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Structure and Properties of Liquid Fe-C Alloys at High Pressures by Experiments and First-Principles Calculations

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ABSTRACT

It is believed that the core formation processes sequestered a large majority of Earth's carbon into its metallic core. Incorporation of carbon to liquid iron may significantly influence its properties under physicochemical conditions pertinent to the deep magma ocean and thus the chemical evolution of terrestrial planets and moons. Compared to available experimental data on the physical properties of crystalline iron alloys under pressure, there is a remarkable lack of data on the properties of liquid iron-rich alloys, due to experimental challenges. Here we review experimental and computational results on the structure and properties of iron or iron-nickel liquids alloyed with carbon upon compression. These laboratory data provide an important foundation on which the interpretation of ultrahigh pressure laboratory data and the verification of theoretical data will have to be based. The low-pressure data can be used to validate results from theoretical calculations at the same conditions, and high-pressure calculations can be used to estimate and predict liquid properties under core conditions. Availability of the liquid properties of Fe-C liquids will provide essential data for stringent tests of carbon-rich core composition models for the outer core.

4.1. INTRODUCTION

As the remotest and most dynamic region of the planet and accounting for 18% of the total planetary volume, the liquid core of the Earth is estimated to be mostly composed of iron (Fe) and 5% to 10% nickel (Ni), with a minor fraction of light impurities that lower its density and melting point with respect to pure Fe (Birch, 1964; Li & Fei, 2014; McDonough & Sun, 1995; Poirier, 1994). The estimates of the core density deficit relative to solid Fe vary between 6% and 10% for the outer core (O. L. Anderson & Isaak, 2002; Anderson & Ahrens,

1994; Fei et al., 2016; Jephcoat & Olson, 1987; Shanker et al., 2004; Stevenson, 1981; Stixrude, Cohen, et al., 1997). Knowledge on the nature and abundance of the light alloying elements (S, O, C, Si, H) in the core has significant implications for planetary accretion and differentiation history, bulk composition and chemical evolution of the planet, and dynamic processes in the outer core for the generation of the Earth's magnetic field (Li & Fei, 2014, and references therein; Stevenson, 2010). Furthermore, the composition of the core holds the key for answering the fundamental questions in geophysics and planetary sciences: "How has the core evolved to its current state?" and "What is the role of the core in the planet's internal processes and dynamics?" As in the Earth, the presence of liquid cores has been identified in other planets such as Mercury (Margot et al., 2007) and Mars (Fei & Bertka, 2005), as well as the moons of planets in the solar system such as the Moon

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(Weber et al., 2011) and Ganymede (Bland et al., 2008; Hauck et al., 2006). The advent of space exploration of terrestrial-like planets and moons also gives rise to tremendous interest in the internal structures of these bodies, and particularly the possible existence of cores and their composition and internal dynamics.

Carbon is the fourth most abundant element in the solar system but is depleted by three orders of magnitude in the silicate Earth. Most of Earth's carbon resides in the deep interior, but the fact that carbon is readily outgassed makes these estimates difficult and controversial. A significant fractionation of Earth's carbon may have partitioned into the core during differentiation (Chen & Li, 2016; Dasgupta & Walker, 2008; Nakajima et al., 2009). Carbon has been suggested to be among the principal light elements in the core, partly due to its cosmochemical abundance, occurrence of Fe carbide phases in meteorites, and high affinity and solubility in Fe-Ni liquids during core-mantle differentiation (Chen & Li, 2016; Wood, 1993; Wood et al., 2013). Recent advances in high-pressure and synchrotron techniques have permitted both static and dynamic high-pressure experiments on crystalline iron alloys under pressure-temperature (P-T) conditions found at the center of the Earth (Li & Fei, 2014). For the solid inner core, the phase stability, thermal equation-of-state, and sound velocities of relevant solid Fe-carbide phases, under or approaching core conditions, have been extensively investigated (Chen et al., 2012, 2018; Fiquet et al., 2009; Gao et al., 2008; Lai et al., 2018; Liu et al., 2016; Mookherjee, 2011; Mookherjee et al., 2011; Nakajima et al., 2009; Prescher et al., 2012, 2015; Sata et al., 2010). In contrast, for much of the liquid outer core, such experimental investigations and discussion are still significantly lacking, largely due to the huge gap in the P-T space accessible to experiment at actual core conditions. Furthermore, there are very limited experimental data on thermoelastic properties of Fe-C liquids even at low pressures (Kuwabara et al., 2015; Lai et al., 2017; Shibasaki et al., 2015; Shibasaki & Kono, 2018; Terasaki et al., 2006, 2010). These properties of iron-light-element liquids are usually investigated under 10 GPa in the laboratory, far below the expected conditions of the outer core.

The elastic and viscoelastic properties of liquid Fe alloys, such as the density, sound velocities, attenuation,

and viscosity, are a prerequisite for the interpretation of the behavior of the outer core and for constructing core composition models. To account for the density deficit for the outer core, and to understand buoyancy effects accompanying inner core crystallization and hence core dynamics, it is critical to measure the density of Fe-rich liquids under high P-T conditions in the laboratory. Recent advances in experimental techniques allow measurement of the liquid properties at relatively low pressures. For instance, using sink/float or X-ray absorption methods, the densities of several liquid Fe-rich alloys have been measured under static high-pressure conditions (mostly <10 GPa), i.e. Fe-S liquids (Nishida et al., 2008; Sanloup, Guyot, Gillet, Fiquet, Mezouar, et al., 2000; Tateyama et al., 2011), Fe-C liquids (Sanloup et al., 2011; Terasaki et al., 2010), and Fe-Si liquids (Sanloup et al., 2004; Tateyama et al., 2011; Yu & Secco, 2008) (see Table 4.1).

Likewise, recent advances in high-performance computation permit calculations of structure, equations of state, viscosity, and sound velocity of melts at high temperatures and pressures, using first-principles molecular dynamics (MD) simulations (Lai et al., 2017; Stixrude, Cohen, et al., 1997). Simulations of systems of in the order of 1000 atoms and up to tens of pico-seconds become practical and are expected to be adequate to calculate the properties of the melts with acceptable accuracies. First-principles simulations of Fe-Ni-C liquids are, however, limited in the literature (Alfé, 2010; Alfé et al., 2000; Belashchenko, 2014; Côté et al., 2012; Desjarlais, 2013; Lai et al., 2017; Sobolev & Mirzoev, 2013; Vočadlo et al., 2000; Zhang & Yin, 2012). In concert with current high P-T experimental capabilities, it is desirable to systematically investigate the density, sound velocity, viscosity, and structure of Fe-Ni-C liquids under moderate pressures by experiments and approaching core conditions by theoretical calculations, an approach to avoid long extrapolations of low-pressure properties in order to have a better understanding of the carbon inventory in planetary cores. The ambient and low-pressure experimental data can serve as a baseline for higher pressure materials properties and can be directly applied to the modeling for planetary cores of smