¹ at ICB, 2,600 km, and CMB, respectively.

3.4 Model/observation comparison approach

A radial seismic radial profile cannot be directly compared with the $V_P(P,T)$ and $\rho(P,T)$ predictions of the thermodynamic model, because we do not know a priori the structure of P(r) or T(r). Previous studies have derived P(r) by integrating the seismically-constrained density profile (given $(dP/dr) = -\rho(r)g(r)$) and T(r) for an assumed adiabatic profile using some model of the Grüneisen parameter (using $dT/T = \gamma(\rho)d\rho/\rho$ to establish $T(\rho)$, and the seismic $\rho(r)$ to translate this to T(r)). As such, the radial seismic model can be transformed to a function of pressure and its velocity and density predictions compared to a thermodynamic model in $P - V_P$ and $P-\rho$ spaces, separately (Umemoto and Hirose, 2020). We note that this comparison suffers from three notable shortcomings: (i) the considerable uncertainty inherent in the seismically-derived density profile leads to an accumulation of uncertainty in pressure and temperature, (ii) using the P(r) function to convert the radial seismic velocity profile badly degrades the precision and resolution of the velocity profile, and (iii) this approach encourages evaluation of models as fits to the density and velocity profiles separately when in fact these variables are closely coupled and a valid model must fit both simultaneously.

To address these challenges, we propose a novel approach using the Adams-Williamson equation to integrate radius into the thermodynamic model under the assumption of an adiabatic and homogeneous outer core. Given a proposed set of model parameters, including the boundary conditions at the ICB (P, T, r) and the mass of the inner core) and the composition of the outer core (concentrations of Ni, S, C, Si, O, and H; the balance is Fe), our new method enables a complete and internally consistent derivation from our thermodynamic model of the velocity and density structure as a function of radius across the whole outer core. This model output can then be directly compared to a radial seismic model in the most model-independent way, without the error accumulation effect discussed above. The solution of the Adams-Williamson equation and the knowledge of the Grüneisen parameter allow P(r) and T(r) to be obtained directly from the thermodynamic model, rather than being tied to a seismically-derived radial density model. This offers a fresh perspective on the thermal structure of the Earth's outer core and the mass and moment of inertia contributed by the Earth's core, independent of the construction of a core density model from normal modes. On the other hand, we must acknowledge that the outer core may not, in fact, be homogeneous and adiabatic. A failure of the Adams-Williamson approach to yield an acceptable fit to a seismic model may indicate any combination of the following conclusions: (a) that the seismic

model is incorrect, beyond its stated uncertainty range, (b) that the thermodynamic model is incorrect or does not include the actual core composition, (c) that the core is compositionally layered and hence has density gradients that are not equal to the adiabatic compressibility, or (d) that the core P - T profile deviates strongly from adiabatic, perhaps due to non-convecting boundary layers.

The uncertainty of the velocity (or density) profile derived from the thermodynamic model can be estimated using the Monte Carlo method. This involves randomly generating a set of pressures and energies based on the values and uncertainties of the ab initio data on pure Fe and reference binaries, then regressing the EOS and non-ideal mixing coefficients of the thermodynamic model to the trial data set, and finally integrating the Adams-Williamson equation to produce a candidate pair of density and velocity profiles. The ensemble of such profiles for a given choice of ICB boundary conditions and outer core composition yields the uncertainty of density and velocity, propagated from the ab initio simulation results. As shown in Figure 3.1a, the uncertainty velocity for pure iron ranges from 0.010 to 0.025 km s^{-1} . This uncertainty is less than that of the seismic models of the outer core, where nominal uncertainties are typically less than 0.045 km s⁻¹ (Kennett, 2020; Kennett et al., 1995; Wit et al., 2013). This level of uncertainty is also more than sufficient to resolve the differences of 0.7 to 0.11 km/s between PREM and ak135 at the ICB and CMB. Therefore, our new approach is satisfactory for comparison to and between seismic velocity models.

The compositional and thermal state of the Earth's outer core can be inferred by identifying the plausible range of model parameters that result in a velocity profile agreeing with an observed seismic model. Given the extensive number of model parameters that need to be determined, this problem is optimally addressed through Bayesian inference using the Metropolis-Hastings MCMC approach (Hastings, 1970; Metropolis et al., 1953). To ensure that the result is geochemically and geophysically acceptable for the Earth's outer core, we set a prior range for the model parameters. Specifically, we bound the temperature at the ICB between 4500 K to 5500 K, based on the melting temperature of metal at ~330 GPa (Dobrosavljevic et al., 2022; Morard et al., 2017; Sinmyo et al., 2019; D. Zhang et al., 2016). Given the weak constraints on possible H contents in the outer core, we also perform separate H-free simulations. Constraints from chondritic meteorites (Allègre et al., 2001; McDonough and Sun, 1995) indicate that the Fe/Ni molar ratio may range from 10 to 16 and that the molar ratio of (Fe+Ni)/(Fe+Ni+S+Si+O+C) may range from 0.6 to 1. For the fiducial case, we fix the pressure at ICB (P_{ICB}) to be 329 GPa and adopt the mass of the inner core (M_{IC}) from the PREM model, 0.984 × 10²³ kg. To test the sensitivity to these two parameters, we also conduct separate "unshackled" simulations that relax these constraints as much as possible: letting P_{ICB} vary from 325-335 GPa and bounding M_{IC} only by the constraints that the inner core be more dense than the outer core at the ICB and less dense than pure iron at the pressure of the center of the Earth (Fei et al., 2016). Meanwhile, to reduce the cost of computing the σ^r factor in the likelihood function $f(d|\mathbf{x})$, we set σ^r to a uniform value of 0.015 km/s for each radius, based on the average uncertainty of velocity variations in pure iron liquid. The resulting MCMC simulations yield a population of accepted samples, representing the posterior distribution of plausible model parameters based on a chosen radial seismic velocity model and our new thermodynamic model. We will discuss the MCMC simulation results for PREM and ak135 in turn in the following sections.

3.5 Comparison to PREM model

We begin with the fiducial case. The optimal fit (minimum E(x) value) among 500,000 MCMC steps yields composition Fe_{66.74}Ni_{6.45}C_{0.98}H_{25.82} (in mol%), with the total content of S, Si, and O being less than 0.01 mol%, and $T_{ICB} = 4518$ K. The yellow solid line in Fig. 3.1b shows the velocity profile for this optimal fit, which lies fully within the 1 σ range of uncertainties for the PREM model (cyan shaded range).

This optimal fit does not represent the only set of model parameters capable of fitting the PREM model. All accepted MCMC samples (N = 22,387), shown below the diagonal of Fig. 3.2, are considered statistically equivalent fits to the PREM model. The posterior distribution of each model parameter for the fit to PREM is shown along the diagonal of Fig. 3.2. The result confirms the expectation that Fe and Ni are the primary elements in the Earth's core, constituting 73.67 ± 0.70 mol% (1 σ uncertainty), illustrated by the blue bars in Fig. 3.3a. Although our prior bounds allowed Fe/Ni ratios from 10 – 16, all accepted samples have Fe/Ni ratios less than 13.9, with a broad distribution showing a weak maximum at Fe/Ni = 10.9 (Figure 3.3b). The major light element is H, constituting 23.66 ± 1.59 mol%, with 99% of accepted samples falling in the range 18.55 – 26.66 mol%. The remaining four light elements considered in our model (C, Si, S, and O) account in total for 2.68±1.26 mol% (Fig. 3.3c). Although the optimal fit suggests a significant presence of C with the other three elements nearly absent, the posterior distribution indicates that these four elements can substitute for each other, as evidenced by a considerable number of accepted samples where the content of any one of these four elements is near zero (Fig. 3.2). These four elements exhibit the highest probability at contents approaching zero, with their respective distributions predominantly (99%) bounded to <1.5 mol% for Si, <3.2 mol% for S, <6.0 mol% for O, and <3.0 mol% for C. For comparison, when Umemoto and Hirose (2020) fit their thermodynamic model to the PREM $P - V_P$ and $P - \rho$ profiles assuming $T_{ICB} = 5400K$ and Fe/Ni = 16, they obtained a 'best' estimate outer core composition with 5.9 mol% O, 0.4 mol% Si, 0.7 mol% S and 25.3 mol% H. This solution falls within our accepted posterior distribution range. In contrast to the compositional parameters, whose posterior distributions are much narrower than the prior acceptable ranges, T_{ICB} is very weakly constrained, with accepted fits spanning the entire prior range (4,500 K - 5,500 K) and a slight inclination towards lower temperatures (60% of accepted samples have $T_{ICB} \leq 5000$ K).

The trade-offs among model parameters for the fiducial case (i.e., with P_{ICB} fixed at 329 GPa, M_{IC} fixed at 0.984 × 10²³ kg, and H permitted) are illustrated in two-dimensional distributions of the accepted MCMC samples above the diagonal of Fig. 3.2. The intercorrelation among these parameters is indicated by the Pearson correlation coefficients (*R*) between each pair of parameters (Table B.1). Except for the Ni-Si pair (p – value = 0.55) all other pairs of model parameters are significantly correlated at the α = 0.01 level according to Student's t-test. Among all the correlation coefficients, H content and T_{ICB} exhibit the strongest correlation (*R* = -0.77), with the other correlation coefficients spanning from -0.6 to +0.6.

Although the fiducial case predicts that H is the dominant light element, the presence of H as a light element in the Earth's core remains a matter of debate, so we carried out an MCMC fit for an H-free case. The posterior distribution of model parameters for the H-free case (Fig. 3.4) includes 18,309 accepted samples with an optimal composition of Fe_{70.95}Ni_{6.18}S_{22.80}O_{0.04}Si_{0.03} and $T_{ICB} = 5295$ K. As with the fiducial case, the velocity profile of the optimal H-free fit lies entirely within the 1 σ uncertainty range of PREM (pink dashed line in Fig. 3.1b). The H-free model fits require more Fe+Ni (77.33 ± 0.24 mol%; green bars in Fig. 3.3a) and a lower Fe/Ni ratio (≤ 11.9) than the fiducial case. Among the light elements, S is preferred over Si, O, and C; the minimum accepted S content is 10.19 mol% and the S distribution in the accepted population is 20.12 ± 1.82 mol%. The other three



Figure 3.2: Distributions of model parameters for accepted samples of the MCMC fit to the PREM model in the fiducial case (H included, P_{ICB} fixed at 329 GPa, M_{IC} fixed at 0.984 × 10²³ kg). The frames along the diagonal show the probability histograms of each model parameter, the lower triangle shows 2-D scatter diagrams, and the upper triangle shows 2-D probability histograms. The model parameters are T_{ICB} and the mole % of Ni, H, Si, O, C, and S. The dependent mole % of Fe is also shown. The red filled star marks the optimal fit (i.e., with the smallest misfit E(x)) to the PREM model among the 400,000 MCMC steps.

elements have highest probability near zero, with 99% of accepted samples having $O \le 4.2 \mod \%$, Si \le 6.4 \mod \%, and C ≤ 1.8 mol%. The H-free case yields a strong preference for higher T_{ICB} than the fiducial case, with 99% of accepted samples having $T_{ICB} \ge 5150$ K.

The "unshackled" PREM case, which relaxes the prior constraints on P_{ICB} and M_{IC} as much as possible, yields a best-fit solution quite similar to that of the fiducial case, with outer core composition of Fe_{69.47}Ni_{5.66}C_{4.21}Si_{0.03}S_{0.01}H_{20.62} and T_{ICB} of 4506 K. For this best-fit case, P_{ICB} is 326 GPa (vs. 329 GPa in the fiducial case) and M_{IC} is 0.95 × 10²³ kg (vs. 0.984 × 10²³ in the fiducial case).

In addition to outer core composition and T_{ICB} , each realization of the model outputs a predicted mass of the core, moment of inertia of the core, pressure at the CMB, and temperature at the CMB. The distributions of these variables for the fiducial, H-free, and "unshackled" simulations runs are shown in Fig. 3.3 (d)-(f).



Figure 3.3: Comparison of the probability density functions for accepted MCMC samples in the fiducial, H-free, and unshackled cases. The plotted model parameters are (a) total mole percent of Fe and Ni, (b) the ratio of Fe/Ni, (c) total mole percent of light elements excluding H (i.e. O, C, Si, and S), (d) the mass of the whole Earth's core, (e) the moment of inertia of the outer core, (f) pressure at the CMB, and (g) temperature at the CMB. The distributions are the statistics results for the accept samples that fit to the PREM model. The blue bins with broad bar widths represent the fiducial case and are fitted with Gaussian distributions (when this is a reasonable description of the distribution) shown by the blue solid lines. The pink bins with moderate bar widths represent the H-free case and are fitted with Gaussian distributions shown by the pink solid lines. The green bins with thin bar widths represent the unshackled case and are fitted with Gaussian distributions shown by the pink solid lines.

In the fiducial case, the first three quantities are normally distributed, with values of $(1.981 \pm 0.005) \times 10^{24}$ kg, $(9.625 \pm 0.022) \times 10^{36}$ kg m², and 127.7 ± 0.9 GPa, respectively. Even if we relax the constraints on the inner core mass and ICB



Figure 3.4: Distributions of model parameters for accepted samples of the MCMC fit to the PREM model in the H-free case (H content fixed to 0, P_{ICB} fixed at 329 GPa, M_{IC} fixed at 0.984 × 10²³ kg). The frames along the diagonal show the probability histograms of each model parameter, the lower triangle shows 2-D scatter diagrams, and the upper triangle shows 2-D probability histograms. The model parameters are T_{ICB} and the mole % of Ni, Si, O, C, and S. The dependent mole % of Fe is also shown. The red filled star marks the optimal fit (i.e., with the smallest misfit E(x)) to the PREM model among the 400,000 MCMC steps.

pressure as in the unshackled case (as shown by the pink bars in Figure 3.3), the averages of these three quantities are almost unaffected, but their variances become larger. Regarding T_{CMB} , the MCMC simulations containing H result in this value being almost uniformly distributed between 3450 K and 4200 K without any obvious trend. The distributions of accepted H-free models, however, have some notable differences from the H-bearing cases. The core mass and moment of inertia both significantly decrease, reaching (1.908 ± 0.002) × 10²⁴ kg and (8.916 ± 0.009) × 10³⁶ kg m², respectively, while P_{CMB} sees a large increase to 141.8 ± 0.4 GPa. At the same time, in the H-free model T_{CMB} is no longer uniformly distributed and instead yields a normal distribution 3966 ± 68 K, with bounds of 3580 K and 4110 K. It should be noted that these distributions are entirely derived based on the PREM velocity model for the outer core and are completely independent of other observations. Since the H-bearing and H-free models yield such notably different values of core mass, core moment of inertia, and P_{CMB} , other observations that

constrain these three parameters can, in turn, constrain whether hydrogen is, in fact, a feasible light element in the Earth's outer core.

3.6 Comparison to ak135 model

In contrast to the PREM model, which we can be successfully fitted within its uncertainty over the whole range of outer core radii, it is not possible to achieve such a fit to the ak135 model. Even in the unshackled case, the velocity profile resulting from the optimal fit (with model parameters Fe_{69.47}Ni_{5.66}C_{4.21}Si_{0.03}S_{0.01}H_{20.62}, $P_{ICB} = 326 \text{ GPa}, T_{ICB} = 4506 \text{ K}, \text{ and } M_{IC} = 0.95 * 10^{23} \text{ kg})$ is faster than the ak135 reference model at both the top and bottom of the outer core region by 0.07 km s^{-1} (Fig. 3.1c). This error exceeds the uncertainty range within which the model can fit its seismic travel time data set (Kennett et al., 1995). This difference may stem from our use of the Adams-Williamson equation, which assumes that the Earth's outer core is adiabatic, homogeneous, and has a shear modulus of exactly zero. It appears that the ak135 velocity structure, derived entirely by fitting body wave travel times with no a priori physical constraints, is not consistent with these assumptions, given the EOS of any metallic liquid within our modeled range. Similar conclusions have been reached by a number of studies based on more generalized EOS formulations, as well as through the detailed study of seismic phases that specifically target the outermost (or innermost) outer core (Gubbins et al., 2008; Helffrich and Kaneshima, 2010; Helffrich and Kaneshima, 2013; Hernlund and Mcnamara, 2015).

Considering that reduced concentrations of light elements or increased temperatures can decrease velocity, the slow anomalies in ak135 (relative to our best fitting self-consistent Adams-Williamson model) at the top and bottom of the core may indicate the presence of layers with either non-adiabatic temperature gradients (i.e. sub-adiabatic near CMB and super-adiabatic near ICB) or light element depletion (or both). As shown in Fig. 3.5, we quantified the magnitude of the excess temperature or light element depletion at the ICB (inner core boundary) that would be needed to bring the model into alignment with ak135. A positive temperature anomaly of at least 1300 K or a 6 mol% depletion in light element concentration would reduce the model velocity at the ICB by 0.07 km s⁻¹ and align with the ak135 model. This magnitude of temperature anomaly relative to the adiabat appears quite unreasonable: increasing the CMB temperature by more than 1000 K would eliminate the temperature difference across the outer core and suppress the convection necessary to support the geodynamo, while increasing the ICB temperature by more than 1000 K would exceed the melting point of even pure iron and be inconsistent with a solid inner core. Therefore, we prefer the notion that vertical structure in the concentration of light elements might explain the anomalous velocity regions at the top and bottom of the outer core in the ak135 model. A depletion of light elements at the bottom of the outer core, while seemingly inconsistent with the idea that light elements are excluded from the growing inner core, could potentially be explained by a translational mode of the inner core in which crystallization happens on one side of the inner core and melting on the opposite side due to asymmetry (Alboussière et al., 2010). This novel mechanism is able to drive compositional convection within the Earth's outer core but form a stable low velocity dense layer at the bottom of the outer core. Meanwhile, depletion of light elements at the top of the outer core could be evidence of ongoing exchange between core and mantle across the CMB (Badro et al., 2016; Deng et al., 2023; Hirose et al., 2017; Liu et al., 2020; Pozzo et al., 2019), an alternative mechanism for supporting compositional convection in the core.



Figure 3.5: The magnitude of perturbation to (a) temperature and (b) light element concentration necessary to obtain an acceptable fit to the seismic velocity of the ak135 model at the ICB. The blue filled squares show the velocity at the ICB in the optimal fit to the whole outer core profile of ak135, with a composition of $Fe_{69.47}Ni_{5.66}C_{4.21}Si_{0.03}S_{0.01}H_{20.62}$, $P_{ICB} = 326$ GPa and $T_{ICB} = 4506$ K. The ak135 model velocity at the ICB is shown by the red filled circles, with uncertainty bounds marked by the red shaded area. In (a) the composition is fixed but T_{ICB} is varied from 4,000 to 8,000 K. In (b) T_{ICB} is fixed but the total concentration of light elements is varied from 15 to 30 mole %, keeping the ratios the same as in $C_{4.21}Si_{0.03}S_{0.01}H_{20.62}$ and keeping the Fe/Ni ratio at 12.27.

3.7 Comparison to EPOC-V model

In the fiducial case, the velocity profile derived from the optimal fit (with model parameters $Fe_{69.60}Ni_{5.90}C_{2.99}O_{0.02}S_{0.02}Si_{0.01}H_{21.46}$, and $T_{ICB} = 4505$ K) exceeds the EPOC-V model by 0.025 km s⁻¹ at CMB and 0.014 km s⁻¹ at ICB, but slower in the middle of the outer core region (reaching a maximum difference at r=2600 km) by ~0.008 km s⁻¹ (Fig. 3.1d). This discrepancy is significantly larger than the uncertainty of the EPOC-V model. However, EPOC-V assumes that PREM represents the 1D structure outside the outer core and does not account for the propagation of the uncertainties of PREM into the model, resulting in an underestimation of velocity uncertainties of the outer core. We instead considered the uncertainty in the velocity profile derived from our new thermodynamic model, and the results show that its 1-sigma range (0.020, 0.022 and 0.035 km s⁻¹ at ICB, 2600 km and CMB, respectively) is sufficient to encompass its discrepancy relative to EPOC-V. Although the Vinet EOS (Vinet et al., 1987) used in the EPOC-V model has a different formulation than the third-order BM EOS we used to construct the thermodynamic model in this work, both forms have proven suitable for fitting DFT data for pure iron liquid under core pressures and temperatures (Figs. 2.7a and 2.4a). Thus, the optimal fit still adequately represents the posterior distribution of plausible model parameters based on the EPOC-V model.

Compared with the "fiducial" PREM model (blue bars in Fig. 3.6), the EPOC-V model fits (pink bars in Fig. 3.6) require more Fe+Ni with 75.85 ± 0.39 mol% and a lower Fe/Ni ratio (99% of accepted MCMC samples have Fe/Ni in the range 10.77 - 12.24). H remains the dominant light element, but its amount is smaller than that of PREM model, constituting 20.48 ± 0.93 mol%. The remaining four light elements account for 3.67 ± 0.76 mol%. C is selected over Si, O, and S, with a concentration of 2.79 ± 0.78 mol% and 99% of accepted samples within 0.03 - 4.16mol%. The remaining three elements still have highest probability near zero, with 99% of accepted samples having $O \le 5.5 \text{ mol}\%$, $Si \le 1.6 \text{ mol}\%$, and $S \le 2.2 \text{ mol}\%$. The EPOC-V model strongly favors a lower T_{ICB} than the PREM model, with 99% of accepted samples having $T_{ICB} \leq 5075$ K. For the other model outputs (including the mass of the core, temperature at the CMB, pressure at the CMB, and moment of inertia of the core), the values all exhibit strong normal distribution characteristics: $(1.998 \pm 0.003) \times 10^{24}$ kg, 124.3 ± 0.6 GPa, 3513 ± 87 K, and (9.3466 ± 0.014) \times 10³⁶ kg m², respectively. The first two values are greater than those of PREM model fits, while the latter two are lower.



Figure 3.6: Comparison of the probability density functions of model parameters and outputs between 'fiducial' prem model and 'fiducial' EPOV-C model. Model parameters and outputs includes: the mole % of Fe, Ni, H, Si, O, C, and S, temperature at ICB, total mole percent of Fe and Ni, the ratio of Fe/Ni, total mole percent of light elements excluding H (i.e. O, C, Si, and S), the mass of the whole Earth's core, the moment of inertia of the outer core, pressure at the CMB, and temperature at the CMB. The blue bins with broad bar widths represent the PREM model and are fitted with Gaussian distributions (when this is a reasonable description of the distribution) shown by the blue solid lines. The pink bins with thin bar widths represent the EPOC-V model and are fitted with Gaussian distributions shown by the pink solid lines.

The "H-free" EPOC-V case yields a best-fit solution with an optimal composition of Fe_{71.10}Ni_{6.92}S_{20.15}C_{1.82}Si_{0.01} and $T_{ICB} = 4514$ K. Compared to "H-free" PREM model (blue bars in Fig. 3.7), a larger Fe content (71.61 ± 0.56 mol%) is required by the EPOC-V model (pink bars in Fig. 3.7), while the Ni content remains the same (6.67 ± 0.25 mol%). S is still favored as the major light element over Si, O and C, with a content of 15.30 ± 3.81 mol%, but there are a small number of S-free accepted samples. The other three elements still have highest probability near zero,



Figure 3.7: Same as Figure 3.6 for the 'H-free' case.

3.8 Comparison to ek137 model and more seismic models with no a priori Adams-Williamson constraint

As with the ak135 model, we cannot find a fit to the ek137 model, even in the unshackled case. As shown in Fig. 3.1e, the velocity profile resulting from the optimal fit (with model parameters $Fe_{67.80}Ni_{6.35}C_{3.58}O_{0.04}H_{22.23}$, $P_{ICB} = 325$ GPa, $T_{ICB} = 4504$ K and $M_{IC} = 0.95 \times 10^{23}$ kg) is faster than the ek137 model by 0.06 km s⁻¹ at ICB and by 0.03 km s⁻¹ at CMB, but slower in the middle of the outer core region by 0.02 km s⁻¹ (at r = 2450 km). The velocity difference at the ICB is statistically significant, as it exceeds both the uncertainty of the derived velocity profile (0.023 km s⁻¹) and that of ek137 seismic reference model (0.015 km s⁻¹), suggesting that a super-adiabatic or light element-depleted layer near the ICB should be considered. However, the discrepancies at the CMB and the middle of the outer core region can be alternatively explained by the uncertainties (0.032 km s⁻¹ at CMB and 0.020 km s⁻¹ at 2450 km) of the velocity profile propagated from the

thermodynamic model.

The seismic velocity structure in the outermost outer core remains a matter of dispute. The body wave travel time and amplitude anomalies suggest the presence of stratification, with velocities up to 0.10 km s⁻¹ lower than PREM in the outermost outer core (Helffrich and Kaneshima, 2010; Helffrich and Kaneshima, 2013; Hernlund and Mcnamara, 2015; Ma and Tkalčić, 2023). This slow anomaly at the top of the outer core has been further validated with improved fits to the frequencies of normal modes (Tent et al., 2020). If the interpretation of these observations is correct, the reduced uncertainties of our thermodynamic model compared to previous methods confirms that such seismically anomalous layers must be compositionally anomalous as well. However, some studies also reject non-Adams-Williamson structure at top of outer core (Alexandrakis and Eaton, 2010; Frost et al., 2024; X. Zhang and Wen, 2023); these studies typically argue that much of the signal interpreted as stratification at top of outer core might instead come from the 3D structure of heterogeneous mantle.

3.9 Conclusions and future perspective

In this chapter, we developed a method based on the Adams-Williamson equation to transform our thermodynamic equation of state into the radial velocity and density structure of a homogeneous, adiabatic outer core, for optimal comparison to radial seismic velocity models of the Earth, free of the loss of precision that comes from the use of density models to transform pressure into radius. The family of acceptable model parameters and the correlations among them are then obtained using a Markov chain Monte Carlo approach.

Considering the PREM and EPOC-V models, which are constructed in a manner consistent with the Adams-Williamson equation for a homogenous, adiabatic outer core, we find a range of acceptable model parameters that yield good fits to the seismic model, within its stated precision over the full radius range of the outer core. The most favored models have H as the main light element and very weak constraints on the temperature at the inner core boundary. However, models that exclude H can also fit the PREM and EPOC-V model, with little control on the relative proportions of C, Si, S, and O but relatively tight constraints on the temperature at the inner core boundary.

By contrast, the ak135 and ek137 models, which are fit to body wave travel times with no a priori constraint on whether their velocity structure implies a reasonable

liquid EOS, cannot be fit within their stated precision by our approach. The velocity structure of ak135 near the top and bottom of the outer core, as well as of ek137 at the bottom of the outer core, are too slow to be consistent with the velocity across the middle of the outer core, according to our model for any homogeneous and adiabatic liquid composition within the considered set of light elements. We cannot at this time explain exactly why this is the case. We might consider that ak135 and ek137 do not accurately describe the velocity structure of the outer core, perhaps because mantle structure has been aliased into the core, and indeed the seismological community still debates whether this is the case. However, the majority of recent seismological studies suggest the presence of anomalous layers at the bottom and probably top of the outer core. We might question our model and the methods used to construct it, but it has been validated against available experimental results and constructed in the most internally-consistent manner yet applied to this problem. Or we might conclude that the outer core is inhomogeneous and/or non-adiabatic. The magnitude of temperature anomalies that would be required to eliminate the model misfit appears unreasonably large, and so radial compositional zoning seems to be the most plausible explanation. Our model offers quantifiable estimates of the magnitude of compositional variation required to fit radial seismic models that do not assume Adams-Williamson behavior, such as ak135 and ek137.

Our current conclusions regarding the composition and thermal state of the outer core are exclusively derived from the liquid outer core. The best approach to narrowing the parameter trade-off range may be to supplement our consideration of the liquid phase and the outer core with accurate phase equilibria calculations that define the conditions of solid-liquid coexistence at the ICB. Because a solid phase and a liquid phase coexist across this boundary and are likely in chemical and thermal equilibrium there, the phase diagram has the potential to eliminate T_{ICB} as a free parameter — given outer core composition and P_{ICB} , the temperature would be fixed by the equilibrium constraint. Moreover, such a model would predict the phase and composition of the solid inner core, allowing seismic results on V_P , V_S , and ρ of the whole inner core, as well as density jump at ICB, to help constrain the model. Such multicomponent phase equilibria are challenging, but not impossible, to construct given a self-consistent thermodynamic model of solid metal alloys from ab initio methods and this will be a productive future research direction.

We have noticed that, at the current stage, seismic models constructed based on different assumptions and datasets inevitably influence our conclusions regarding the composition and thermal structure of Earth's outer core. At the same time, seismic models are typically parameterized without incorporating constraints from the physical behavior of materials, yet they are widely used to infer outer core properties. Therefore, we propose to directly infer the composition, thermal state, velocity, and density structure of Earth's outer core from seismic observations. This can be achieved by embedding a thermodynamic model into a direct seismic forward modeling framework (e.g., MINEOS), allowing us to search for compositional and thermal profiles that reproduce the observed seismic properties. In this way, the resulting compositional and thermal states are directly constrained by seismic observations, and the corresponding velocity and density profiles will be more physically grounded. This one-step inversion avoids the artificial separation of first inverting for velocity structure and then fitting composition, thereby preventing the accumulation of errors in traditional 2-step inversion framework. We aim to complete this work in the future.

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Chapter 4

THE PARTITION COEFFICIENTS OF IODINE AND PLUTONIUM BETWEEN METAL LIQUID AND SILICATE MELT

4.1 Introduction

Earth must have accreted from diverse materials, but the nature and temporal sequence of delivery of these potential building blocks remain heavily debated (Dauphas, 2017; Rubie et al., 2011; Burkhardt et al., 2021; Piani et al., 2020; Halliday and Porcelli, 2001; Fitoussi et al., 2016). To investigate these questions, the isotopes of Xenon (Xe), the heaviest stable noble gas, are particularly useful. Indeed, since ¹²⁹Xe* comes from radioactive beta-decay of now extinct volatile ¹²⁹I ($t_{1/2} = 15.7$ Myr), and ¹³⁶Xe*^{Pu} from spontaneous fission of extinct refractory ²⁴⁴Pu ($t_{1/2} = 80$ Myr), the ¹²⁹Xe*/¹³⁶Xe*^{Pu} ratio evolve as a function of both time and reservoirs compositions (i.e., I/Pu ratio) early in Earth's history. As such, study of the ¹²⁹Xe*/¹³⁶Xe*^{Pu} in silicate reservoirs of the Earth has the potential to place strong constraints on Earth's accretion and evolution (Mukhopadhyay, 2012; Pető et al., 2013; Parai and Mukhopadhyay, 2015; Caracausi et al., 2016; Jackson et al., 2018; Tucker et al., 2012; Mukhopadhyay and Parai, 2019). According to recent high-precision analyses of Xe isotopes, OIB samples (plume mantle sources, originating from as deep as the core mantle boundary) display a uniformly low ¹²⁹Xe*/¹³⁶Xe*^{Pu} (by a factor of ~2.8) compared to MORB samples (upper mantle sources) (Mukhopadhyay, 2012; Pető et al., 2013; Parai and Mukhopadhyay, 2015; Mukhopadhyay and Parai, 2019). Previous work has shown that these signatures cannot simply result from shallow atmospheric contamination, mixing between subducted atmospheric Xe and MORB Xe, and/or different closure ages of Xe loss between the shallow and deep mantle reservoirs (Mukhopadhyay, 2012; Parai and Mukhopadhyay, 2015; Mukhopadhyay and Parai, 2019). Instead, the low 129 Xe*/ 136 Xe* Pu in the plume reservoir indicates that a low I/Pu was established before ¹²⁹I extinction (i.e., first ~80-100 Myr of the Solar System), and has been preserved thereafter, avoiding re-homogenization, for about 4.45 billion years (Mukhopadhyay, 2012; Caracausi et al., 2016; Mukhopadhyay and Parai, 2019).

Since iodine is thought to be retained since the earliest stages of accretion (Broadley

et al., 2020; Musselwhite and Drake, 2000), two main competing mechanisms have been proposed to explain the I/Pu contrast between MORB and OIB mantle reservoirs: (i) a heterogeneous volatile accretion history for the Earth (Mukhopadhyay, 2012; Caracausi et al., 2016), or (ii) a homogeneous volatile accretion history where partitioning of iodine into liquid metal during core formation was taken into account (Jackson et al., 2018; Armytage et al., 2013). Both models have important ramifications for our understanding of Earth's evolution. In the first case, volatile elements (including iodine) would be depleted in early accreted materials compared to later building blocks of the Earth and inefficiently mixed into the Earth's whole mantle. In the second scenario, a change in the nature of Earth's building blocks is not required since the iodine depletion of the deeper mantle could be achieved through episodes of high-pressure core formation. However, both models also suffer from notable shortcomings. Most importantly, the heterogeneous accretion models (Mukhopadhyay, 2012; Caracausi et al., 2016) did not consider the impact of core formation processes, and neither model considered the geochemical behavior of plutonium at the high P - T conditions relevant to core formation. This last parameter could exert a strong control on the evolution of I/Pu ratios within Earth's reservoirs during its accretion. In the near absence of experimental data on metal-silicate Pu partitioning (Seitz et al., 1979)-due to its highly radioactive nature and lack of access to suitable amount to perform such experiments-Pu has been implicitly assumed to be a rock-loving (lithophile) element independent of temperature and pressure throughout the planetary accretion and core formation processes.

To remedy this situation and assess whether core formation alone without a change in volatile content of building blocks could explain the difference in I/Pu ratios between MORBs and OIBs, we used the two-phase first-principles molecular dynamics (FPMD) method (Y. Zhang and Yin, 2012; Y. Zhang and Guo, 2009; Liu et al., 2020) to determine the partition coefficient of I and Pu between liquid iron and silicate melt. This method has successfully predicted the partition coefficients of C, He, Mg, Si and O (Y. Zhang and Yin, 2012; Liu et al., 2020). Our newly derived partition coefficients can then be used in a multi-stage core formation model to assess whether I/Pu could be efficiently fractionated under different accretion scenarios. Enhanced by a thorough compilation and analysis of available meteorite xenon isotope data, we present a model for the accretion history of the Earth based on I/Pu evidence.

4.2 Methods

First-principles molecular dynamics simulations (FPMD)

Calculations were performed using the two-phase first-principles molecular dynamics (FPMD) method following Y. Zhang and Yin (2012), Y. Zhang and Guo (2009), and Liu et al. (2020), and using the ab-initio total-energy and molecular-dynamics program VASP (Kresse and Furthmüller, 1996). The projector-augmented wave potentials (Blöchl, 1994; Kresse and Joubert, 1999) were employed together with the generalized gradient approximation of the exchange-correlation potential (PAW-PBE) (Perdew et al., 1996), in which 6 valence electrons are considered for O $(2s^22p^4)$, 2 for Mg $(3s^2)$, 14 for Fe $(3p^63d^64s^2)$, 4 for Si $(3s^23p^2)$, 7 for I $(5s^25p^5)$, and 16 for Pu $(6s^26p^66d^25f^47s^2)$. The Plane-wave basis set cutoff was 400 eV. The accuracy for electronic self-consistent iteration was 10^{-4} eV. The Brillouin zone sampling was performed only at the gamma point and Fermi-Dirac smearing was used to consider the temperature effect. Molecular dynamics simulations were performed in the NVT canonical ensemble (i.e., number of atoms, volume, and temperature remain constant during simulation) with a time step of 1 femtosecond. Due to the complex nature of the 5f electron states for Pu, the splitting of the orbital energy level under symmetrical crystal structures might cause spin crossover (Söderlind et al., 2019; Moore and Laan, 2009). However, it would be hard to form symmetrical configuration around Pu in silicate melt or iron metal liquid phases considering the size of Pu. Furthermore, the high pressure and temperature would favor Pu in the nonmagnetic low spin-state even if the 5f could split in liquid (Moore and Laan, 2009). Therefore, in consideration of the of our high computational demands (260 atoms and more than 60,000 steps) FPMD simulations, we did not perform spin-polarized calculations in this work.

The simulation box contained 260 atoms. Oxygen (O), Mg, Fe and Si represent 256 of these atoms, and the other 4 atoms are I or Pu. The relative proportions of O, Mg, Fe and Si were set to match bulk Earth compositional models from McDonough (2014). Most simulations used the the O-rich Earth composition model, which contains 127 O, 51 Mg, 44 Fe, and 34 Si atoms, while the simulation run named 'I3' (see Table 4.1) used the Si-rich Earth composition model, which has same number of Mg and Fe atoms but contains 123 O and 38 Si atoms. The size effect (i.e. number of atoms) has been tested in Y. Zhang and Guo (2009).

The atoms were randomly distributed in a simulation cell and more than 30,000 time steps were used to allow for segregation of liquid iron and silicate melt, and

	liquid iron (mol%)						silicate	melt (me	Oxygen fugacity			
Runs	T(K)	P(GPa)	0	Si	Mg	Fe	Ι	SiO_2	MgO	FeO	Ι	$2\log(X_{\rm FeO}/X_{\rm Fe})$
I1	3641	69.6	10.42	4.84	0.79	79.70	4.24	34.37	54.71	8.67	2.25	-1.93
I2	3450	59.8	11.78	5.11	1.40	78.35	3.36	34.26	54.51	8.57	2.65	-1.92
I3	3247	50.3	3.46	8.78	0.39	85.57	1.80	37.26	56.03	3.25	3.46	-2.84

65

Table 4.1: Results of first-principles molecular dynamics simulations on iodine partitioning.

for the system to reach equilibrium. Another 30,000-50,000 steps were used to calculate the average compositions of the liquid iron and silicate melt phases. For calculating composition of the Fe phase, a polyhedron "alpha shape" (a term used in computational geometry with smaller values of alpha describing more details of an object) was first constructed for the Fe cluster using the randomized incremental algorithm (Clarkson et al., 1993). The alpha shape is derived from the convex hull of iron cluster by using Delaunay triangulation of all Fe atoms, and describes the detail of the iron cluster surface by sifting the Delaunay tetrahedral sets according to the radius of their circumscribed sphere (Fig. 4.1). The periodic boundary condition of the simulation box must be considered here because the iron cluster tends to spontaneously conform to a cylindrical shape, especially at high pressures and temperatures, probably due to a smaller surface area of the cylinder (considering periodic boundary) compared to sphere. Determination of whether an atom (Mg, Si, O, Pu, and I) resided inside the polyhedron was then done using the random ray crossing algorithm (O'Rourke, 1998). More details could be found in Y. Zhang and Yin (2012) and Y. Zhang and Guo (2009).

As discussed in Y. Zhang and Yin (2012), due to the small size of the system size, one needs to consider the surface effect of iron cluster. The surface effect refers to the potential ambiguity in determining whether the iron atoms on the surface of an iron cluster belong to the silicate cluster or the iron cluster. The irregular shape of the Fe cluster makes it difficult to estimate the number of Fe irons in each phase. In keeping with Liu et al. (2020), we used valence balance of the silicate phase to consider this effect. By distinguishing whether an atoms is included in the polyhedron, we already know the number of Si, O, Mg, Pu and I that belong to the iron cluster, $N_{\rm Si}^{Metal}$, $N_{\rm O}^{Metal}$, $N_{\rm Mg}^{Metal}$, $n_{\rm Pu}^{Metal}$, and $N_{\rm I}^{Metal}$, and their numbers in the silicate cluster, $N_{\rm Si}^{Silicate}$, $N_{\rm O}^{Silicate}$, $N_{\rm Mg}^{Silicate}$, $N_{\rm Pu}^{Silicate}$, and $N_{\rm I}^{Silicate}$. Using valence balance in the silicate cluster, we obtain:

$$N_{\rm Fe}^{Silicate} = N_{\rm O}^{Silicate} - 2N_{\rm Si}^{Silicate} - N_{\rm Mg}^{Silicate} - 3/2N_{\rm Pu}^{Silicate},$$
(4.1)



Figure 4.1: Snapshot of atomic configuration in the simulation cell. The iron cluster (large atom symbols) at center marks the liquid metal phase domain and the surrounding area (small atom symbols) is the silicate melt domain. The orange bonds illustrate the surface of the constructed alpha shape of the Fe cluster considering the periodic conditions of the simulation cell. Some Si, O, and Pu atoms (large atom marks) are enclosed in the alpha shape.

where, the valence of Pu in the silicate melt is assumed to be 3 (Hyatt et al., 2014; Vance et al., 2003), and that of iodine is zero (Jackson et al., 2018). Conservation of the number of atoms means that the number of Fe atoms in the iron cluster is then simply:

$$N_{\rm Fe}^{Metal} = N_{\rm Fe}^{Total} - N_{\rm Fe}^{Silicate}.$$
(4.2)

As a result, we know all the numbers of atoms in the two phases at a single snapshot. Here, we use 30,000-50,000 snapshots to calculate the average compositions of the liquid iron and silicate melt phases.

Iodine and plutonium partitioning

Iodine partitioning between silicate melt and iron metal liquid can be described following (Jackson et al., 2018) by reaction:

$$\mathbf{I}^{\text{silicate}} \rightleftharpoons \mathbf{I}^{\text{metal}}.$$
(4.3)

Although IO^{3-} , I_2 and I^- could coexist in the silicate glass (Cicconi et al., 2019), the exchange coefficient of iodine derived by using reaction 4.3 could well describe the

high P - T experiment data (Jackson et al., 2018). The iodine equilibrium exchange partition coefficient (K_d^I) and equilibrium constant (K_I) are defined as:

$$K_d^{\rm I} = \frac{X_{\rm I}^{metal}}{X_{\rm I}^{silicate}},\tag{4.4}$$

$$K_{\rm I} = \frac{\gamma_{\rm I}^{metal} X_{\rm I}^{metal}}{\gamma_{\rm I}^{silicate} X_{\rm I}^{silicate}},\tag{4.5}$$

where X denote mole fraction and γ is the activity coefficient. The natural logarithm of the equilibrium constant K_I is the change in Gibbs free energy, which is:

$$\ln(K_{\rm I}) = -\frac{\Delta H_{\rm I}^0 - T\Delta S_{\rm I}^0 + P\Delta V_{\rm I}^0}{RT} = a_{\rm I} + \frac{b_{\rm I}}{T} + c_{\rm I} \frac{P}{T},$$
(4.6)

where *P* is pressure (in GPa) and *T* is temperature (in K). The parameters *a*, *b* and *c* are related to the changes in the standard state entropy (ΔS_I^0) , enthalpy (ΔH_I^0) and volume (ΔV_I^0) of reactions 4.3. It is noted that equilibrium constants only vary with pressure and temperature, and do not depend on oxygen fugacity conditions. We therefore directly regressed the equilibrium constant (instead of the partition coefficient) as a function of pressure and temperature. Once this functional form has been established, the exchange partition coefficient K_D^I can then be expressed, for any fO_2 condition, as:

$$\ln(K_d^{\rm I}) = \ln(K_{\rm I}) - \ln(\gamma_{\rm I}^{metal}). \tag{4.7}$$

In the above equation, the $\gamma^{silicate}$ term is incorporated into the expression of K_I because activity coefficients in the silicate phase are not strong functions of composition (Fischer et al., 2015) following Jackson et al. (2018). The epsilon formalism of Ma (2001) is used to describe the activity coefficient in the iron-rich metal liquid (the terms of γ_{Fe} and γ_i^0 are also incorporated into parameters *a*, *b*, and *c*):

$$\ln(\gamma_i) = -\epsilon_i^i \frac{1873}{T} ln(1 - X_i) - \sum_{i \neq j} \epsilon_i^j \frac{1873}{T} X_j \left(1 + \frac{ln(1 - X_j)}{X_j} - \frac{1}{1 - X_i} \right) + \sum_{i \neq j} \frac{1873}{T} X_j^2 X_i \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_j} + \frac{X_i}{2(1 - X_i)^2} - 1 \right),$$
(4.8)

where the *i* and *j* are the elements except Fe in iron liquid, and ϵ_i^j is the interaction parameter of elements *i* and *j* at the standard temperature of 1873 K. Under the consideration of the concentration of elements in the metal liquid, ϵ_I^O , ϵ_I^S , and ϵ_I^C are included in the expression of γ_{I}^{metal} . All parameters (i.e. $a_{I} b_{I}$, c_{I} , ϵ_{I}^{O} , ϵ_{I}^{S} , and ϵ_{I}^{C}) were then fitted to exchange coefficients of first-principles calculation and LH-DAC experimental (Jackson et al., 2018) data by the least-square method, and yielded $a_{I} = 1.34 \pm 1.51$, $b_{I} = -(13.4 \pm 4.8) \times 10^{3}$, $c_{I} = 131 \pm 48$, $\epsilon_{I}^{O} = -9.13 \pm 4.16$, and $\epsilon_{I}^{S} = -5.71 \pm 2.29$. Because the model with or without ϵ_{I}^{Si} fits the data equally well based on F-test (probability value: P value > 0.05), ϵ_{I}^{S} was set to 0 in this work. Though the uncentainty of a_{I} is higher than its value, the a_{I} term cannot be neglected because it accounts for the entropy change of reaction (Fischer et al., 2015).

Plutonium partitioning between silicate melt and iron metal liquid can be described as a dissociation reaction:

$$PuO_{3/2}^{\text{silicate}} \rightleftharpoons Pu^{\text{metal}} + 3/2O^{\text{metal}}.$$
(4.9)

As trivalent Pu is verified to be enriched in silicate minerals and glass at high temperature (Hyatt et al., 2014; Vance et al., 2003), we assume Pu to behave similarly in metal-silicate partitioning situations. The plutonium equilibrium exchange partition coefficient (K_d^{Pu}) and equilibrium constant (K_{Pu}) are defined as:

$$K_{d}^{\text{Pu}} = \frac{X_{\text{Pu}}^{metal} (X_{O}^{metal})^{3/2}}{X_{\text{PuO}_{3/2}}^{silicate}},$$
(4.10)

$$K_{\rm Pu} = \frac{\gamma_{\rm Pu}^{metal} X_{\rm Pu}^{metal} (\gamma_{\rm O}^{metal} X_{\rm O}^{metal})^{3/2}}{\gamma_{\rm PuO_{3/2}}^{silicate} X_{\rm PuO_{3/2}}^{silicate}}.$$
(4.11)

Since there are only three FPMD data points for Pu, and no experimental data with detailed composition data to calculate K_d^{Pu} (Seitz et al., 1979), too many parameters would result in over-fitting, and we therefore assumed:

$$\ln(K_d^{\rm Pu}) = \ln(K_{\rm Pu}) = a_{\rm Pu} + \frac{b_{\rm Pu}}{T}.$$
(4.12)

Parameters a_{Pu} and b_{Pu} were fitted to exchange coefficients by the least-square method, and yielded $a_{Pu} = 11.1 \pm 1.1$ and $b_{Pu} = -(56.8 \pm 3.5) \times 10^3$.

In theory, because equilibrium constants do not depend on oxygen fugacity, experiments and FPMD simulations could be performed at any fO_2 conditions and still be used in core-formation modeling. In practice, and to avoid extrapolation, it is preferable to run experiments and FPMD simulations at conditions relvant to the core-formation modeling. This is why our simulations were conducted at fO_2

		liquid iron (mol%)						silicate	melt (mo	Oxygen fugacity		
Runs	T(K)	P(GPa)	0	Si	Mg	Fe	Pu	SiO ₂	MgO	FeO	PuO _{3/2}	$2\log(X_{\rm FeO}/X_{\rm Fe})$
Pu1	2804	24.61	1.02	3.08	0.01	95.50	0.39	35.60	55.47	4.75	4.18	-2.61
Pu2	3450	53.6	9.39	9.13	0.72	79.96	0.80	32.70	55.64	7.68	3.99	-2.03
Pu3	4006	86.1	13.45	8.17	1.56	74.34	2.48	33.55	56.44	6.93	3.08	-2.06

Table 4.2: Results of first-principles molecular dynamics simulations on plutonium partitioning.

values between IW–1.9 and IW–2.9 (Tables 4.1 and 4.2). These values cover the range of values used in typical core-formation models (Dauphas, 2017; Badro et al., 2015; Fischer et al., 2017), and encompass our preferred accretion model whereby Earth mainly accreted from differentiated planesimals thought to be very reduced. That range is similar to the conditions of the more oxidized piston cylinder experiment (IW–1.9) in Jackson et al. (2018), and is only ~1 to 2 log units below (i.e., more reduced than) those of the DAC experiment (IW–0.5 to IW–2.0). Overall, all available data (FPMD and experiments) focused on the quite reducing conditions thought to have been relevant to core formation on Earth (IW–1.5 to IW–2.5; e.g., Fischer et al. (2015) and Righter et al. (2020)). Thus, when possible (i.e., for iodine), all data is considered to build the equilibrium constant fit as function of pressure and temperature.

A final quality control on our simulations was performed by calculating the major element equilibrium constants obtained in our FPMD simulations. As shown in Fig. 4.2, the equilibrium constants for Si, O, and Mg from our new FPMD data are fully consistent with previous FPMD data and experimental data obtained at fO_2 ranging from IW-0.4 to IW-4.0. This excellent agreement further demonstrates (i) the adequacy of our FPMD method, and (ii) the feasibility of regressing equilibrium constant to obtain partition coefficients, even with a limited number of simulations.

Core formation modelling

Core formation was modeled as a multi-stage process during Earth's accretion (Badro et al., 2015; Wade and Wood, 2005). In the fiducial model of this work, the Earth was accreted to its present mass in 0.1 % increments (i.e., 1000 steps). The metal fraction in the impactor was set to 0.325 in the fiducial model. Each impact was assumed to generate a magma ocean at the top of the proto-Earth, within which the metal in the impactor fully equilibrated with the entire magma ocean (including the silicate in the impactor) under the pressure and temperature of the base of the magma ocean (Dauphas and Schauble, 2016; Badro et al., 2015). After equilibrium, the equilibrated liquid metal was assumed to descend rapidly to the



Figure 4.2: Comparison of equilibrium constants from new FPMD simulations with those from previous experiment and FPMD simulations. The central thick straight lines are the fitting equations of equilibrium constant in Liu et al. (2020). The blue open circles are experimental data (Jackson et al., 2018; Blanchard et al., 2017; Mann et al., 2009; Fischer et al., 2015; Wade and Wood, 2005; Siebert et al., 2012; Badro et al., 2016; Badro et al., 2018; Bouhifd and Jephcoat, 2011; Chabot et al., 2005; Chabot and Agee, 2003; Corgne et al., 2008; Geßmann and Rubie, 1998; Hillgren et al., 1996; Ito et al., 1995; Jana and Walker, 1997; Ricolleau et al., 2011; Suer et al., 2017; Tsuno et al., 2013; Du et al., 2017), the blue filled circles are pervious FPMD data (Liu et al., 2020), and the red filled circles are new FPMD data from present study. The equilibrium constants are derived by using exchange coefficients and activity coefficients with $\epsilon_{Si}^{O} = -8.3$, $\epsilon_{O}^{O} = -5.8$ and $\epsilon_{Mg}^{O} = -16.4$. See (Liu et al., 2020) for more details. (a) Equilibrium constant of reaction SiO₂^{Sil} + 2 Fe^{Met} $\approx _2$ FeO^{Sil} + Si^{Met}. (b) Equilibrium constant of reaction FeO^{Sil} \rightleftharpoons Fe^{Met} + O^{Met}. (c) Equilibrium constant of reaction MgO^{Sil} \rightleftharpoons Mg^{Met} + O^{Met}.

core through the solid mantle without further equilibration (Wade and Wood, 2005), and the equilibrated magma ocean mixed with the solid mantle to form a new mantle (Dauphas, 2017). The above assumptions, while necessarily simplistic, were made as extreme examples to enable the expression of the largest core-formation induced I/Pu fractionation. The rationale being that if even such scenario cannot explain the I/Pu contrast between MORBs and OIBs, then more realistic scenarios (e.g., invoking partial equilibration) would not either.

During this incremental accretion process, the pressure at the base of the magma ocean increased with the fraction of mass accreted (f), following (Badro et al., 2015):

$$P = P_{fin} \times f^{3/2},$$
 (4.13)

where P_{fin} is the equilibrium pressure of the magma ocean at the last accretion. Using this equilibrium pressure, the temperature was determined based on a cold liquidus geotherm constructed through the melting of chondritic mantle (Andrault et al., 2011) in the fiducial model. The fraction of mantle mass involved in the magma ocean (f_{mo}) was parameterized as a function of P_{fin} following (Dauphas, 2017):

$$f_{mo} = \frac{r_{earth}^{3} - \left(r_{earth} - (r_{earth} - r_{core}) * \frac{P_{fin}}{P_{CMB}}\right)^{3}}{r_{earth}^{3} - r_{core}^{3}}.$$
 (4.14)

In which, the radius of the Earth (r_{earth}) is 6371 km, the radius of the Earth's core (r_{core}) is 3485 km, and the pressure at CMB (P_{CMB}) is 135 GPa. In the fiducial model, P_{fin} is assumed to be 60 GPa.

During the multi-stage core formation process, the distribution of elements was calculated by mass balance using their partition coefficients. The concentrations of O, Si, Co, Cr, V, and Ni were first derived at each step. The partition coefficient of these elements were taken from Siebert et al. (2012) and Siebert et al. (2013) following Badro et al. (2015). In each accreting building block, the bulk concentrations of these elements (except for O and Fe) relative to Al were those of the bulk Earth's composition assuming 5 wt% Si in core (McDonough and Sun, 1995), following Dauphas (2017). In principle, the oxygen fugacity of the Earth would vary as accretion proceeds due to loss of O to space (Lodders, 2000), which would affect the size of the Earth core (Righter et al., 2020). Since it is hard to precisely evaluate the O escape to space during accretion, to test how oxygen fugacity affects the accretion process, we assume a constant core mass fraction during Earth's accretion and the concentration of O and Fe were instead controlled by predetermined evolution scenarios of the FeO content in the magma ocean. These evolution histories were constructed by linear interpolation between different meteorites as a starting point and present Earth's mantle as an ending point (Fig. 1 in Badro et al. (2015)). The fiducial model used the FeO in EH chondrite as the starting point (Path 2 of Fig. 1 in Badro et al. (2015)). This fiducial model illustrates a scenario in which the Earth started accretion from a plausible reduced redox condition but does not mean that the Earth formed through accretion of EH chondrites. Then, the distribution of Pu and I were determined based on the pressure, temperature and metal compositions for each step using the equilibrium constants obtained in this chapter.

Besides the fiducial model, a series of simulations were performed in which key input parameters were varied to test the sensitivity of these parameters on the simulation outcomes. These runs tested different (i) P_{fin} values (60, 70 and 80 GPa) that determine the equilibrium pressure, (ii) mantle liquidus geotherm (hot (Fiquet et al., 2010) and cold (Andrault et al., 2011)) that determines the equilibrium temperature, and (iii) evolution scenario of FeO content of the magma ocean (Paths 2, 9, 10, 11, 12, 13 and 14 of Fig. 1 in Badro et al. (2015)) that ensure the oxygen fugacity conditions are varied. A special accretion scenario of equilibrium pressure was also constructed to verify whether high pressure episodes in the middle stages of accretion could efficiently fractionate I and Pu. In this scenario, equilibrium pressures during the first 50% of the accretion was the pressure at the CMB of the proto-Earth ($P_{fin} = 135$ GPa) and the pressure during the last 50% accretion linearly decreased from the highest pressure (85 GPa) to a final equilibrium pressure (40 GPa). We also tested whether the change of core size would affect I/Pu fractionation during accretion process. Heterogeneous volatile accretion simulations were performed by multiplying iodine concentration of building block materials in Phase 2 while Pu concentration was assumed to remain constant throughout Earth's accretion.

Meteoritic Xe analysis

Xenon has nine isotopes (i.e., ¹²⁴Xe, ¹²⁶Xe, ¹²⁸Xe, ¹²⁹Xe, ¹³⁰Xe, ¹³¹Xe, ¹³²Xe, ¹³⁴Xe, and ¹³⁶Xe) whose relative abundances represent a mixture of 6 components (Table C.1): (1) spallogenic Xenon (noted here sp), (2) initial or primordial Xenon (init) that can be represented by solar wind or Phase-Q, (3) atmospheric Xenon (air); (4) uranium-fission Xenon (U), (5) plutonium-fission Xenon (Pu), and (6) iodine-decay Xenon. Except for the iodine-decay component, ¹³²Xe is present in all other components. So, we can normalize to ¹³²Xe (avoiding issues from divisions by zero) and decompose the isotopic composition in a sample as the sum of contributions from the first five components as:

$$\begin{pmatrix} {}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{meterorite} = X_{sp} \left({}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{sp} + X_{init} \left({}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{init} + X_{air} \left({}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{air} + X_{Pu} \left({}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{Pu} + X_{U} \left({}^{i}Xe \\ \overline{132}Xe \end{pmatrix}_{U},$$

$$(4.15)$$

where i is 124, 126, 128, 130, 131, 134, or 136, X is the molar proportion of 132 Xe in the sample from each component. For the solution of X to be physically relevant, the following additional constraints are considered:

$$X_{sp} + X_{init} + X_{air} + X_{Pu} + X_U = 1, (4.16)$$

$$\begin{pmatrix} \frac{129}{132} \frac{Xe}{Xe} \end{pmatrix}_{meterorite} \geq X_{sp} \left(\frac{129}{132} \frac{Xe}{Xe} \right)_{sp} + X_{init} \left(\frac{129}{132} \frac{Xe}{Xe} \right)_{init} + X_{air} \left(\frac{129}{132} \frac{Xe}{Xe} \right)_{air} + X_{Pu} \left(\frac{129}{132} \frac{Xe}{Xe} \right)_{Pu} + X_U \left(\frac{129}{132} \frac{Xe}{Xe} \right)_U,$$

$$(4.17)$$

$$0 \le X_j \le 1,\tag{4.18}$$

where *j* is sp, init, air, Pu, and U, respectively. There are five unknowns and seven equations. The linear least-squares solutions to this system of equation with constraints was analytically derived by using the method of Lagrange multipliers. Following Parai and Mukhopadhyay (2015), each endmember and sample isotope ratio was weighted by normalization to the 1σ derivations on the meteorite compositions. Once the solution of the least-squares decomposition was obtained, the ¹²⁹Xe*/¹³⁶Xe*^{Pu} for a given sample was calculated as follows:

$$\frac{129 X e^*}{136 X e^*} = \frac{\left(\frac{129 X e}{136 X e}\right)_{meteorite} - \sum_j X_j \left(\frac{129 X e}{136 X e}\right)_j}{X_{Pu} \left(\frac{129 X e}{136 X e}\right)_{Pu}}.$$
(4.19)

A Monte Carlo method was used to propagate the uncertainties in mixing proportions for each endmember. Specifically, 10^5 Monte Carlo simulations are applied for each sample by repeatedly sampling its compositions based on isotopic values and uncertainties. There are 9 chondrite and 15 achondrites data used in this work (Tables C.1-C.3), and this exercise points to the need for further high-precision Xe isotope investigation of meteorites.

4.3 Results on partitioning coefficient of I and Pu

The FPMD simulations were ran at pressures ranging from 25 to 85 GPa along the mantle liquidus (Andrault et al., 2011). These values were chosen to cover the range of P - T conditions relevant to Earth's accretion according to the current prevailing literature (Badro et al., 2015; Fischer et al., 2017). Each simulation started with 256 Mg, Si, O, and Fe atoms (in proportions reflecting the bulk Earth composition, see Methods) and 4 I or Pu atoms placed randomly in the simulation boxes. After 30,000 steps of equilibration, the atoms are segregated into two phases, a liquid iron phase and a silicate melt phase. A polyhedron "alpha shape" of Fe cluster is constructed to mark the boundary between the two phases (Fig. 4.1). Atomic configurations from the next 30,000-50,000 simulation steps are used to calculate the average compositions of the liquid iron and silicate melt phases (Tables 4.1 and 4.2).

Partitioning of iodine and plutonium between silicate melt and metal liquid takes place according to the reactions (4.3) and (4.9). The corresponding equilibrium

constants, K_{Pu} and K_I , are of the form, $\ln(K) = a + \frac{b}{T} + c\frac{P}{T}$, where *T* is temperature (in K) and *P* is pressure (in GPa), and were derived by fitting the exchange coefficients (K_d) of our data and previous laser-heated diamond anvil cell (LH-DAC) experimental data of iodine (Jackson et al., 2018) using least-squares regression, yielding:

$$\ln(K_{\rm I}) = (1.34 \pm 1.51) - (13.4 \pm 4.8) \frac{1000}{T} + (131 \pm 48) \frac{P}{T}$$
(4.20)

$$\ln(K_{\rm Pu}) = (11.1 \pm 1.1) - (56.8 \pm 3.5) \frac{1000}{T}.$$
(4.21)

The first-principles calculation data we obtained for iodine are fully consistent with previous experimental data (Fig. 4.3a), further justifying the adequacy of our FPMD method for estimating elemental partition coefficients (Y. Zhang and Guo, 2009; Y. Zhang and Yin, 2012). Most importantly, our results show that, like iodine, Pu becomes less lithophile at higher temperature (Fig. 4.3b). This temperature dependency of K_{Pu} is in line with the similar behavior of another actinide, uranium, observed in LH-DAC experiments (Blanchard et al., 2017; Chidester et al., 2022).



Figure 4.3: High-pressure metal-silicate equilibrium constants for iodine and plutonium, as a function of temperature. Filled squares are ab initio data from this study (see Tables 4.1 and 4.1), while open circles denote experimental data from Jackson et al. (2018). The curves are least-square fits to all available data using Eq (4.20) and (4.21). (a) Equilibrium constant of iodine, all data are corrected to the cold mantle liquidus geotherm constructed through the melting of chondritic mantle (Andrault et al., 2011). (b) Equilibrium constant of plutonium. The P - T conditions of the FPMD simulations were chosen to be most relevant to the accretion model and avoid extrapolation.

4.4 I/Pu partitioning during core formation and mantle ¹²⁹Xe*/¹³⁶Xe*^{Pu} observations

Both I and Pu tend to partition into the metal phase under high pressures and temperatures relevant to core formation (Fig. 4.3). However, given that the I and Pu partition coefficients ($D = X_{metal}/X_{silicate}$) have different $P - T - X_{O}^{metal}$ (oxygen molar fraction in metal phase) dependency (Fig. 4.4 and 4.5), the silicate mantle would lose I and Pu to the core in variable proportions during metal-silicate equilibration events. To assess whether core formation could sufficiently fractionate I and Pu to explain the ¹²⁹Xe*/¹³⁶Xe*^{Pu} offsets between the OIB and the MORB mantle sources, we run a series of multistage core-formation simulations (Badro et al., 2015), whose results would be discussed in the following sections.

As the criteria for identifying the Earth accretion and core formation scenarios, the extent of I/Pu difference between the deep and shallow mantle reservoirs underlying the observation of 129 Xe*/ 136 Xe* Pu must be clarified. To explain the lower 129 Xe*/ 136 Xe* Pu in the plume mantle, a factor of 2.8 depletion of I/Pu would be required, assuming a synchronous closure time of Xe loss for the whole mantle (Parai and Mukhopadhyay, 2015; Jackson et al., 2018). This is a conservative assumption because (i) prolonged Xe loss from the mantle to the atmosphere would tend to decrease the upper mantle 129 Xe*/ 136 Xe* Pu and require an even higher initial I/Pu ratio in the upper mantle to account for the observed contrast between MORB and OIB 129 Xe*/ 136 Xe* Pu ratios (Mukhopadhyay and Parai, 2019), and (ii) a later closure time of the plume mantle source compared to the upper mantle would be physically difficult to explain.

4.5 Homogeneous volatile accretion

First, we assume a homogeneous volatile accretion scenario, meaning that in each simulation all building blocks are assumed to have the same I/Pu ratio (i.e., volatile content). Equilibrium pressure, temperature and oxygen fugacity during accretion were varied to test the sensitivity of the simulation outcomes (Figs. 4.6-4.9). Under the assumption of homogeneous volatile accretion (i.e., constant I/Pu in Earth's building blocks), we find that core formation processes do not result in substantial fractionation of I from Pu in Earth's mantle. Indeed, I and Pu partition into the metal phase very similarly during core formation processes (e.g., Fig. 4.6a and Fig 4.10), and mantle I/Pu ratios barely vary during accretion, with the mantle I/Pu ratio of the fully accreted Earth being only 8% lower than that of the initial proto-mantle (Fig. 4.6b). This is the case, even when the equilibrium pressure



Figure 4.4: Metal-silicate partition coefficients for iodine and plutonium as a function of temperature at different $P - T - X_{O}^{metal}$ conditions. Partition coefficients $(D = X_{metal} / X_{silicate})$ for iodine (solid lines) and plutonium (dashed lines) are derived from equilibrium constants for given $P - T - X_{O}^{metal}$ conditions. The pressures and temperatures are connected by either a cold liquidus geotherm (a, b) using chondritic mantle composition (Andrault et al., 2011), or and a hot liquidus geotherm (c, d) constructed by peridotite (Fiquet et al., 2010) which was used in Jackson et al. (2018). X_{Ω}^{metal} is set to be 3 mol% (a, c) and 30 mol% (b, d). The 3 mol% and 30 mol% oxygen in metal correspond to ~1 wt% and 10 wt%, respectively, and cover the range of oxygen concentration consistent with the seismic observations (Badro et al., 2015; Umemoto and Hirose, 2020). Measured D values from this study and previous experimental study (Jackson et al., 2018) are corrected to the given X_{O}^{metal} and the mantle liquidus geotherm according to temperature. It is noted that X_{Ω}^{metal} would change with pressure and temperature during core formation processes. In the more realistic cases, the partition coefficients would evolve with the mass accreted to the Earth considering core formation modelling

of last accretion is assumed to be the upper bound (80 GPa) needed to generate a distribution of other moderately siderophile elements (e.g., Ni, V, Co, and Cr) consistent with observations (Badro et al., 2015) (Fig. 4.7). Even assuming an



Figure 4.5: Metal-silicate partition coefficients for iodine and plutonium as a function of pressure at different $P - T - X_O^{metal}$ conditions. Symbols, notations and assumptions as on Figure 4.4. Measured *D* values from this study and previous experimental study (Jackson et al., 2018) are corrected to the given X_O^{metal} and the mantle liquidus geotherm according to pressure.

extreme accretion scenario with higher equilibration pressure in the middle stage of accretion compared to the late stages (Jackson et al., 2018), the maximum difference between the accreting and the final mantle I/Pu ratios is only ~25 % (Fig. 4.7.b and c). As such, the isotopic Xe signature in the plume mantle source is unlikely to be readily explained by episodes of a high equilibrium pressure during any stage of a homogeneous accretion.

The above calculations were run assuming accretion starting from reduced building materials, but changes in oxygen fugacity during accretion (simulated here using prescribed evolution curves for the FeO content of the magma ocean (Badro et al., 2015) could have a notable effect on the I/Pu ratio of the mantle of the proto-earth (Fig. 4.8). This effect of changes in fO_2 depends on the assumed T of metal-silicate equilibration. When equilibration occurs along the mantle liquidus geotherm based



Figure 4.6: Changes in I and Pu partitioning behaviors and their impact on the I/Pu of Earth's reservoirs as a function of the mass accreted to the Earth. (a) Partition coefficients ($D = X_{metal}/X_{silicate}$) of Iodine and Plutonium between silicate melt and metal liquid during core formation processes. The simulation used the fiducial multi-stage model (i.e., cold liquidus geotherm, 60 GPa maximum pressure and reduced conditions, see Methods for details). Based on these partition coefficients, change in the I/Pu ratio in terrestrial reservoirs was calculated assuming (b) a homogeneous and (c) a heterogeneous volatile accretion scenario. In (b) all materials accreted to the Earth have identical I/Pu ratio, and core formation results in nearly invariant mantellic (mantle and silicate melt in magma oceans) I/Pu ratios during accretion. The high I/Pu in metal fractions (core and liquid metal in magma oceans) rule out a core/metal contribution to the plume mantle as the source of the low ¹²⁹Xe*/¹³⁶Xe*^{Pu}. The I/Pu ratios (y-axis) are normalized to the bulk I/Pu ratio of the building block materials. In (c) materials in the later stages of accretion (Phase 2) are enriched in iodine compared to those in the earlier stages of accretion (Phase 1, see enrichment factor on each colored curve). The y-axis shows the mantle I/Pu ratio normalized to the bulk I/Pu ratio of the material accreted during Phase 1. Accretion of volatile-enriched materials in Phase 2 can result in an increase in I/Pu ratio in the final mantle relative to the mantle at the end of Phase 1 by a factor 2.8 (horizontal dashed line) or more, which is the lowermost value needed to explain the 129 Xe*/ 136 Xe* Pu offsets between the MORBs and OIBs.

on the melting of a chondritic mantle (cold liquidus geotherm hereafter) (Andrault et al., 2011), the I/Pu ratio for Earth's mantle monotonically decreases throughout Earth's accretion (Fig. 4.8a). Regardless of the oxygen fugacity conditions, under the cold liquidus geotherm, isolation of an early formed mantle reservoir would yield higher I/Pu ratio in OIBs than MORBs, the opposite to what is observed. In contrast, at the very high temperatures following the liquidus geotherm constructed through the melting profiles of peridotite (hot liquidus geotherm hereafter) (Fiquet et al., 2010), and for the most oxidized evolution scenarios ($Log(fO_2) \sim IW-0.6$, where IW is the iron-wüstite buffer), metal-silicate equilibration would lead to a 4.5 times



Figure 4.7: Pressure and temperature sensitivity tests for homogeneous volatile accretion scenarios. Model runs assume a reduced oxygen fugacity condition in which the FeO concentration in the magma ocean linearly increase with mass fraction accreted to the Earth from 0.6 mol% to 5.8 mol% (Path 2 of Fig.1 in ref. (Badro et al., 2015). Materials accreted to the Earth have identical I/Pu ratios during all stages of accretion. (a) Equilibrium pressures as a function of mass fraction accreted, for different accretion scenarios. The red, yellow, and blue lines are three examples of incrementally increasing equilibrium pressure with different final pressures (P_{fin}). The green line is an example of accretion scenario in which equilibrium pressures during the first 50% of Earth's accretion is the pressure at the CMB of the proto-Earth and the pressure during the last 50% of Earth's accretion linearly decreases from 85 GPa to 40 GPa. (b-c) Variations of the mantle I/Pu ratio (normalized to the I/Pu ratio of the bulk accretion materials) as a function of the mass fraction accreted assuming an equilibrium temperature that follows (b) the cold liquidus geotherm constructed through the melting of chondritic mantle (Andrault et al., 2011), or (c) the hot liquidus geotherm based on the melting profiles of peridotite (Fiquet et al., 2010). Curves color coded as in (a).

lower I/Pu ratio in the middle stages of accretion compared to the final mantle (Fig. 4.8b). If some part of the mantle in this intermediate stage was not involved in the subsequent accretion process and preserved throughout Earth's history, these relics of proto-Earth mantle could explain the lower 129 Xe*/ 136 Xe* Pu in the plume mantle. However, elemental and isotopic evidence suggest that Earth mainly accreted under less oxidizing conditions (i.e., between IW-4.5 and IW-1.5) (Dauphas, 2017; Rubie et al., 2011; Labrosse et al., 2015; Fischer et al., 2017; Righter et al., 2020), not to mention that accretion under oxidizing conditions would yield



Figure 4.8: Variations of the mantle I/Pu ratio as a function of the mass fraction accreted to the Earth under homogeneous volatile accretion scenarios for different fO_2 conditions and equilibrium T. In all runs the equilibrium incrementally increases to a final value of 60 GPa, and materials accreted to the Earth have identical I/Pu ratios during all stages of accretion. Colors denote the predetermined oxygen fugacity evolution scenarios of the FeO concentration in the magma ocean, which are constructed by linear interpolation between different meteorites compositions (i.e., EH chondrites (initial redox: IW-4.5), H chondrites (IW-1.4), HED chondrites (IW-1.3), L chondrites (IW-1.2), LL chondrites (IW-1.0), CV chondrites (IW-0.8), and CI chondrites (IW-0.6)) as a starting point and the present Earth's mantle as an ending point (Paths 2, 9, 10, 11, 12, 13, and 14 of Fig.1 in Badro et al. (2015)). These models illustrate scenarios in which the Earth started accretion under the entire plausible range of redox conditions, but does not mean that the Earth formed by accretion of the type of meteorites in the legend. (a-b) Variations of the mantle I/Pu ratio (normalized to the I/Pu ratio of the bulk accretion materials) for different evolution scenario of FeO content in the magma ocean and an equilibrium temperature following (a) the cold liquidus geotherm (Andrault et al., 2011), and (b) the hot liquidus geotherm Fiquet et al. (2010). Though the composition of peridotite cannot reflect the bulk mantle, its melting profile could represent the upper-limit of equilibrium temperatures during core formation. It is noted that the change of core size would also affect the oxygen fugacity during accretion process. However, our result shows that core size would not have notable impact on I/Pu differentiation, and thus the change of impactor core fraction during accretion does not affect our result (Fig. 4.11).

a much smaller terrestrial core than observed (Righter et al., 2006). Considering only the plausible range of oxygen fugacity relevant to Earth's accretion (starting from a value between IW-4.5 and IW-1.5), even in the hot liquidus geotherm case, our simulations reveal that iodine is unlikely to be sufficiently fractionated from Pu



Figure 4.9: Variations of I/Pu ratio with mass fraction accreted to the Earth under homogeneous and heterogeneous accretion scenarios in an equilibrium temperature that follows hot liquidus geotherm. Same as Fig. 4.6 in the main text, except simulations are made under an equilibrium temperature that follows the hot liquidus geotherm. (a) Though the composition of peridotite cannot reflect the bulk mantle, its melting profile could represent the upper-limit of equilibrium temperatures during core formation. The lowermost I/Pu ratio of magma ocean metal (0.55), which is twice lower compared to the mantle during the late stages of accretion (~1.1), could be treated as the lower limit for the I/Pu ratio in the liquid metal droplet that never settled to the Earth's core. (b) In the later stages of accretion (Phase 2), iodine content in the material accreted to the Earth are higher (see enrichment factor on each colored curve) than during the earlier stages of accretion (Phase 1).

during a homogeneous volatile accretion to explain the 2.8 times lower I/Pu recorded in the plume mantle (Fig. 4.8b).

Incorporation of intrusions from Earth's liquid outer core and/or suspended liquid metallic droplets into part of the silicate mantle has been proposed as the possible source of the plume mantle (Mundl et al., 2017). If metal-silicate equilibration happened at temperatures following the cold liquidus geotherm, both Earth's core and the liquid metal in the magma ocean would have consistently higher I/Pu ratios than the values in the bulk mantle (Fig. 4.6b). In this scenario, any core/metal contribution to the plume mantle would lead to a higher ¹²⁹Xe*/¹³⁶Xe*^{Pu} after decay of ¹²⁹I and ²⁴⁴Pu, again opposite to what is observed between MORBs and OIBs. Accretion under the hot liquidus geotherm, treated as the upper limit for the equilibrium temperatures, can produce I/Pu ratio 2 times lower in the magma ocean liquid metal (i.e., the metal after silicate-metal equilibration but before segregation



Figure 4.10: Variations of I and Pu partitioning between silicate melt and metal liquid as a function of the mass accreted to the Earth. (a-b) The simulations are made under the fiducial model as described in the Methods. (c-d) The simulations are made assuming an episode of high-pressure equilibration in the middle of Earth's accretion (green line in Fig 4.7.a). The pressures and temperatures during accretion processes are connected following (a,c) the cold liquidus geotherm (Andrault et al., 2011) and (b,d) the hot liquidus geotherm (Fiquet et al., 2010). The solid lines are I partition coefficients, and the dashed lines are Pu partition coefficients. Both I and Pu become less lithophile (D values approaches 1) as equilibration pressure increasing, and even become moderately siderophile at highest equilibration pressure (D values above 1).

into the Earth's core) or in the proto-core compared to the mantle during the middle and late stages of accretion (Fig. 4.9). This value is only 30% lower than the factor of 2.8 difference observed between OIBs and MORBs but assumes that the plume mantle Xe derives entirely from the core/metal. In the much more likely scenario where the plume mantle initially contained some Xe, incorporation of Xe from the metal/core could not produce the 2.8 times offset observed between the MORB and plume mantle reservoirs. Overall, these results suggest that the Xe anomalies in the plume mantle are unlikely to be due to incorporation of Xe from the core and/or the



Figure 4.11: Variations of the mantle I/Pu ratio as a function of the mass fraction accreted to the Earth under homogeneous volatile accretion scenarios for different metal fraction in the impactor (f_{core}). The simulations are made based on the fiducial model as described in the Methods. This figure shows that changes in the f_{core} of impactors and the accreting Earth would only marginally impact the I/Pu ratio during differentiation (less than 20%). As such, changes in impactor core fraction during accretion do not affect the results presented in this work.

presence of suspended droplets of magma ocean metal liquids that never settle to the Earth's core (Mundl et al., 2017; Z. Zhang et al., 2016).

4.6 Heterogeneous volatile accretion

We now consider a scenario of heterogeneous volatile accretion with core formation processes, whereby the volatile content (i.e., I/Pu ratio) of Earth's building blocks is no longer kept constant over time. Moderately volatile siderophile elements in the Earth's mantle suggest that volatile elements may be delivered to the Earth in the later stages of the accretion process (Rubie et al., 2011; Schönbächler et al., 2010; Mann et al., 2009; Wang et al., 2013), implying that the material accreted to Earth during early stages of accretion (Phase 1) likely had a lower I/Pu ratio than material accreted in the later stages of accretion (Phase 2) (see Fig 4.6c). Specifically, our Phase 2 not only includes the later stage of core formation process but also the late veneer (i.e., the last ~0.5% mass of accretion that dominates the highly siderophile element budget of the bulk silicate Earth), as they are thought to have delivered

the same volatile-rich (high I/Pu ratio) building block materials to Earth (Dauphas, 2017). It is important to note that the late veneer does not participate in the core formation process, and the additional volatiles it delivers are directly added to the mantle. In such heterogeneous accretion scenarios, the I/Pu ratio in Earth's mantle at the end of its accretion history (end of Phase 2) could be much higher than the I/Pu ratio in the proto-Earth mantle at the end of Phase 1. At the core mantle boundary (CMB), a small portion of the proto-Earth mantle before addition of volatile-rich material, if isolated from the subsequent accretion process and Earth's dynamical evolution (Mundl et al., 2017; Peters et al., 2018; Hyung and Jacobsen, 2020) thereafter, could be the source of the depleted I/Pu mantle reservoirs sampled by OIBs (Fig. 4.6c), while the rest of the mantle enriched by the subsequent Phase 2 accretion processes would represent the reservoirs with higher I/Pu ratio sampled by MORBs.

Figure 4.6c shows an illustrative calculation of a heterogeneous volatile accretion history where addition of volatile-rich materials (with high I/Pu) starts after 60 % of Earth's accretion. In this example, the material accreted in Phase 2 only needs to have ~ 6 times higher I/Pu than that accreted in Phase 1 to explain the ¹²⁹Xe*/¹³⁶Xe*^{Pu} contrast between OIBs and MORBs. Evidently, onset of Phase 2 at a later time would require a higher I/Pu in the late accreted material to still explain the 2.8 times difference in Xe isotope ratios between MORBs and OIBs. The relationship between the timing of onset of Phase 2 (no later than 99.5 wt% Earth's final mass accreted as it includes late veneer) and the mantle's I/Pu enrichment (i) after core formation processes (which could be treated as the endmember scenario in which the late veneer happened after ¹²⁹I extinction and cannot deliver any ¹²⁹Xe to the Earth) and (ii) after the entire accretion history are respectively shown in Fig. 4.13 and Fig. 4.12, along with independent constraints on these variables. Though some earlier works suggested that a large fraction (30-40 wt%) of Earth's building blocks were volatile-rich, recent estimates (Burkhardt et al., 2021) based on a multielement comparison between the isotopic composition of bulk Earth and meteorites indicate that volatile-rich materials account for $< \sim 15$ wt% of the bulk Earth, and most likely only ~4 wt%. On Figure 4.12, the full range of allowable mass fraction of accretion of volatile-rich materials is thus shown to the right of the grey vertical line, and reveals that I/Pu ratios in Phase 2 materials must be more than an order of magnitude higher than in Phase 1 materials to explain the minimum I/Pu differences between MORBs and OIBs (horizontal black line).



Figure 4.12: Final MORB mantle's I/Pu ratio (normalized to the mantle I/Pu at the end of Phase 1) as a function of the starting time of Phase 2 of accretion. Each curve represents a different extent of iodine enrichment (curve labels) in the Phase 2 materials relative to Phase 1 materials. As Phase 2 includes late veneer (last 0.5 wt% of accretion process), its starting time should be earlier than 99.5 wt% of Earth's final mass accreted. Simulations conditions as in Figure 2. The horizontal black line denotes a I/Pu ratio in the final mantle that is 2.8× higher than at the end of Phase 1. The vertical lines shows the upper limit (15 wt%) on the mass fraction of volatile-rich material accreted by the Earth late in its history, as constrained by nucleosynthetic anomalies data (ε Mo, and correlations with ε Cr, ε Nd, and ε Zr) on meteorites (3). Large I/Pu enrichments in the MORB mantle (compared to the mantle at the end of Phase 1) are only achieved if volatile-poor, differentiated planetesimals (with I/Pu ratios 40 to 7500× lower than chondrites, Tables S4-5 of Liu et al. (2023)) constitute the main building blocks of the Earth during Phase 1 (blue area). In contrast, accretion histories involving undifferentiated chondrites (whose I/Pu ratios only differ by a factor of ~ 10, Tables S4-5 of Liu et al. (2023)) as the main material in Phase 1 (red area), fail to yield a $2.8 \times$ difference in mantellic I/Pu ratio. To date, there are no known planetary materials with I/Pu enrichment between 12-40× (Tables S4-5 of Liu et al. (2023)) although such materials could produce large I/Pu enrichments in the MORB mantle.

The high iodine enrichment, relative to Pu, in Phase 2 materials indicates that accretion histories for the Earth involving only chondrites are very unlikely. Indeed, deconvolving I-decay and Pu-fission Xe from thoroughly compiled available Xe isotopic data of different meteorites (Table C.1) only suggests a small range (within a factor ~10) of 129 Xe*/ 136 Xe* Pu among chondrites (Tables C.2–C.3). Independently, the latest data in carbonaceous, enstatite and ordinary chondrites shows that iodine abundances do not vary significantly across the board (Clay et al., 2017), and the



Figure 4.13: Mantle's I/Pu ratio right after core formation processes (normalized to the mantle I/Pu at the end of Phase 1) as a function of Phase 2 starting time. The mantle's I/Pu ratio after core formation could be treated as the endmember scenario in which late veneer happened after 129I extinction and cannot deliver any ¹²⁹Xe to the Earth. The simulations conditions and the meaning of curves are same as that in Figure 4.12.

vast majority have iodine content within a factor 10 of each other (Bekaert et al., 2020). Finally, while some studies also suggested that comets could accrete to the Earth during late veneer (Dauphas et al., 2000; Marty et al., 2017), the fact that the iodine content of comets (67 P/C-G) appears to be of same order of magnitude as that of chondrites (Clay et al., 2017; Bekaert et al., 2020; Marty et al., 2017), further strengthen the conclusion that chondrites are very unlikely to be the primary building block materials during Phase 1.

4.7 Accretion model of differentiated planetesimal

Compared to chondrites, achondrites have 40-7500 times lower ¹²⁹Xe*/¹³⁶Xe*^{Pu} (Tables S4-5 of Liu et al. (2023)), and thus much lower I/Pu ratios. This high extent of iodine deficiency compared to plutonium in achondrites is in line with the idea that most parent bodies of achondrites are highly volatile depleted and refractory enriched (Halliday and Porcelli, 2001). In a scenario where the parent bodies of achondrites represent Earth's main building blocks in Phase 1, the Xe isotopic offsets between MORBs and OIBs can be readily generated by late accretion of any type of chondrites. Most achondrites originated from volatile-depleted and refractory-enriched asteroids (Halliday and Porcelli, 2001), which are themselves the remnants of differentiated planetesimals. Meanwhile, volatile-poor differentiated

planetesimals have been suggested to be the archetypal first-generation planetary embryos formed in the innermost Solar System within < 2 Myr of its formation (as defined by the age of Calcium, Aluminum-rich inclusions) (Tissot et al., 2022). Our results thus support a heterogeneous accretion history of the Earth, whereby earlyformed, volatile-poor differentiated planetesimals represent Earth's main building blocks (Fitoussi et al., 2016) (> 85%), and chondrites, which are comparatively volatile-rich, represent late-accreted materials and only account for a small fraction (< 15%) of Earth's mass (Fig. 4.14).

Isotopic constraints indicate that Earth accreted from both NC (non-carbonaceous, volatile-poor inner solar system material) and CC (carbonaceous, volatile-rich outer solar system material) materials (Burkhardt et al., 2021; Johansen et al., 2021). Our results further suggest that the NC material primarily consists of early differentiated planetesimals so as to create large enough volatile difference among Earth's building blocks. Because silicon preferentially partitions into the Earth's core over magnesium at high pressure, the Mg/Si ratio in the mantle would increase during the accretion process (Fig. 4.15). As a result, at the CMB, the portion of proto-Earth mantle isolated from the later stages of accretion would have a higher viscosity (due to lower Mg/Si ratio) compared with the final mantle (Ballmer et al., 2017): a feature that could help preserve the chemical records of early accretion of volatile-poor differentiated planetesimal at the base of the mantle until today. Our heterogeneous accretion model also readily explains the fact that present-day plume mantle reservoirs have a uniformly low ratio of potassium (a volatile, incompatible element) over uranium (a refractory, incompatible element) compared to the MORB mantle, without resorting to complex geochemical or geodynamical processes such as crust recycling or mantle convection (Arevalo et al., 2009; Nielsen, 2010). Finally, our model sheds light on the origin of Earth's water, as it requires that chondrites represent the main material delivered to Earth in the last 1 to 15% of its accretion (Burkhardt et al., 2021; Fitoussi et al., 2016). Independent constraints from Mo nucleosynthetic anomalies require such late accreted materials to come from the carbonaceous supergroup (Burkhardt et al., 2021). Taken together, these results indicate that carbonaceous chondrites must have represented a non-negligible fraction of the volatile-enriched materials in Phase 2 and thus play a substantial role in the water delivery to Earth. This is in agreement with recent evidence from H and N isotopes that independently point to delivery of 4-15 % of CI-like materials to the Earth during the late stages of accretion (Piani et al., 2020). A coherent picture is therefore emerging where Earth accreted mostly dry and gained its water and



Phase 1: Continuous accretion of differentiated planetesimals

Figure 4.14: Schematic representation of the heterogeneous accretion history of the Earth that is consistent with the more siderophile behavior of I and Pu at high P - T conditions (this work). As core formation alone does not result in I/Pu fractionations sufficient to explain the ~ 3 times lower 129 Xe*/ 136 Xe* Pu ratio observed in OIBs compared to MORBs (Fig. 4.6b), a scenario of heterogeneous accretion has to be invoked in which volatile-depleted differentiated planetesimals constitute the main building blocks of the Earth for most of its accretion history (Phase 1), before addition of, comparatively, volatile-rich undifferentiated materials (chondrite and possibly comet) during the last stages of accretion (Phase 2). Isolation and preservation, at the CMB, of a small portion of the proto-Earth mantle before addition of volatile-rich material would explain the lower I/Pu ratio of plume mantle, while the mantle involved in the last stages of the accretion would have higher, MORB-like, I/Pu ratios. Since the low I/Pu mantle would also have an inherently lower Mg/Si (Fig. 4.15), its higher viscosity could help to be preserved at the CMB until today.

volatiles only late in its accretion history, highlighting the impact that small differences in formation history (e.g., changes in the nature of minor building blocks) can have on a planet's evolution and habitability.



Figure 4.15: Variations of mantle Mg/Si ratio as a function of the mass fraction accreted to the Earth. The simulation is made under the fiducial model as described in Methods. Si enters the metallic core at high P - T equilibration, and thus results in a high Mg/Si mantle during the late stage of accretion.

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Chapter 5

THE PARTITION COEFFICIENTS OF SAMARIUM AND NEODYMIUM BETWEEN SILICATE MELT AND METAL LIQUID

[This chapter is temporarily embargoed.]

Appendix A

SUPPLEMENTARY TABLES FOR CHAPTER II

Table A.1: DFT data of pure iron used for pressure correction based on DAC experiments (Kuwayama et al., 2020).

P (GPa)	<i>T</i> (K)	ρ (Mg/m ³)	ρ (Mg/m ³)	V (Å ³)	$P_{\rm DFT}$ (GPa)
		(Exp.)	(Fit)	(per 108 atoms)	
21.5	2600	7.91	7.98	1266.17	-1.06
31.3	2870	8.24	8.30	1215.46	8.37
40.6	2880	8.64	8.59	1159.19	19.10
40.7	3060	8.48	8.66	1181.06	16.82
52.7	3250	8.93	8.93	1121.54	31.14
52.8	3340	9.19	8.88	1089.81	40.94
68.5	3530	9.32	9.31	1074.61	48.47
69.8	3540	9.30	9.37	1076.92	47.66
73.8	3630	9.53	9.42	1050.93	56.92
106.3	4250	10.01	10.07	1000.54	84.04
116.1	4350	10.10	10.24	991.62	89.42

<i>T</i> (K)	a (Å)	$V(Å^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	$P_{\rm raw}$ (GPa)	$E_{\rm raw}~({\rm eV})$
Fe ₁₀₈													
4000	9.4	830.584	212.98	1.96	4000.00	7.45	-555.85	4.90	3.83	24.02	9.32	207.64	-599.84
4000	9.5	857.375	186.63	2.12	4000.21	80.24	-580.31	5.31	4.48	28.25	10.84	177.60	-622.93
4000	9.6	884.736	164.40	1.93	4000.36	94.05	-604.33	4.80	3.74	23.02	8.91	153.59	-645.26
4000	9.7	912.673	144.58	2.04	4000.85	153.27	-622.92	5.32	4.16	28.28	10.13	131.96	-661.80
4000	9.8	941.192	127.81	1.99	4000.71	128.56	-639.75	5.21	3.97	27.11	9.80	113.42	-676.23
4000	9.9	970.299	113.56	1.99	4000.67	148.12	-652.81	5.12	3.98	26.23	9.52	97.49	-686.52
4000	10.0	1000.000	99.34	2.26	4000.90	168.27	-665.49	5.85	5.10	34.26	12.39	81.72	-696.07
4500	9.2	778.688	283.15	2.28	4499.97	5.20	-468.40	5.80	5.18	33.61	12.87	278.77	-514.27
4500	9.3	804.357	247.94	2.22	4500.00	4.77	-508.07	5.66	4.94	32.01	12.27	242.16	-553.13
4500	9.4	830.584	220.28	2.36	4500.01	5.22	-530.34	5.99	5.56	35.88	13.78	212.94	-574.33
4500	9.5	857.375	193.04	2.30	4500.02	4.22	-556.96	5.83	5.30	34.01	13.15	184.00	-599.58
4500	9.6	884.736	171.20	2.36	4500.02	4.44	-579.99	5.88	5.59	34.57	13.62	160.38	-620.92
4500	9.7	912.673	150.92	2.09	4500.06	46.15	-599.46	5.17	4.37	26.77	10.50	138.30	-638.34
4500	9.8	941.192	132.90	2.25	4500.00	3.76	-619.72	5.53	5.07	30.55	12.15	118.51	-656.20
5000	9.1	753.571	327.36	2.46	5000.01	5.28	-406.88	6.71	6.05	44.98	15.89	324.17	-453.34
5000	9.3	804.357	255.45	2.59	5000.00	4.81	-480.93	7.03	6.73	49.45	17.81	249.68	-525.99
5000	9.4	830.584	225.86	2.36	5000.02	4.93	-509.40	5.98	5.56	35.71	13.65	218.52	-553.39
5000	9.5	857.375	199.31	2.32	5000.01	5.00	-533.87	5.92	5.39	35.03	13.38	190.27	-576.50
5000	9.6	884.736	176.86	2.47	5000.02	5.37	-558.37	6.20	6.09	38.48	14.97	166.05	-599.30
5000	9.7	912.673	156.25	2.17	5000.01	7.67	-578.85	5.25	4.69	27.61	11.04	143.63	-617.73

Table A.2: Ab initio simulation results for reference metals.

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	$\sigma_T(\mathbf{K})$	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	$P_{\rm raw}$ (GPa)	$E_{\rm raw}~({\rm eV})$
5500	9.0	729.000	375.91	2.99	5500.01	5.78	-341.43	8.17	8.91	66.77	23.89	373.67	-388.31
5500	9.1	753.571	333.43	2.81	5500.00	5.60	-384.70	8.12	7.90	65.97	22.32	330.23	-431.17
5500	9.2	778.688	295.29	2.67	5499.98	5.13	-423.48	6.96	7.15	48.41	18.17	290.91	-469.35
5500	9.3	804.357	261.43	2.42	5500.01	4.85	-458.94	6.41	5.87	41.07	14.96	255.66	-504.00
5500	9.4	830.584	231.99	2.32	5500.00	4.79	-486.69	6.03	5.38	36.35	13.51	224.65	-530.68
5500	9.7	912.673	162.34	2.62	5500.02	4.60	-555.85	6.45	6.88	41.56	16.55	149.72	-594.73
6000	9.0	729.000	383.00	2.68	6000.00	5.87	-315.80	7.48	7.16	55.98	19.25	380.77	-362.68
6000	9.1	753.571	339.78	3.02	6000.01	5.74	-360.77	8.42	9.14	70.96	24.85	336.58	-407.23
6000	9.2	778.688	302.37	2.78	5999.98	5.50	-398.15	7.78	7.73	60.59	21.08	297.98	-444.03
6000	9.3	804.357	267.65	2.85	6000.00	4.90	-435.81	7.42	8.15	55.10	20.74	261.88	-480.87
6000	9.4	830.584	237.59	3.07	5999.99	4.64	-464.85	7.82	9.42	61.10	23.54	230.25	-508.84
6000	9.7	912.673	167.16	2.44	5999.99	3.89	-535.99	6.17	5.97	38.06	14.62	154.54	-574.88
Fe ₉₀ Ni	18												
4000	9.4	830.584	214.02	2.07	4000.25	77.79	-505.06	5.16	4.29	26.63	10.33	206.68	-549.05
4000	9.5	857.375	188.90	2.08	4000.37	99.01	-528.14	5.37	4.33	28.86	10.76	179.86	-570.76
4000	9.6	884.736	165.55	2.01	4000.52	121.63	-553.98	5.11	4.02	26.12	9.69	154.74	-594.90
4000	9.7	912.673	145.61	2.09	4000.90	152.26	-572.94	5.39	4.37	29.01	10.51	132.99	-611.82
4000	9.8	941.192	129.52	2.10	4001.10	186.46	-588.15	5.53	4.40	30.60	10.60	115.13	-624.63
4000	9.9	970.299	114.62	2.06	4001.82	221.59	-603.32	5.87	4.23	34.49	10.87	98.55	-637.03
4000	10.0	1000.000	101.42	2.03	4002.26	261.05	-615.65	5.92	4.12	35.06	10.36	83.80	-646.24
4500	9.2	778.688	282.39	2.35	4499.99	10.31	-420.19	6.08	5.51	36.93	13.91	278.00	-466.07
4500	9.3	804.357	250.08	2.31	4500.00	14.60	-452.07	6.02	5.33	36.19	13.53	244.31	-497.13
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Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	T _{DFT} (K)	σ_T (K)	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
4500	9.4	830.584	221.77	2.26	4500.03	20.71	-478.98	5.56	5.11	30.94	12.23	214.43	-522.97
4500	9.5	857.375	194.96	2.16	4500.02	27.42	-506.40	5.42	4.66	29.38	11.33	185.92	-549.03
4500	9.6	884.736	172.44	2.18	4500.08	37.15	-529.72	5.39	4.76	29.08	11.42	161.63	-570.65
4500	9.7	912.673	152.26	2.25	4500.08	48.69	-548.84	5.43	5.07	29.47	11.83	139.64	-587.72
4500	9.8	941.192	135.57	2.29	4500.11	62.37	-565.84	5.85	5.27	34.16	12.98	121.18	-602.31
5000	9.1	753.571	328.36	2.69	5000.01	5.73	-354.09	6.95	7.24	48.29	18.28	325.16	-400.56
5000	9.2	778.688	290.62	2.41	5000.01	5.43	-392.66	6.44	5.81	41.42	14.98	286.23	-438.54
5000	9.3	804.357	255.74	2.88	5000.01	5.24	-431.03	7.56	8.32	57.20	21.36	249.97	-476.09
5000	9.4	830.584	226.96	2.42	4999.99	5.52	-458.82	5.93	5.85	35.20	13.99	219.62	-502.81
5000	9.5	857.375	200.68	2.45	5000.01	5.89	-485.00	6.21	6.01	38.51	14.83	191.64	-527.63
5000	9.6	884.736	178.30	2.36	4999.98	7.31	-507.78	5.74	5.55	32.91	13.17	167.49	-548.70
5000	9.7	912.673	158.04	2.23	5000.01	9.10	-527.02	5.49	4.99	30.15	11.97	145.42	-565.91
5500	9.0	729.000	377.98	2.73	5500.00	6.61	-287.66	7.15	7.46	51.13	18.91	375.75	-334.54
5500	9.1	753.571	334.66	2.62	5499.99	5.42	-331.94	6.84	6.88	46.79	17.48	331.46	-378.41
5500	9.2	778.688	297.00	2.72	5500.01	5.18	-369.35	7.23	7.39	52.29	19.20	292.61	-415.23
5500	9.3	804.357	262.90	2.62	5499.98	5.55	-405.55	6.80	6.86	46.23	17.40	257.12	-450.61
5500	9.4	830.584	233.60	2.36	5500.01	4.74	-434.95	6.14	5.57	37.75	14.05	226.26	-478.94
5500	9.5	857.375	206.38	2.89	5499.98	4.84	-463.63	7.43	8.36	55.26	21.05	197.34	-506.25
5500	9.6	884.736	183.53	2.60	5500.01	4.55	-487.56	6.51	6.76	42.34	16.54	172.71	-528.49
5500	9.7	912.673	163.46	2.58	5500.01	4.62	-506.35	6.46	6.64	41.71	16.25	150.85	-545.24
6000	9.0	729.000	384.03	3.05	5999.98	6.12	-265.69	8.12	9.31	65.90	24.12	381.80	-312.57
6000	9.1	753.571	341.61	2.89	6000.00	5.81	-307.15	7.62	8.35	58.00	21.36	338.41	-353.62
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Table A.2: (continued)

102

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	$\sigma_T(\mathbf{K})$	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
6000	9.2	778.688	302.77	2.70	6000.00	5.39	-347.88	7.12	7.31	50.76	18.76	298.38	-393.76
6000	9.3	804.357	268.42	3.14	5999.99	5.16	-384.78	7.96	9.84	63.43	24.49	262.64	-429.84
6000	9.4	830.584	238.81	2.92	6000.01	5.18	-414.91	7.49	8.55	56.09	21.38	231.47	-458.90
6000	9.5	857.375	211.97	3.03	6000.00	4.75	-442.10	7.52	9.16	56.59	22.33	202.93	-484.72
6000	9.6	884.736	189.02	2.49	6000.01	4.61	-466.77	6.38	6.19	40.69	15.45	178.20	-507.70
6000	9.7	912.673	168.00	2.66	5999.99	4.27	-487.49	6.64	7.09	44.10	17.21	155.38	-526.37
Fe ₉₀ S ₁₈	3												
4000	9.4	830.584	214.60	2.74	4000.00	6.80	-491.62	5.73	7.51	32.85	14.73	207.25	-535.61
4000	9.5	857.375	189.91	2.33	4000.01	7.67	-516.50	4.96	5.43	24.58	10.70	180.87	-559.12
4000	9.6	884.736	168.14	2.57	4000.98	176.95	-539.22	6.05	6.61	36.61	14.07	157.32	-580.15
4000	9.7	912.673	148.61	2.15	4000.13	59.03	-560.21	4.60	4.63	21.16	9.17	135.99	-599.09
4000	9.8	941.192	131.90	2.18	4000.19	66.01	-576.32	4.86	4.76	23.58	9.62	117.52	-612.80
4000	9.9	970.299	118.31	2.17	4000.14	74.86	-590.03	4.71	4.72	22.18	9.22	102.24	-623.74
4500	9.3	804.357	248.14	2.75	4499.99	7.25	-443.97	5.82	7.54	33.92	14.83	242.37	-489.03
4500	9.4	830.584	220.42	2.47	4500.01	6.94	-470.82	5.74	6.10	32.95	13.14	213.08	-514.81
4500	9.5	857.375	197.00	2.76	4499.98	6.68	-493.53	6.17	7.63	38.12	15.97	187.96	-536.15
4500	9.6	884.736	174.54	2.55	4499.99	6.66	-517.48	5.44	6.52	29.64	12.83	163.72	-558.41
4500	9.7	912.673	155.73	2.48	4500.04	40.60	-536.68	5.37	6.17	28.84	12.12	143.11	-575.56
4500	9.8	941.192	138.62	2.83	4499.98	6.37	-553.93	5.63	8.04	31.69	14.97	124.23	-590.41
5000	9.1	753.571	327.22	3.02	5000.03	8.06	-345.66	7.11	9.15	50.54	19.65	324.02	-392.12
5000	9.2	778.688	289.48	2.84	5000.01	7.32	-384.92	6.79	8.07	46.05	17.80	285.10	-430.80
5000	9.3	804.357	255.73	2.66	5000.01	7.20	-419.67	6.15	7.05	37.85	14.86	249.95	-464.74
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Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
5000	9.4	830.584	227.07	3.08	4999.99	7.23	-448.36	7.04	9.49	49.63	20.06	219.73	-492.35
5000	9.5	857.375	201.95	2.72	5000.02	6.38	-474.27	6.03	7.41	36.36	15.20	192.91	-516.89
5000	9.6	884.736	179.68	2.66	5000.00	6.42	-498.26	5.92	7.10	35.09	14.76	168.87	-539.19
5000	9.7	912.673	161.10	2.69	5000.02	26.64	-516.52	6.22	7.24	38.71	15.62	148.48	-555.40
5500	9.0	729.000	377.42	3.27	5500.02	8.07	-277.46	7.29	10.71	53.19	21.63	375.19	-324.34
5500	9.1	753.571	333.36	2.76	5500.03	8.27	-325.38	6.65	7.59	44.17	16.24	330.16	-371.85
5500	9.2	778.688	295.75	2.90	5500.01	7.19	-363.42	6.70	8.41	44.93	18.13	291.37	-409.29
5500	9.3	804.357	262.53	3.08	5499.98	7.20	-397.82	7.08	9.49	50.11	19.87	256.75	-442.88
5500	9.4	830.584	234.04	3.00	5500.00	7.27	-425.08	6.55	9.01	42.93	18.28	226.70	-469.07
5500	9.5	857.375	207.87	2.99	5500.00	6.60	-453.52	6.69	8.91	44.75	18.66	198.83	-496.14
5500	9.6	884.736	185.90	3.04	5500.02	6.40	-475.76	6.87	9.22	47.25	19.63	175.08	-516.69
5500	9.7	912.673	166.25	2.78	5499.98	9.73	-496.83	6.05	7.71	36.60	15.42	153.63	-535.71
6000	8.9	704.969	429.61	3.97	6000.01	9.49	-214.26	9.34	15.78	87.32	33.93	428.13	-261.41
6000	9.0	729.000	382.98	3.48	6000.00	8.58	-257.74	8.45	12.08	71.34	26.53	380.74	-304.62
6000	9.1	753.571	339.81	3.38	6000.00	7.74	-302.75	7.89	11.42	62.29	24.49	336.61	-349.21
6000	9.2	778.688	301.51	3.13	6000.00	7.28	-343.03	7.19	9.79	51.69	20.26	297.13	-388.91
6000	9.3	804.357	269.70	3.07	6000.01	6.74	-373.84	7.13	9.43	50.89	20.18	263.92	-418.90
6000	9.5	857.375	213.55	3.22	6000.00	6.83	-432.59	7.17	10.34	51.38	21.50	204.51	-475.21
6000	9.7	912.673	172.01	2.98	6000.01	7.14	-475.87	6.63	8.91	43.89	18.58	159.39	-514.76
6000	9.5	857.375	211.97	3.03	6000.00	4.75	-442.10	7.52	9.16	56.59	22.33	202.93	-484.72
6000	9.6	884.736	189.02	2.49	6000.01	4.61	-466.77	6.38	6.19	40.69	15.45	178.20	-507.70

Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	T _{DFT} (K)	σ_T (K)	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
6000	9.7	912.673	168.00	2.66	5999.99	4.27	-487.49	6.64	7.09	44.10	17.21	155.38	-526.37
Fe ₉₀ Si	18												
4000	9.4	830.584	217.16	2.55	4000.00	7.13	-520.56	6.57	6.51	43.11	16.35	209.82	-564.55
4000	9.5	857.375	190.63	1.96	4000.06	33.04	-548.02	5.04	3.83	25.42	9.47	181.59	-590.64
4000	9.6	884.736	167.91	2.15	4000.03	39.13	-574.13	5.48	4.63	29.98	11.38	157.09	-615.05
4000	9.7	912.673	149.41	2.16	4000.06	49.87	-591.38	5.49	4.68	30.10	11.50	136.79	-630.26
4000	9.8	941.192	132.41	2.20	4000.18	58.71	-609.55	5.31	4.83	28.21	11.27	118.03	-646.03
4000	9.9	970.299	117.21	2.06	4000.11	65.32	-625.66	4.85	4.23	23.48	9.50	101.14	-659.37
4500	9.3	804.357	251.82	2.44	4500.00	6.37	-471.26	6.29	5.96	39.62	14.93	246.04	-516.32
4500	9.4	830.584	222.33	2.26	4500.00	6.45	-501.79	5.69	5.10	32.39	12.54	214.99	-545.78
4500	9.5	857.375	195.19	2.45	4500.00	6.74	-530.05	6.22	5.99	38.66	14.84	186.15	-572.67
4500	9.6	884.736	175.00	2.05	4500.01	6.30	-549.31	5.12	4.22	26.19	10.15	164.18	-590.24
4500	9.7	912.673	155.61	2.28	4500.04	42.23	-568.52	6.01	5.19	36.14	13.17	142.99	-607.40
4500	9.8	941.192	138.08	1.95	4499.97	5.67	-587.62	4.86	3.81	23.66	9.09	123.69	-624.10
5000	9.2	778.688	292.26	2.41	5000.00	7.17	-410.62	6.37	5.81	40.62	14.77	287.88	-456.49
5000	9.3	804.357	258.26	2.67	5000.01	6.96	-448.21	6.83	7.11	46.59	17.56	252.48	-493.27
5000	9.4	830.584	228.50	2.59	4999.99	6.55	-479.72	7.05	6.72	49.70	17.73	221.16	-523.71
5000	9.5	857.375	202.26	2.24	5000.02	6.40	-504.63	5.88	5.03	34.63	12.68	193.22	-547.25
5000	9.6	884.736	180.13	2.41	4999.99	6.22	-529.38	6.04	5.81	36.48	14.02	169.31	-570.31
5000	9.7	912.673	160.19	2.87	5000.01	5.36	-549.70	6.98	8.22	48.73	19.60	147.57	-588.58
5500	9.0	729.000	377.05	2.90	5500.02	8.49	-306.81	7.86	8.42	61.84	21.98	374.82	-353.69
5500	9.1	753.571	335.38	2.52	5500.02	7.84	-350.73	6.90	6.34	47.67	16.58	332.18	-397.20
												Continued of	n next page

Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	$\sigma_T(\mathbf{K})$	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
5500	9.2	778.688	298.27	2.67	5500.01	7.55	-388.03	6.92	7.13	47.93	17.72	293.89	-433.90
5500	9.3	804.357	264.28	2.88	5500.00	6.67	-425.81	7.12	8.31	50.69	19.88	258.51	-470.87
5500	9.4	830.584	234.90	2.60	5500.01	6.19	-455.57	6.75	6.76	45.55	16.93	227.56	-499.56
5500	9.5	857.375	208.25	2.78	5500.02	6.62	-483.42	7.02	7.76	49.23	19.01	199.21	-526.05
5500	9.6	884.736	185.74	2.63	5499.99	6.45	-508.10	7.07	6.90	49.93	17.99	174.92	-549.03
5500	9.7	912.673	165.53	2.74	5500.01	6.25	-528.79	6.93	7.48	48.01	18.37	152.91	-567.67
6000	8.9	704.969	433.28	2.77	6000.00	8.70	-233.34	7.79	7.65	60.65	20.63	431.80	-280.49
6000	9.0	729.000	383.26	3.01	6000.02	8.48	-285.55	7.98	9.06	63.74	23.18	381.03	-332.42
6000	9.1	753.571	340.73	3.05	6000.01	7.87	-329.31	8.14	9.31	66.24	24.08	337.53	-375.77
6000	9.2	778.688	303.87	2.87	6000.00	7.25	-367.08	7.90	8.21	62.39	21.79	299.49	-412.96
6000	9.3	804.357	270.04	3.12	6000.01	7.53	-404.60	8.12	9.73	65.88	24.71	264.27	-449.66
6000	9.4	830.584	240.30	2.70	5999.99	6.53	-435.03	7.08	7.29	50.19	18.39	232.96	-479.02
6000	9.5	857.375	212.88	2.89	6000.00	6.73	-464.09	7.45	8.35	55.54	20.80	203.84	-506.72
6000	9.6	884.736	190.91	2.72	6000.02	6.57	-487.77	6.89	7.40	47.47	18.13	180.09	-528.70
6000	9.7	912.673	171.25	2.84	5999.99	6.13	-507.18	7.43	8.06	55.13	20.50	158.63	-546.07
6000	9.6	884.736	189.02	2.49	6000.01	4.61	-466.77	6.38	6.19	40.69	15.45	178.20	-507.70
6000	9.7	912.673	168.00	2.66	5999.99	4.27	-487.49	6.64	7.09	44.10	17.21	155.38	-526.37
Fe ₉₀ C ₁	8												
4000	8.8	681.472	341.72	2.45	4000.05	25.27	-464.73	5.45	6.01	29.66	11.72	340.79	-512.06
4000	9.0	729.000	259.94	2.40	4000.18	60.22	-538.32	5.84	5.77	34.12	12.33	257.71	-585.20
4000	9.2	778.688	198.30	2.32	4000.05	34.72	-592.55	5.49	5.37	30.12	11.02	193.92	-638.43
4000	9.3	804.357	172.07	2.60	4000.01	32.50	-616.38	5.49	6.74	30.18	12.74	166.29	-661.44
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Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	T _{DFT} (K)	σ_T (K)	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
4000	9.4	830.584	151.06	2.28	3999.99	28.95	-633.33	4.65	5.20	21.66	9.59	143.72	-677.32
4000	9.5	857.375	132.15	2.46	4000.09	52.68	-647.68	4.96	6.05	24.61	10.48	123.11	-690.30
4000	9.6	884.736	116.15	2.13	4000.16	64.55	-661.00	4.29	4.53	18.38	7.79	105.33	-701.93
4000	9.7	912.673	101.50	2.40	4000.05	34.71	-673.28	4.91	5.76	24.10	10.97	88.88	-712.17
4000	9.8	941.192	89.66	2.23	4000.05	44.03	-681.77	4.63	4.98	21.40	8.98	75.28	-718.25
4500	8.8	681.472	348.78	2.79	4500.06	29.74	-441.42	6.14	7.81	37.68	15.67	347.85	-488.75
4500	9.0	729.000	266.73	2.88	4500.03	32.26	-516.91	6.03	8.27	36.38	15.78	264.50	-563.79
4500	9.2	778.688	204.23	2.66	4500.09	39.75	-571.08	5.67	7.08	32.15	13.52	199.85	-616.96
4500	9.3	804.357	178.68	2.70	4500.10	54.08	-593.30	5.40	7.28	29.18	13.13	172.90	-638.37
4500	9.4	830.584	156.64	2.54	4500.01	21.61	-612.75	5.47	6.45	29.88	12.43	149.30	-656.74
4500	9.5	857.375	137.67	2.44	4500.01	37.56	-627.57	5.20	5.94	27.03	10.99	128.64	-670.19
4500	9.6	884.736	121.67	2.41	4500.12	55.45	-640.64	5.20	5.82	27.08	10.98	110.86	-681.56
4500	9.7	912.673	107.70	2.60	4500.26	89.25	-651.15	5.69	6.74	32.40	13.25	95.08	-690.03
4500	9.8	941.192	94.83	2.57	4500.13	62.12	-662.10	5.27	6.62	27.72	12.03	80.44	-698.57
5000	8.8	681.472	354.28	3.10	5000.03	22.14	-421.46	7.07	9.61	50.01	19.78	353.35	-468.80
5000	9.0	729.000	273.66	2.99	5000.00	23.44	-493.57	6.78	8.95	45.97	18.33	271.43	-540.45
5000	9.2	778.688	211.16	2.91	5000.01	20.85	-549.08	6.52	8.47	42.55	16.98	206.77	-594.96
5000	9.3	804.357	185.14	2.71	5000.08	39.86	-572.12	5.86	7.34	34.31	14.19	179.36	-617.18
5000	9.4	830.584	162.60	2.56	5000.05	30.07	-591.06	5.97	6.55	35.68	13.36	155.25	-635.05
5000	9.5	857.375	143.77	2.72	5000.04	27.58	-606.44	5.89	7.38	34.75	13.97	134.73	-649.06
5000	9.6	884.736	126.84	2.78	5000.04	28.51	-622.17	6.02	7.71	36.21	15.24	116.02	-663.10
5000	9.7	912.673	112.08	2.64	4999.98	19.32	-634.31	5.75	6.96	33.02	13.32	99.46	-673.19
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Table A.2: (continued)

107

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	$\sigma_T(\mathbf{K})$	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
5000	9.8	941.192	99.76	2.71	5000.08	51.35	-642.78	5.38	7.36	28.92	13.03	85.37	-679.26
5500	8.8	681.472	362.18	3.20	5500.04	22.94	-397.27	7.39	10.25	54.64	20.88	361.25	-444.61
5500	9.0	729.000	279.24	3.24	5500.00	21.24	-474.36	7.25	10.49	52.57	21.18	277.01	-521.24
5500	9.2	778.688	216.74	3.14	5500.03	21.78	-528.71	6.95	9.89	48.32	19.92	212.36	-574.59
5500	9.3	804.357	190.48	2.76	5499.99	15.73	-552.48	5.97	7.61	35.60	14.98	184.70	-597.54
5500	9.4	830.584	168.48	3.10	5499.99	20.54	-571.35	6.83	9.60	46.69	19.53	161.14	-615.34
5500	9.5	857.375	149.18	2.94	5500.01	23.61	-587.31	6.58	8.66	43.25	17.50	140.14	-629.93
5500	9.6	884.736	131.86	3.02	5500.06	27.63	-603.02	6.26	9.12	39.24	17.12	121.04	-643.95
5500	9.7	912.673	117.41	2.74	5499.97	24.80	-614.36	6.14	7.52	37.73	15.15	104.79	-653.24
5500	9.8	941.192	104.53	2.93	5500.04	26.46	-624.42	6.07	8.60	36.83	16.42	90.14	-660.89
6000	8.8	681.472	367.83	3.30	6000.02	20.40	-377.60	8.13	10.88	66.13	23.63	366.90	-424.93
6000	9.0	729.000	286.08	3.57	6000.02	15.85	-451.97	8.02	12.73	64.39	25.97	283.85	-498.85
6000	9.2	778.688	222.53	3.18	6000.01	18.60	-509.00	7.09	10.13	50.22	20.59	218.15	-554.88
6000	9.3	804.357	197.33	3.15	5999.97	18.47	-530.84	6.70	9.93	44.83	19.16	191.56	-575.90
6000	9.4	830.584	174.12	3.06	6000.01	20.98	-550.65	7.09	9.36	50.24	19.66	166.78	-594.64
6000	9.5	857.375	154.09	2.94	6000.01	20.53	-568.30	6.48	8.64	41.97	17.15	145.06	-610.92
6000	9.6	884.736	137.25	3.04	6000.04	25.49	-582.52	6.65	9.22	44.26	18.54	126.43	-623.45
6000	9.7	912.673	122.55	3.03	6000.01	24.99	-594.94	6.18	9.17	38.23	16.97	109.93	-633.82
6000	9.8	941.192	109.57	2.72	6000.05	30.69	-605.10	5.75	7.39	33.06	13.85	95.19	-641.58
Fe ₇₆ O ₃	2												
4000	8.8	681.472	289.95	2.88	4000.00	20.99	-424.90	5.22	8.28	27.20	11.71	289.02	-472.23
4000	8.9	704.969	252.65	2.97	4000.04	25.92	-459.38	4.80	8.83	23.08	11.78	251.17	-506.53
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Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V({\rm \AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
4000	9.0	729.000	221.53	2.84	4000.00	20.25	-487.07	4.77	8.08	22.74	11.16	219.30	-533.95
4000	9.1	753.571	193.67	2.70	4000.02	31.11	-512.34	4.46	7.31	19.89	9.81	190.48	-558.80
4000	9.2	778.688	169.62	2.53	4000.06	30.21	-533.63	4.29	6.40	18.36	7.85	165.24	-579.51
4000	9.3	804.357	149.45	2.64	4000.01	24.87	-551.73	4.46	6.95	19.91	9.06	143.67	-596.79
4000	9.4	830.584	130.74	2.82	4000.11	42.95	-568.40	4.79	7.94	22.93	11.12	123.40	-612.39
4000	9.5	857.375	115.06	2.48	4000.04	34.80	-582.40	4.45	6.14	19.78	8.37	106.02	-625.02
4000	9.6	884.736	101.55	2.48	4000.13	52.46	-594.73	4.23	6.17	17.90	7.98	90.74	-635.66
4500	8.8	681.472	296.10	3.30	4500.03	17.05	-405.11	5.23	10.87	27.36	13.65	295.17	-452.44
4500	8.9	704.969	260.04	3.00	4500.01	15.60	-439.63	5.01	8.97	25.08	12.44	258.56	-486.79
4500	9.0	729.000	228.00	2.90	4500.02	17.38	-467.89	5.08	8.39	25.77	11.84	225.77	-514.77
4500	9.1	753.571	199.41	3.17	4500.03	23.21	-492.56	5.40	10.05	29.12	14.33	196.21	-539.02
4500	9.2	778.688	175.82	3.17	4500.03	22.16	-514.09	5.83	10.08	33.95	16.07	171.44	-559.96
4500	9.3	804.357	154.18	2.78	4500.00	22.71	-534.18	4.69	7.73	21.99	10.53	148.41	-579.24
4500	9.4	830.584	135.65	2.83	4500.06	38.54	-550.22	4.50	7.98	20.29	10.55	128.31	-594.21
4500	9.5	857.375	119.98	2.64	4500.03	41.89	-564.82	4.45	6.97	19.77	9.17	110.94	-607.44
4500	9.6	884.736	106.47	2.91	4500.14	56.08	-576.77	4.79	8.49	22.90	11.50	95.65	-617.70
5000	8.8	681.472	302.72	3.59	5000.01	16.20	-385.80	6.40	12.90	40.98	17.40	301.79	-433.14
5000	8.9	704.969	266.32	3.75	5000.05	15.10	-419.59	6.34	14.03	40.14	20.11	264.84	-466.75
5000	9.0	729.000	233.93	3.22	4999.99	15.47	-448.49	5.45	10.34	29.72	13.76	231.70	-495.36
5000	9.1	753.571	205.95	3.24	5000.01	14.28	-473.77	5.49	10.50	30.11	15.33	202.76	-520.24
5000	9.2	778.688	180.99	3.04	4999.99	15.74	-496.14	5.07	9.26	25.69	12.48	176.60	-542.02
5000	9.3	804.357	159.97	3.05	5000.03	18.54	-516.06	5.37	9.33	28.79	13.52	154.20	-561.12
												Continued or	n novt nogo

Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
5000	9.4	830.584	141.89	2.92	5000.00	15.88	-531.12	5.46	8.53	29.78	12.89	134.55	-575.11
5000	9.5	857.375	125.43	2.81	5000.04	20.37	-546.24	5.10	7.92	26.02	11.79	116.39	-588.86
5000	9.6	884.736	111.17	3.00	5000.04	28.79	-559.73	4.96	9.02	24.58	12.88	100.36	-600.66
5500	8.8	681.472	308.38	3.51	5500.01	15.52	-367.34	6.35	12.33	40.29	18.20	307.46	-414.67
5500	8.9	704.969	271.95	3.39	5500.01	14.22	-401.37	5.86	11.51	34.35	16.76	270.47	-448.53
5500	9.0	729.000	239.77	3.52	5500.01	14.15	-430.06	6.24	12.39	38.90	18.63	237.54	-476.94
5500	9.1	753.571	211.26	3.32	5500.01	13.74	-455.63	5.49	11.05	30.10	15.98	208.06	-502.09
5500	9.2	778.688	186.34	3.59	5500.00	13.86	-478.17	5.92	12.91	35.11	18.47	181.96	-524.04
5500	9.3	804.357	165.37	3.33	5500.01	14.51	-497.70	5.88	11.10	34.60	16.80	159.60	-542.76
5500	9.4	830.584	146.49	3.06	5500.02	15.36	-514.90	5.53	9.38	30.55	14.13	139.15	-558.89
5500	9.5	857.375	130.16	3.07	5500.03	13.65	-528.95	5.50	9.42	30.20	13.84	121.13	-571.57
5500	9.6	884.736	115.93	2.99	5500.01	16.42	-542.73	5.28	8.93	27.86	12.69	105.11	-583.66
6000	8.8	681.472	314.85	3.68	6000.01	14.36	-347.63	6.31	13.55	39.87	19.31	313.92	-394.96
6000	8.9	704.969	278.43	4.03	5999.98	15.41	-382.59	6.91	16.28	47.80	24.41	276.95	-429.74
6000	9.0	729.000	245.14	3.72	5999.99	13.79	-412.52	6.31	13.81	39.85	20.15	242.90	-459.40
6000	9.1	753.571	216.28	3.74	6000.01	15.28	-437.95	6.46	13.97	41.69	21.17	213.08	-484.42
6000	9.2	778.688	191.37	3.30	6000.01	13.37	-461.19	5.96	10.90	35.57	16.79	186.98	-507.07
6000	9.3	804.357	170.09	3.38	6000.00	12.47	-481.18	6.13	11.45	37.53	17.79	164.31	-526.24
6000	9.4	830.584	151.03	3.19	6000.01	13.54	-497.37	5.76	10.20	33.14	15.67	143.69	-541.37
6000	9.5	857.375	134.50	3.33	6000.01	14.20	-512.08	5.98	11.07	35.81	16.80	125.46	-554.70
6000	9.6	884.736	120.45	3.04	6000.02	14.47	-526.16	5.34	9.26	28.48	13.21	109.63	-567.09
Fe ₇₆ H ₁	8												

Table A.2: (continued)

<i>T</i> (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	$\sigma_T(\mathbf{K})$	<i>E</i> (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
4000	8.1	531.441	417.52	3.74	4003.45	257.23	-268.85	8.51	14.00	72.44	29.95	417.51	-316.40
4000	8.2	551.368	360.42	4.56	4003.36	257.89	-316.62	10.35	20.82	107.21	45.42	360.41	-364.17
4000	8.3	571.787	316.48	2.88	4003.69	280.28	-345.88	6.90	8.31	47.55	17.75	316.45	-393.42
4000	8.4	592.704	275.24	2.71	4002.71	244.05	-375.24	5.97	7.33	35.68	14.38	275.17	-422.78
4000	8.5	614.125	237.31	3.08	4003.10	262.95	-403.84	6.90	9.50	47.57	19.12	237.16	-451.36
4000	8.6	636.056	205.66	2.70	4003.16	265.44	-427.62	6.30	7.29	39.63	14.99	205.36	-475.11
4000	8.7	658.503	177.61	2.53	4003.32	268.87	-448.31	5.98	6.41	35.78	13.08	177.07	-495.74
4000	8.9	704.969	131.95	2.39	4002.98	264.34	-478.72	5.56	5.73	30.91	11.11	130.47	-525.88
4000	9.1	753.571	96.97	2.39	4002.61	252.51	-500.61	5.48	5.69	30.02	10.93	93.77	-547.07
4500	8.1	531.441	419.02	4.20	4503.15	250.62	-262.27	9.78	17.64	95.60	39.22	419.01	-309.82
4500	8.2	551.368	372.17	2.93	4503.29	258.64	-286.97	6.76	8.58	45.74	17.66	372.16	-334.51
4500	8.3	571.787	324.35	2.95	4503.51	272.24	-324.26	6.84	8.73	46.77	18.05	324.32	-371.80
4500	8.4	592.704	281.73	2.95	4503.01	250.71	-356.92	6.63	8.69	43.93	17.53	281.66	-404.46
4500	8.5	614.125	244.19	2.84	4503.33	265.33	-384.40	6.61	8.06	43.63	16.70	244.04	-431.92
4500	8.6	636.056	211.79	2.97	4503.23	267.15	-409.69	6.69	8.85	44.81	17.69	211.49	-457.19
4500	8.7	658.503	184.38	2.66	4502.86	253.78	-428.88	6.10	7.05	37.20	14.24	183.83	-476.31
4500	8.9	704.969	137.26	2.60	4503.44	288.51	-462.22	6.20	6.74	38.48	13.62	135.78	-509.38
4500	9.1	753.571	102.01	2.42	4503.12	277.75	-484.08	5.70	5.85	32.48	11.28	98.81	-530.55
5000	8.1	531.441	433.66	3.48	5003.23	252.89	-224.82	7.87	12.10	61.95	25.02	433.65	-272.37
5000	8.2	551.368	378.72	3.29	5003.37	263.79	-268.27	7.54	10.82	56.81	22.46	378.71	-315.81
5000	8.3	571.787	330.89	3.04	5003.75	277.72	-305.46	7.09	9.22	50.26	19.21	330.86	-353.01
5000	8.4	592.704	288.10	3.38	5003.66	273.68	-338.36	7.55	11.46	57.03	23.14	288.03	-385.89
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Table A.2: (continued)

T (K)	a (Å)	$V(\text{\AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
5000	8.5	614.125	250.98	3.16	5003.58	277.49	-364.87	7.25	10.01	52.53	20.56	250.83	-412.39
5000	8.6	636.056	218.38	3.08	5003.71	287.99	-390.69	6.99	9.51	48.84	18.98	218.08	-438.19
5000	8.7	658.503	190.06	2.97	5004.14	303.29	-411.64	6.86	8.80	47.05	17.58	189.51	-459.07
5000	8.9	704.969	143.27	2.73	5003.31	281.38	-444.08	6.27	7.47	39.30	14.48	141.79	-491.24
5000	9.1	753.571	107.16	2.62	5003.28	285.19	-467.28	5.94	6.87	35.32	12.75	103.96	-513.75
5500	8.1	531.441	438.43	4.14	5502.84	240.68	-210.63	9.45	17.17	89.34	36.81	438.43	-258.17
5500	8.2	551.368	385.96	3.36	5503.50	262.67	-247.66	7.64	11.28	58.36	23.10	385.95	-295.20
5500	8.3	571.787	337.52	3.29	5502.89	249.21	-286.48	7.38	10.83	54.40	21.99	337.50	-334.02
5500	8.4	592.704	294.85	3.30	5503.15	260.44	-319.02	7.53	10.92	56.77	22.60	294.78	-366.56
5500	8.5	614.125	257.18	3.17	5503.20	261.49	-346.52	7.09	10.04	50.21	20.08	257.03	-394.04
5500	8.6	636.056	224.79	2.94	5503.56	284.36	-371.72	6.93	8.66	47.98	17.74	224.49	-419.21
5500	8.7	658.503	196.23	3.07	5503.34	276.49	-392.82	7.04	9.41	49.53	18.90	195.68	-440.25
5500	8.9	704.969	148.29	3.15	5503.65	292.90	-427.56	7.06	9.94	49.88	19.43	146.81	-474.71
5500	9.1	753.571	111.94	3.02	5503.39	287.56	-451.19	6.73	9.13	45.29	17.37	108.74	-497.65
6000	8.1	531.441	447.04	3.85	6002.47	226.37	-186.75	8.58	14.80	73.57	30.31	447.03	-234.30
6000	8.2	551.368	392.04	3.59	6002.56	231.53	-229.81	8.04	12.89	64.71	26.57	392.03	-277.36
6000	8.3	571.787	344.52	3.62	6002.42	224.24	-266.73	8.07	13.08	65.06	26.71	344.49	-314.27
6000	8.4	592.704	301.29	3.75	6002.67	240.74	-300.46	8.03	14.06	64.46	27.75	301.22	-347.99
6000	8.5	614.125	263.44	3.37	6002.79	245.84	-328.02	7.52	11.34	56.60	22.98	263.29	-375.55
6000	8.6	636.056	230.86	3.21	6002.88	254.05	-353.49	7.08	10.28	50.15	20.24	230.56	-400.99
6000	8.7	658.503	201.48	3.31	6003.10	264.05	-376.56	7.35	10.99	53.98	21.85	200.93	-423.99
6000	8.9	704.969	153.55	3.23	6003.25	276.72	-410.42	7.35	10.46	54.09	21.01	152.07	-457.57
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Table A.2: (continued)

112

						Table	A.2: (conti	inued)					
T (K)	a (Å)	$V({\rm \AA}^3)$	P (GPa)	σ_P (GPa)	$T_{\rm DFT}$ (K)	σ_T (K)	E (eV)	σ_E (eV)	$\operatorname{cov}(P, P)$	$\operatorname{cov}(E, E)$	$\operatorname{cov}(P, E)$	P _{raw} (GPa)	$E_{\rm raw}~({\rm eV})$
6000	9.6	884.736	120.45	3.04	6000.02	14.47	-526.16	5.34	9.26	28.48	13.21	109.63	-567.09

Fe	С	0	Si	S	Ni	Н	T (K)	$V(\text{\AA}^3)$	P _{DFT} (GPa)	σ_P (GPa)	P _I (GPa)	P _{II} (GPa)	P _{III} (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
99	9	0	0	0	0	0	4000	857.38	159.73	2.27	158.90	160.22	159.41	-0.36	0.22	-0.14
99	0	0	0	9	0	0	4000	912.67	147.57	2.15	147.09	147.07	146.45	-0.22	-0.23	-0.52
99	0	0	0	0	9	0	4000	912.67	145.90	2.14	146.10	146.09	145.47	0.09	0.09	-0.20
99	0	9	0	0	0	0	4000	857.38	165.19	2.01	164.77	167.43	165.37	-0.21	1.11	0.09
99	0	0	0	0	0	9	4000	753.57	236.13	2.07	238.72	253.31	237.49	1.25	8.32	0.66
90	0	0	0	0	0	18	4000	753.57	171.16	2.70	175.27	191.79	172.53	1.53	7.65	0.51
81	0	0	0	0	0	27	4000	753.57	120.30	2.32	122.14	130.26	119.95	0.79	4.29	-0.15
72	0	0	0	0	0	36	4000	753.57	80.17	2.48	76.44	68.74	79.75	-1.50	-4.60	-0.17
63	0	0	0	0	0	45	4000	753.57	50.04	2.52	31.10	7.22	51.92	-7.53	-17.01	0.75
90	0	18	0	0	0	0	4000	704.97	314.16	2.83	315.32	321.68	316.23	0.41	2.65	0.73
90	0	18	0	0	0	0	4000	729.00	275.57	2.59	276.48	282.14	277.35	0.35	2.54	0.69
90	0	18	0	0	0	0	4000	753.57	241.43	2.37	242.50	247.53	243.33	0.45	2.57	0.80
90	0	18	0	0	0	0	4000	778.69	212.64	2.48	212.73	217.21	213.52	0.04	1.84	0.35
90	0	18	0	0	0	0	4000	804.36	186.25	2.52	186.65	190.64	187.40	0.16	1.75	0.46
90	0	18	0	0	0	0	4000	830.58	163.83	2.35	163.78	167.34	164.49	-0.02	1.49	0.28
90	0	18	0	0	0	0	4000	857.38	144.35	2.47	143.72	146.90	144.39	-0.26	1.03	0.02
90	0	18	0	0	0	0	4000	884.74	127.56	2.42	126.10	128.95	126.74	-0.60	0.57	-0.34
90	0	18	0	0	0	0	4000	912.67	112.57	2.26	110.63	113.18	111.25	-0.86	0.27	-0.59
90	0	18	0	0	0	0	4500	681.47	364.87	2.67	365.71	372.86	366.57	0.31	2.99	0.64
90	0	18	0	0	0	0	4500	704.97	321.19	2.84	321.19	327.54	322.01	0.00	2.24	0.29
90	0	18	0	0	0	0	4500	729.00	281.90	2.85	282.26	287.90	283.04	0.12	2.10	0.40
90	0	18	0	0	0	0	4500	753.57	248.44	2.90	248.17	253.20	248.91	-0.09	1.64	0.16
90	0	18	0	0	0	0	4500	778.69	218.06	2.91	218.32	222.79	219.02	0.09	1.63	0.33
90	0	18	0	0	0	0	4500	804.36	193.14	2.95	192.14	196.13	192.81	-0.34	1.02	-0.11
90	0	18	0	0	0	0	4500	830.58	169.86	2.73	169.19	172.75	169.82	-0.24	1.06	-0.01
90	0	18	0	0	0	0	4500	857.38	150.17	2.29	149.04	152.22	149.64	-0.49	0.89	-0.23

Table A.3: Comparison of DFT pressure with model predictions.

Fe	С	0	Si	S	Ni	Н	T (K)	$V({\rm \AA}^3)$	P _{DFT} (GPa)	σ_P (GPa)	$P_{\rm I}~({\rm GPa})$	P_{II} (GPa)	$P_{\rm III}$ (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	0	18	0	0	0	0	4500	884.74	132.83	2.44	131.35	134.19	131.91	-0.61	0.56	-0.38
90	0	18	0	0	0	0	4500	912.67	117.82	2.39	115.80	118.36	116.34	-0.84	0.23	-0.62
90	0	18	0	0	0	0	5000	681.47	371.51	3.02	371.68	378.83	372.45	0.06	2.42	0.31
90	0	18	0	0	0	0	5000	704.97	327.85	2.97	327.06	333.41	327.80	-0.26	1.87	-0.02
90	0	18	0	0	0	0	5000	729.00	288.89	2.63	288.02	293.67	288.72	-0.33	1.81	-0.07
90	0	18	0	0	0	0	5000	753.57	254.80	2.88	253.84	258.87	254.50	-0.33	1.41	-0.10
90	0	18	0	0	0	0	5000	778.69	224.91	2.72	223.89	228.37	224.51	-0.37	1.27	-0.15
90	0	18	0	0	0	0	5000	804.36	198.43	2.60	197.64	201.62	198.22	-0.31	1.23	-0.08
90	0	18	0	0	0	0	5000	830.58	175.92	2.71	174.59	178.15	175.14	-0.49	0.83	-0.29
90	0	18	0	0	0	0	5000	857.38	155.58	2.46	154.37	157.55	154.88	-0.49	0.80	-0.28
90	0	18	0	0	0	0	5000	884.74	138.30	2.49	136.60	139.44	137.08	-0.68	0.46	-0.49
90	0	18	0	0	0	0	5000	912.67	123.11	2.66	120.98	123.53	121.44	-0.80	0.16	-0.63
90	0	18	0	0	0	0	5500	681.47	377.87	3.32	377.66	384.80	378.34	-0.06	2.09	0.14
90	0	18	0	0	0	0	5500	704.97	334.82	3.19	332.93	339.28	333.58	-0.59	1.40	-0.39
90	0	18	0	0	0	0	5500	729.00	294.56	3.21	293.80	299.44	294.40	-0.24	1.52	-0.05
90	0	18	0	0	0	0	5500	753.57	260.64	3.25	259.52	264.54	260.09	-0.35	1.20	-0.17
90	0	18	0	0	0	0	5500	778.69	230.77	2.60	229.47	233.95	230.01	-0.50	1.22	-0.29
90	0	18	0	0	0	0	5500	830.58	181.21	2.46	180.01	183.56	180.47	-0.49	0.95	-0.30
90	0	18	0	0	0	0	5500	857.38	160.94	2.40	159.70	162.87	160.13	-0.52	0.81	-0.34
90	0	18	0	0	0	0	5500	884.74	143.63	2.96	141.85	144.69	142.25	-0.60	0.36	-0.46
90	0	18	0	0	0	0	5500	912.67	127.97	2.68	126.16	128.70	126.54	-0.67	0.27	-0.53
90	0	18	0	0	0	0	6000	658.50	434.95	3.19	434.90	442.94	435.52	-0.01	2.51	0.18
90	0	18	0	0	0	0	6000	681.47	384.43	3.71	383.64	390.77	384.22	-0.21	1.71	-0.05
90	0	18	0	0	0	0	6000	704.97	340.81	3.31	338.80	345.15	339.36	-0.61	1.31	-0.44
90	0	18	0	0	0	0	6000	729.00	301.27	3.39	299.56	305.20	300.09	-0.50	1.16	-0.35
90	0	18	0	0	0	0	6000	778.69	236.31	2.97	235.06	239.52	235.51	-0.42	1.08	-0.27
90	0	18	0	0	0	0	6000	830.58	186.21	2.99	185.42	188.96	185.80	-0.26	0.92	-0.14
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	T (K)	$V(Å^3)$	P _{DFT} (GPa)	σ_P (GPa)	P _I (GPa)	P _{II} (GPa)	$P_{\rm III}$ (GPa)	$\Delta P_{\rm I}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	0	18	0	0	0	0	6000	857.38	166.26	3.09	165.03	168.19	165.38	-0.40	0.62	-0.29
90	0	18	0	0	0	0	6000	884.74	148.29	2.92	147.11	149.93	147.43	-0.40	0.56	-0.30
90	0	18	0	0	0	0	6000	912.67	132.82	2.99	131.35	133.87	131.63	-0.49	0.35	-0.40
99	0	0	9	0	0	0	4000	804.36	244.21	1.99	244.90	244.88	243.84	0.35	0.34	-0.19
99	0	0	9	0	0	0	4000	857.38	187.57	2.03	189.93	189.92	189.12	1.16	1.16	0.76
99	0	0	9	0	0	0	4000	912.67	146.82	1.92	147.40	147.38	146.76	0.30	0.29	-0.03
99	0	0	9	0	0	0	4000	970.30	115.32	1.88	114.39	114.38	113.90	-0.49	-0.50	-0.75
99	0	0	9	0	0	0	4500	753.57	321.83	2.41	322.08	322.06	320.69	0.10	0.10	-0.47
99	0	0	9	0	0	0	4500	804.36	250.99	2.31	250.71	250.70	249.63	-0.12	-0.12	-0.59
99	0	0	9	0	0	0	4500	857.38	192.61	2.85	195.56	195.56	194.73	1.04	1.04	0.74
99	0	0	9	0	0	0	4500	912.67	152.27	2.25	152.87	152.85	152.20	0.27	0.26	-0.03
99	0	0	9	0	0	0	4500	970.30	120.31	1.98	119.71	119.70	119.19	-0.30	-0.31	-0.56
99	0	0	9	0	0	0	5000	753.57	326.78	3.34	328.09	328.08	326.68	0.39	0.39	-0.03
99	0	0	9	0	0	0	5000	804.36	256.77	2.20	256.53	256.52	255.42	-0.11	-0.11	-0.61
99	0	0	9	0	0	0	5000	857.38	200.30	2.60	201.21	201.20	200.34	0.35	0.34	0.01
99	0	0	9	0	0	0	5000	912.67	158.72	2.41	158.33	158.32	157.65	-0.16	-0.17	-0.45
99	0	0	9	0	0	0	5000	970.30	125.61	2.38	125.02	125.01	124.48	-0.25	-0.25	-0.47
99	0	0	9	0	0	0	5500	753.57	333.82	2.49	334.11	334.10	332.67	0.12	0.11	-0.46
99	0	0	9	0	0	0	5500	804.36	262.36	2.88	262.35	262.34	261.22	-0.00	-0.01	-0.40
99	0	0	9	0	0	0	5500	857.38	205.77	2.53	206.85	206.83	205.95	0.42	0.42	0.07
99	0	0	9	0	0	0	5500	912.67	163.14	2.69	163.80	163.79	163.09	0.25	0.24	-0.02
99	0	0	9	0	0	0	5500	970.30	130.25	2.63	130.34	130.33	129.78	0.03	0.03	-0.18
99	0	0	9	0	0	0	6000	753.57	339.80	3.16	340.13	340.12	338.66	0.10	0.10	-0.36
99	0	0	9	0	0	0	6000	804.36	268.47	2.81	268.17	268.16	267.01	-0.11	-0.11	-0.52
99	0	0	9	0	0	0	6000	857.38	211.25	2.84	212.48	212.47	211.57	0.43	0.43	0.11
99	0	0	9	0	0	0	6000	912.67	168.27	2.76	169.27	169.26	168.54	0.36	0.36	0.10
99	0	0	9	0	0	0	6000	970.30	135.32	2.67	135.65	135.64	135.07	0.12	0.12	-0.09
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	<i>T</i> (K)	$V(Å^3)$	P _{DFT} (GPa)	σ_P (GPa)	P _I (GPa)	$P_{\rm II}$ (GPa)	P _{III} (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	6	12	0	0	0	0	4000	884.74	123.38	2.41	122.63	124.51	123.04	-0.31	0.47	-0.14
90	6	0	0	12	0	0	4000	884.74	149.76	2.43	150.09	150.83	150.83	0.14	0.44	0.44
90	6	0	12	0	0	0	4000	884.74	151.58	2.31	150.53	151.44	151.44	-0.45	-0.06	-0.06
90	9	9	0	0	0	0	4000	884.74	121.33	2.40	120.88	122.30	121.19	-0.19	0.40	-0.06
90	9	0	0	9	0	0	4000	884.74	141.30	2.40	141.19	142.04	142.04	-0.04	0.31	0.31
90	9	0	9	0	0	0	4000	884.74	142.15	2.22	141.47	142.49	142.49	-0.31	0.15	0.15
90	12	6	0	0	0	0	4000	884.74	119.67	2.36	119.14	120.08	119.34	-0.23	0.17	-0.14
90	12	0	0	6	0	0	4000	884.74	132.75	2.54	132.49	133.24	133.24	-0.10	0.19	0.19
90	12	0	6	0	0	0	4000	884.74	132.91	2.28	132.64	133.54	133.54	-0.12	0.28	0.28
90	0	12	0	6	0	0	4000	884.74	140.75	2.38	139.59	142.11	140.64	-0.49	0.57	-0.05
90	0	0	12	6	0	0	4000	884.74	167.20	2.25	169.02	169.03	169.03	0.81	0.81	0.81
90	0	9	0	9	0	0	4000	884.74	147.26	2.16	146.57	148.69	147.59	-0.32	0.66	0.15
90	0	0	9	9	0	0	4000	884.74	167.21	2.67	168.87	168.88	168.88	0.63	0.63	0.63
90	0	6	0	12	0	0	4000	884.74	154.07	2.35	153.70	155.27	154.53	-0.16	0.51	0.20
90	0	0	6	12	0	0	4000	884.74	166.71	2.42	168.72	168.73	168.73	0.83	0.84	0.84
100	0	4	4	0	0	0	4000	884.74	158.87	2.04	156.81	158.10	156.91	-1.01	-0.38	-0.96
78	0	24	6	0	0	0	4000	884.74	116.76	2.44	116.22	118.20	118.41	-0.22	0.59	0.68
80	4	16	4	4	0	0	4000	884.74	122.51	2.27	121.87	123.56	124.05	-0.28	0.46	0.68
90	4	5	4	5	0	0	4000	884.74	145.81	2.35	144.30	145.93	145.32	-0.64	0.05	-0.21
90	0	6	12	0	0	0	4000	778.69	257.19	2.27	256.24	258.84	257.61	-0.42	0.73	0.18
90	0	6	12	0	0	0	4000	804.36	226.07	2.06	225.61	227.94	226.86	-0.22	0.90	0.38
90	0	6	12	0	0	0	4000	830.58	200.17	2.14	198.68	200.78	199.83	-0.70	0.28	-0.16
90	0	6	12	0	0	0	4000	857.38	175.93	1.92	175.01	176.89	176.06	-0.48	0.50	0.07
90	0	6	12	0	0	0	4000	884.74	155.47	2.12	154.17	155.87	155.14	-0.61	0.19	-0.16
90	0	6	12	0	0	0	4000	912.67	138.10	2.18	135.81	137.36	136.72	-1.05	-0.34	-0.64
90	0	6	12	0	0	0	4000	941.19	123.05	2.09	119.61	121.06	120.49	-1.64	-0.95	-1.22
90	0	6	12	0	0	0	4500	778.69	262.66	3.24	261.96	264.55	263.29	-0.22	0.58	0.20
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	T (K)	$V(Å^3)$	P _{DFT} (GPa)	σ_P (GPa)	P _I (GPa)	P _{II} (GPa)	P _{III} (GPa)	$\Delta P_{\rm I}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	0	6	12	0	0	0	4500	804.36	233.32	2.25	231.22	233.56	232.45	-0.94	0.11	-0.39
90	0	6	12	0	0	0	4500	830.58	205.64	2.55	204.21	206.31	205.33	-0.56	0.26	-0.12
90	0	6	12	0	0	0	4500	857.38	183.29	2.25	180.43	182.34	181.48	-1.28	-0.42	-0.81
90	0	6	12	0	0	0	4500	884.74	161.79	2.61	159.52	161.24	160.48	-0.87	-0.21	-0.50
90	0	6	12	0	0	0	4500	912.67	143.78	2.18	141.09	142.65	141.98	-1.23	-0.52	-0.82
90	0	6	12	0	0	0	5000	729.00	343.54	3.27	342.71	345.92	344.27	-0.25	0.73	0.23
90	0	6	12	0	0	0	5000	753.57	303.83	2.62	302.75	305.64	304.19	-0.41	0.69	0.13
90	0	6	12	0	0	0	5000	778.69	269.79	2.68	267.67	270.27	268.98	-0.79	0.18	-0.30
90	0	6	12	0	0	0	5000	804.36	239.03	2.37	236.84	239.18	238.05	-0.92	0.06	-0.42
90	0	6	12	0	0	0	5000	830.58	212.00	2.73	209.74	211.84	210.84	-0.83	-0.06	-0.42
90	0	6	12	0	0	0	5000	857.38	187.90	2.49	185.89	187.79	186.90	-0.81	-0.05	-0.40
90	0	6	12	0	0	0	5000	884.74	167.74	2.47	164.88	166.61	165.82	-1.16	-0.46	-0.78
90	0	6	12	0	0	0	5000	912.67	149.70	2.33	146.36	147.94	147.24	-1.43	-0.75	-1.05
90	0	6	12	0	0	0	5500	729.00	350.07	2.96	348.62	351.84	350.16	-0.49	0.60	0.03
90	0	6	12	0	0	0	5500	753.57	310.70	2.84	308.56	311.45	309.97	-0.75	0.27	-0.26
90	0	6	12	0	0	0	5500	778.69	276.06	2.81	273.38	275.98	274.67	-0.96	-0.03	-0.49
90	0	6	12	0	0	0	5500	804.36	244.86	2.83	242.46	244.80	243.64	-0.85	-0.02	-0.43
90	0	6	12	0	0	0	5500	830.58	218.26	2.71	215.26	217.38	216.35	-1.11	-0.32	-0.70
90	0	6	12	0	0	0	5500	857.38	194.21	2.50	191.33	193.24	192.32	-1.15	-0.39	-0.75
90	0	6	12	0	0	0	5500	884.74	173.09	2.32	170.24	171.97	171.16	-1.23	-0.48	-0.83
90	0	6	12	0	0	0	5500	912.67	155.04	2.67	151.65	153.23	152.51	-1.27	-0.68	-0.95
90	0	6	12	0	0	0	6000	704.97	401.63	3.19	400.28	403.87	401.95	-0.42	0.71	0.10
90	0	6	12	0	0	0	6000	729.00	357.09	3.27	354.52	357.75	356.05	-0.78	0.20	-0.32
90	0	6	12	0	0	0	6000	753.57	317.16	3.05	314.36	317.26	315.75	-0.92	0.03	-0.46
90	0	6	12	0	0	0	6000	778.69	281.55	3.07	279.10	281.70	280.36	-0.80	0.05	-0.39
90	0	6	12	0	0	0	6000	804.36	250.49	2.80	248.09	250.43	249.24	-0.86	-0.02	-0.45
90	0	6	12	0	0	0	6000	830.58	223.71	2.78	220.80	222.91	221.86	-1.05	-0.29	-0.67
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	T (K)	$V({\rm \AA}^3)$	P _{DFT} (GPa)	σ_P (GPa)	$P_{\rm I}~({\rm GPa})$	P_{II} (GPa)	$P_{\rm III}$ (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\mathrm{III}}/\sigma_P$
90	0	6	12	0	0	0	6000	857.38	199.44	2.69	196.78	198.68	197.75	-0.99	-0.28	-0.63
90	0	6	12	0	0	0	6000	912.67	159.79	2.93	156.95	158.52	157.77	-0.97	-0.44	-0.69
90	0	9	9	0	0	0	4000	778.69	245.38	2.14	244.96	248.43	246.58	-0.19	1.42	0.56
90	0	9	9	0	0	0	4000	804.36	216.29	2.29	215.50	218.61	216.99	-0.34	1.01	0.31
90	0	9	9	0	0	0	4000	830.58	191.36	1.97	189.61	192.42	190.99	-0.89	0.54	-0.19
90	0	9	9	0	0	0	4000	857.38	168.26	2.46	166.87	169.39	168.14	-0.56	0.46	-0.05
90	0	9	9	0	0	0	4000	884.74	148.77	2.22	146.86	149.14	148.04	-0.86	0.17	-0.33
90	0	9	9	0	0	0	4000	912.67	131.65	2.25	129.25	131.32	130.35	-1.06	-0.14	-0.58
90	0	9	9	0	0	0	4000	941.19	117.71	2.55	113.70	115.63	114.78	-1.57	-0.82	-1.15
90	0	9	9	0	0	0	4500	778.69	251.22	2.58	250.64	254.11	252.23	-0.22	1.12	0.39
90	0	9	9	0	0	0	4500	804.36	222.27	2.34	221.09	224.20	222.54	-0.51	0.82	0.11
90	0	9	9	0	0	0	4500	830.58	196.27	2.20	195.12	197.92	196.46	-0.52	0.75	0.08
90	0	9	9	0	0	0	4500	857.38	174.89	2.27	172.27	174.81	173.52	-1.15	-0.04	-0.60
90	0	9	9	0	0	0	4500	884.74	154.54	2.61	152.19	154.48	153.34	-0.90	-0.02	-0.46
90	0	9	9	0	0	0	4500	912.67	136.88	2.49	134.52	136.58	135.57	-0.95	-0.12	-0.53
90	0	9	9	0	0	0	5000	729.00	329.96	2.85	328.54	332.86	330.39	-0.50	1.02	0.15
90	0	9	9	0	0	0	5000	753.57	291.63	2.68	290.07	293.95	291.76	-0.58	0.86	0.05
90	0	9	9	0	0	0	5000	778.69	258.17	2.71	256.32	259.79	257.87	-0.69	0.60	-0.11
90	0	9	9	0	0	0	5000	804.36	228.44	2.54	226.67	229.79	228.09	-0.70	0.53	-0.14
90	0	9	9	0	0	0	5000	830.58	202.64	2.76	200.62	203.42	201.92	-0.74	0.28	-0.26
90	0	9	9	0	0	0	5000	857.38	180.22	2.46	177.69	180.23	178.90	-1.03	0.00	-0.54
90	0	9	9	0	0	0	5000	884.74	160.07	2.40	157.53	159.81	158.64	-1.06	-0.10	-0.60
90	0	9	9	0	0	0	5000	912.67	143.12	2.38	139.75	141.84	140.79	-1.41	-0.54	-0.98
90	0	9	9	0	0	0	5500	729.00	336.81	3.14	334.41	338.74	336.22	-0.77	0.61	-0.19
90	0	9	9	0	0	0	5500	753.57	297.90	2.92	295.85	299.72	297.50	-0.70	0.63	-0.14
90	0	9	9	0	0	0	5500	778.69	264.50	2.79	261.99	265.47	263.51	-0.90	0.35	-0.36
90	0	9	9	0	0	0	5500	804.36	234.44	2.80	232.26	235.38	233.64	-0.78	0.34	-0.28
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	<i>T</i> (K)	$V(\text{\AA}^3)$	P _{DFT} (GPa)	σ_P (GPa)	P _I (GPa)	P _{II} (GPa)	P _{III} (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	0	9	9	0	0	0	5500	830.58	208.78	3.07	206.11	208.92	207.38	-0.87	0.05	-0.46
90	0	9	9	0	0	0	5500	857.38	185.41	2.45	183.12	185.64	184.28	-0.94	0.09	-0.47
90	0	9	9	0	0	0	5500	884.74	165.35	2.61	162.87	165.15	163.93	-0.95	-0.08	-0.54
90	0	9	9	0	0	0	5500	912.67	147.53	2.58	145.04	147.10	146.01	-0.97	-0.17	-0.59
90	0	9	9	0	0	0	6000	704.97	386.54	3.23	384.36	389.19	386.30	-0.68	0.82	-0.07
90	0	9	9	0	0	0	6000	729.00	342.38	3.07	340.29	344.61	342.06	-0.68	0.73	-0.11
90	0	9	9	0	0	0	6000	753.57	303.88	3.26	301.62	305.50	303.24	-0.69	0.50	-0.20
90	0	9	9	0	0	0	6000	778.69	269.97	3.22	267.68	271.15	269.15	-0.71	0.37	-0.25
90	0	9	9	0	0	0	6000	804.36	240.72	3.03	237.84	240.97	239.19	-0.95	0.08	-0.51
90	0	9	9	0	0	0	6000	830.58	213.89	2.87	211.62	214.42	212.84	-0.79	0.19	-0.36
90	0	9	9	0	0	0	6000	857.38	190.51	2.85	188.54	191.06	189.65	-0.69	0.19	-0.30
90	0	9	9	0	0	0	6000	912.67	152.87	2.91	150.30	152.35	151.24	-0.88	-0.18	-0.56
90	0	12	6	0	0	0	4000	778.69	234.60	2.22	233.95	238.02	235.56	-0.29	1.54	0.43
90	0	12	6	0	0	0	4000	804.36	206.34	2.43	205.64	209.29	207.13	-0.29	1.21	0.32
90	0	12	6	0	0	0	4000	830.58	181.50	2.21	180.79	184.06	182.16	-0.32	1.16	0.30
90	0	12	6	0	0	0	4000	857.38	160.02	2.17	158.95	161.90	160.22	-0.49	0.87	0.09
90	0	12	6	0	0	0	4000	884.74	141.29	2.29	139.76	142.41	140.94	-0.67	0.49	-0.15
90	0	12	6	0	0	0	4000	912.67	125.24	2.34	122.87	125.27	123.98	-1.01	0.01	-0.54
90	0	12	6	0	0	0	4000	941.19	111.80	2.24	107.98	110.20	109.06	-1.71	-0.72	-1.22
90	0	12	6	0	0	0	4500	778.69	240.60	2.42	239.59	243.67	241.16	-0.42	1.27	0.23
90	0	12	6	0	0	0	4500	804.36	212.54	2.59	211.19	214.85	212.63	-0.52	0.89	0.03
90	0	12	6	0	0	0	4500	830.58	187.38	2.57	186.25	189.53	187.58	-0.44	0.84	0.08
90	0	12	6	0	0	0	4500	857.38	165.97	2.42	164.34	167.28	165.56	-0.68	0.54	-0.17
90	0	12	6	0	0	0	4500	884.74	147.36	2.61	145.06	147.72	146.20	-0.88	0.14	-0.45
90	0	12	6	0	0	0	4500	912.67	131.13	2.46	128.09	130.50	129.16	-1.24	-0.26	-0.80
90	0	12	6	0	0	0	5000	729.00	315.93	3.10	314.70	319.80	316.50	-0.40	1.24	0.18
90	0	12	6	0	0	0	5000	753.57	278.53	3.08	277.70	282.25	279.34	-0.27	1.21	0.27
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Table A.3: (continued)

Fe	С	0	Si	S	Ni	Н	T (K)	$V({\rm \AA}^3)$	P _{DFT} (GPa)	σ_P (GPa)	$P_{\rm I}~({\rm GPa})$	P_{II} (GPa)	$P_{\rm III}$ (GPa)	$\Delta P_{\mathrm{I}}/\sigma_P$	$\Delta P_{\mathrm{II}}/\sigma_P$	$\Delta P_{\rm III}/\sigma_P$
90	0	12	6	0	0	0	5000	778.69	246.46	2.76	245.24	249.32	246.75	-0.44	1.04	0.10
90	0	12	6	0	0	0	5000	804.36	218.42	2.73	216.75	220.40	218.13	-0.61	0.73	-0.11
90	0	12	6	0	0	0	5000	830.58	193.91	2.50	191.71	195.00	192.99	-0.88	0.43	-0.37
90	0	12	6	0	0	0	5000	857.38	171.66	2.61	169.72	172.67	170.89	-0.74	0.39	-0.29
90	0	12	6	0	0	0	5000	884.74	152.53	2.22	150.37	153.02	151.45	-0.97	0.22	-0.49
90	0	12	6	0	0	0	5000	912.67	135.64	2.47	133.34	135.73	134.34	-0.93	0.04	-0.52
90	0	12	6	0	0	0	5500	729.00	322.23	2.82	320.54	325.64	322.28	-0.60	1.21	0.02
90	0	12	6	0	0	0	5500	753.57	285.23	2.92	283.44	287.99	285.03	-0.61	0.95	-0.07
90	0	12	6	0	0	0	5500	778.69	252.89	2.95	250.88	254.96	252.34	-0.68	0.70	-0.19
90	0	12	6	0	0	0	5500	804.36	223.86	3.02	222.31	225.96	223.64	-0.52	0.69	-0.08
90	0	12	6	0	0	0	5500	830.58	198.70	2.86	197.20	200.47	198.41	-0.53	0.62	-0.10
90	0	12	6	0	0	0	5500	857.38	177.24	2.81	175.11	178.05	176.23	-0.76	0.29	-0.36
90	0	12	6	0	0	0	5500	884.74	157.87	2.66	155.68	158.33	156.71	-0.82	0.17	-0.44
90	0	12	6	0	0	0	5500	912.67	140.77	2.46	138.58	140.96	139.52	-0.89	0.08	-0.51
90	0	12	6	0	0	0	6000	704.97	370.63	3.28	368.81	374.51	370.65	-0.56	1.18	0.01
90	0	12	6	0	0	0	6000	729.00	328.05	3.30	326.39	331.48	328.07	-0.50	1.04	0.00
90	0	12	6	0	0	0	6000	753.57	291.16	3.17	289.18	293.74	290.72	-0.62	0.81	-0.14
90	0	12	6	0	0	0	6000	778.69	258.53	3.16	256.53	260.61	257.93	-0.63	0.66	-0.19
90	0	12	6	0	0	0	6000	804.36	230.06	2.82	227.86	231.51	229.14	-0.78	0.51	-0.33
90	0	12	6	0	0	0	6000	830.58	204.53	2.84	202.66	205.94	203.83	-0.66	0.49	-0.25
90	0	12	6	0	0	0	6000	857.38	182.18	2.84	180.50	183.44	181.56	-0.59	0.44	-0.22
90	0	12	6	0	0	0	6000	912.67	145.67	2.81	143.82	146.19	144.70	-0.66	0.18	-0.35

Table A.3: (continued)

References

Kuwayama, Yasuhiro, Guillaume Morard, Yoichi Nakajima, Kei Hirose, Alfred Q. R. Baron, Saori I. Kawaguchi, Taku Tsuchiya, Daisuke Ishikawa, Naohisa Hirao, and Yasuo Ohishi (2020). "Equation of State of Liquid Iron under Extreme Conditions". In: *Physical Review Letters* 124.16, p. 165701. DOI: 10.1103/PhysRevLett.124.165701.

Appendix B

SUPPLEMENTARY TABLES FOR CHAPTER III

	Н	Ni	С	0	Si	S	T _{ICB}
Н	1.0000	0.0939	0.0744	-0.5323	-0.3330	-0.4952	-0.7676
Ni	0.0939	1.0000	0.0252	-0.2072	0.0057	-0.0197	-0.0391
С	0.0744	0.0252	1.0000	-0.5508	-0.2810	-0.2214	0.3729
0	-0.5323	-0.2072	-0.5508	1.0000	0.0212	-0.0885	0.1712
Si	-0.3330	0.0057	-0.2810	0.0212	1.0000	0.1100	0.2407
S	-0.4952	-0.0197	-0.2214	-0.0885	0.1100	1.0000	0.2735
$T_{\rm ICB}$	-0.7676	-0.0391	0.3729	0.1712	0.2407	0.2735	1.0000

Table B.1: Correlation matrix among resulted model parameters.

Appendix C

SUPPLEMENTARY TABLES FOR CHAPTER IV

					132 Xe =	100				
		¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe	Reference
Endmen	nbers									
Spalloge	nic Xe	71.69	120.5	183.1	192.8	118.1	454.2	5.301	0.3614	Hohenberg et al. (1981)
Solar Wi	nd Xe	0.4816	0.4222	8.412	104.1	16.49	82.63	36.98	29.99	Meshik et al. (2020)
Phase-Q	Xe	0.455	0.4057	8.22	104.2	16.19	81.85	37.88	31.64	Busemann et al. (2000)
Air Xe		0.3537	0.33	7.136	98.32	15.14	78.9	38.79	32.93	Basford et al. (1973)
Pu-fissio	n Xe	0	0	0	5.424	0	27.8	106.1	113	Lewis (1975)
J-fissior	n Xe	0	0	0	2.543	0	21.39	147.4	173.4	Macnamara and Thode (1950)
Meteori	tes									
Гуре	name									
CI	Ivuna	0.406	0.38	7.54	125.6	15.5	79.9	38.7	32.8	Riebe et al. (2017)
		±0.003	±0.003	± 0.05	± 0.9	± 0.1	± 0.5	± 0.2	± 0.2	
CO	KAINSAZ	0.4726	0.4151	8.316	110.3	16.27	82.08	38.01	31.94	Alaerts et al. (1979b)
		± 0.0069	± 0.0065	± 0.060	± 0.4	± 0.09	± 0.26	± 0.10	± 0.07	
CV	Bukhara	0.483	0.425	8.351	125.9	16.35	82.34	37.83	31.37	Mahajan et al. (2021)
		± 0.003	± 0.004	±0.026	± 0.2	± 0.02	± 0.11	± 0.04	± 0.13	
СМ	QUE 93005	0.4654	0.4037	8.107	110.45	16.194	82.29	38.81	32.7	Krietsch et al. (2021)
		± 0.0074	± 0.0054	± 0.005	±0.63	±0.096	± 0.50	±0.26	±0.24	
H	GRV053690-2	0.4812	0.385	8.341	121.5	16.39	82.87	38.27	32.08	Wang et al. (2020)
		±0.0680	±0.037	±0.826	±11.2	±1.36	±6.06	±1.99	±1.49	
_	GRV0523149-1	0.495	0.7591	8.317	151.4	16.6	82.21	40	33	Wang et al. (2020)
		±0.102	±0.1368	±0.855	±14.1	±1.42	±6.19	±2.44	±1.56	
L	St. Severin	0.511	0.529	8.007	137	15.74	80.92	38.6	32.52	Alaerts et al. (1979a)
		±0.014	±0.018	±0.073	±1.6	±0.08	±0.29	±0.16	±0.12	
EH	ALH 77295	0.4119	0.3777	7.829	137.34	15.644	80.25	38.838	33.023	Okazaki et al. (2010)
		±0.0040	±0.0026	±0.019	±0.14	±0.027	±0.10	±0.054	±0.051	
										Continued on next page

Table C.1: Xenon end-member compositions and meteoritic data used.

		¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe	Reference
EL	DAG 734	0.4322	0.3747	7.589	152.34	15.588	80.22	38.642	32.661	Okazaki et al. (2010)
		±0.0080	±0.0053	±0.026	±0.29	±0.066	±0.18	±0.091	±0.087	
Angrites	Angra dos Reis ($\rho > 3.2$)	5.86	8.51	15.64	73.1	13.9	79.1	62.8	62	Wasserburg et al. (1977)
		±0.57	±0.83	±1.52	± 0.7	±1.1	±7.3	±6.03	±6	
Angrites	LEW 86010	7.1593	11.3251	18.519	58.89	14.303	76.406	74.515	77.567	Hohenberg et al. (1991)
		±0.0623	±0.0896	±0.129	±0.27	±0.102	±0.349	±0.300	±0.286	
Angrites	Sahara 99555 #3	0.638	0.695	7.02	90.8	14.08	75	45.1	40.1	Busemann et al. (2006)
		±0.018	±0.012	±0.12	±0.9	±0.19	±0.8	±0.5	±0.5	
Angrites	D'Orbigny #3	3.2	5.3	10	47	9.9	56	79	84	Busemann et al. (2006)
		±0.27	±0.5	±0.9	±5	±1.1	±6	±7	±7	
Angrites	NWA1296	0.479	0.514	7.69	96.4	14.93	77.2	44.3	39.1	Nakashima et al. (2018)
		±0.013	±0.018	±0.05	±0.3	±0.23	±0.4	±0.3	±0.2	
Angrites	NWA2999	0.94	1.392	8.57	97.2	15.99	83.2	39.8	33.9	Nakashima et al. (2018)
		±0.024	±0.069	±0.10	±0.6	±0.21	±0.4	±0.2	±0.2	
Angrites	NWA4590	7.937	12.679	20.12	49.3	15.2	71	77.4	80.4	Nakashima et al. (2018)
		±0.211	±0.705	±0.33	±0.7	±0.28	±0.7	±1.1	±0.8	
Angrites	NWA4801	1.847	2.745	9.04	76.8	13.15	76.7	55.5	52.4	Nakashima et al. (2018)
		±0.048	±0.145	±0.14	±0.5	±0.20	±0.5	±0.4	±0.4	
Angrites	NWA4931	3.798	5.783	14.48	88.5	16.99	94.3	49.3	46.3	Nakashima et al. (2018)
		±0.146	±0.372	±0.27	±0.9	±0.29	±0.7	±0.5	±0.4	
HED	V1	1.64	3.18	13.91	97.24	20.87	91.79	44.63	42.06	Mahajan et al. (2019)
		±0.41	±0.36	±0.41	±0.36	±0.30	±0.15	±1.11	±1.63	
HED	V2	0.91	1.49	9.09	98.65	17.99	85.36	40.59	34.36	Mahajan et al. (2019)
		±0.18	±0.13	±0.05	±1.02	±0.13	±0.84	±0.16	±0.28	
HED	P1	1.91	2.84	10.16	94.86	16.42	83.68	43.15	38.32	Mahajan et al. (2019)
		±0.04	±0.02	±0.08	±0.38	±0.06	±0.32	±0.13	±0.19	
HED	P2	10.4	2.52	9.67	93.12	16.24	81.81	43.98	38.86	Mahajan et al. (2019)
										Continued on next page

Table C.1: (continued)

		¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe	Reference
		±0.02	±0.03	±0.12	±0.13	±0.04	±0.21	±0.19	±0.18	
HED	L1	6.96	10.68	21.1	86.1	20.7	95.44	55.25	50.48	Mahajan et al. (2019)
		±0.03	±0.31	±0.3	±0.5	±0.52	±2.08	±0.45	±0.73	
HED	L2	8.08	9.83	20.18	104.8	18.15	87.39	50.7	44.96	Mahajan et al. (2019)
		±0.09	±0.12	±0.92	±1.1	±0.69	±0.51	±1.13	±1.31	

Table C.1: (continued)

Table C.2: Solutions for radiogenic ¹²⁹Xe and plutoniumderived fissiogenic ¹³⁶Xe of different meteorites using Phase-Q as the initial composition. -1σ and $+1\sigma$ give 68% confidence limits.

Types	$(^{129}$ Xe*/ 132 Xe)			(¹³⁶ Xe	textrmPu /	¹³² Xe)	$(^{129}\text{Xe}^*/^{132}\text{Xe})/(^{136}\text{Xe}^{textrmPu}/^{132}\text{Xe})$		
	median	-1σ	+1 σ	median	-1σ	+1 σ	median	+1\sigma	
Chondrites									
CI	0.2536	0.0092	0.0092	0.0031	0.0031	0.0036	80.60	38.76	
СО	0.0629	0.0040	0.0040	0	-	-	-	-	
CV	0.2167	0.0020	0.0020	0	-	-	-	-	
СМ	0.0707	0.0065	0.0065	0	-	-	-	-	
Н	0.1877	0.1128	0.1121	0.0000	0.0000	0.0048	-	63.10	
L	0.5031	0.1423	0.1423	0.0000	0.0000	0.0105	-	61.66	
LL	0.3559	0.0162	0.0162	0.0058	0.0031	0.0023	61.65	46.28	
EH	0.3608	0.0016	0.0016	0.0127	0.0039	0.0009	28.31	26.50	
EL	0.5172	0.0032	0.0032	0.0017	0.0017	0.0032	297.58	106.1	
Achondrites									
Angra dos Reis	0.1083	0.0820	0.0812	0.5222	0.0514	0.0516	0.2074	0.3302	
LEW 86010	0.0879	0.0035	0.0035	0.6888	0.0030	0.0029	0.1277	0.1322	
								Continued on next page	

Types	$(^{129}$ Xe*/ 132 Xe)			(136	$Xe^{Pu}/132$	Xe)	(¹²⁹ Xe*/ ¹³	2 Xe)/(136 Xe ^{textrmPu} / 132 Xe)
	median	-1σ	+1 σ	median	-1σ	+1 σ	median	+1 σ
Sahara 99555	0.0044	0.0044	0.0102	0.1103	0.0058	0.0062	0.0403	0.1258
D'Orbigny	0.0452	0.0452	0.0674	0.7320	0.0955	0.0577	0.0618	0.1425
NWA1296	0.0093	0.0058	0.0051	0.0930	0.0197	0.0107	0.0998	0.1384
NWA2999	0.0000	-	-	0.0239	0.0071	0.0072	-	-
NWA4590	0.0454	0.0097	0.0098	0.7571	0.0090	0.0090	0.0600	0.0721
NWA4801	0.0000	-	-	0.2867	0.0132	0.0068	-	-
NWA4931	0.0000	-	-	0.1317	0.0291	0.0295	-	-
V1	0.0000	-	-	0.0000	0.0000	0.0000	-	-
V2	0.0000	-	-	0.0000	0.0000	0.0059	-	-
P1	0.0035	0.0035	0.0049	0.0492	0.0093	0.0097	0.0710	0.1427
P2	0.0801	0.0019	0.0019	0.2327	0.0017	0.0017	0.3441	0.3495
L1	0.0518	0.0073	0.0071	0.3198	0.0060	0.0060	0.1619	0.1805
L2	0.3131	0.0132	0.0132	0.4016	0.0094	0.0094	0.7797	0.7940

Table C.2: (continued)

- : indicates indeterminate values.

Table C.3: Solutions for radiogenic ¹²⁹Xe and plutoniumderived fissiogenic ¹³⁶Xe of different meteorites using solar wind as the initial composition. -1σ and $+1\sigma$ give 68% confidence limits.

Types	$(^{129}$ Xe*/ 132 Xe)			(¹³⁶ Xe	textrmPu /	¹³² Xe)	$(^{129}\text{Xe}^*/^{132}\text{Xe})/(^{136}\text{Xe}^{textrmPu}/^{132}\text{Xe})$		
	median	-1σ	+1 σ	median	-1σ	+1 σ	median	+1\sigma	
Chondrites									
CI	0.2599	0.0092	0.0092	0.0000	0.0000	0.0097	-	27.60	
СО	0.0757	0.0041	0.0042	0	-	-	-	-	
CV	0.2260	0.0020	0.0021	0	-	-	-	-	
СМ	0.0852	0.0065	0.0065	0	-	-	-	-	
Н	0.1991	0.1125	0.1121	0.0000	0.0000	0.0175	-	17.78	
L	0.5117	0.1417	0.1414	0.0000	0.0000	0.0177	-	36.96	
LL	0.3653	0.0161	0.0161	0.0059	0.0059	0.0110	61.47	22.57	
EH	0.3691	0.0015	0.0016	0.0000	0.0000	0.0022	-	164.8	
EL	0.5234	0.0031	0.0031	0.0000	0.0000	0.0027	-	195.4	
Achondrites									
Angra dos Reis	0.1085	0.0820	0.0812	0.5226	0.0515	0.0516	0.2076	0.3303	
LEW 86010	0.0879	0.0035	0.0035	0.6888	0.0030	0.0029	0.1277	0.1322	
								Continued on next page	

Types	$(^{129}$ Xe*/ 132 Xe)			(136	Xe ^{Pu} / ¹³²	Xe)	(¹²⁹ Xe*/ ¹³	2 Xe)/(136 Xe ^{textrmPu} / 132 Xe)
	median	-1σ	+1 σ	median	-1σ	+1 σ	median	+1\sigma
Sahara 99555	0.0063	0.0063	0.0098	0.1140	0.0073	0.0078	0.0551	0.1324
D'Orbigny	0.0469	0.0469	0.0671	0.7337	0.0960	0.0579	0.0639	0.1439
NWA1296	0.0198	0.0074	0.0070	0.0818	0.0303	0.0267	0.2416	0.2467
NWA2999	0.0000	-	-	0.0251	0.0050	0.0062	-	-
NWA4590	0.0454	0.0097	0.0098	0.7571	0.0090	0.0090	0.0600	0.0721
NWA4801	0.0000	-	-	0.2874	0.0129	0.0067	-	-
NWA4931	0.0000	-	-	0.1321	0.0293	0.0299	-	-
V1	0.0000	-	-	0.0584	0.0255	0.0254	-	-
V2	0.0000	-	-	0.0365	0.0341	0.0127	-	-
P1	0.0036	0.0036	0.0049	0.0496	0.0095	0.0101	0.0716	0.1417
P2	0.0801	0.0019	0.0019	0.2327	0.0017	0.0017	0.3441	0.3495
L1	0.0510	0.0077	0.0073	0.3209	0.0065	0.0073	0.1588	0.1775
L2	0.3131	0.0132	0.0132	0.4016	0.0094	0.0094	0.7797	0.7940

Table C.3: (continued)

- : indicates indeterminate values.

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Appendix D

SUPPLEMENTARY TABLES FOR CHAPTER V

[This chapter is temporarily embargoed.]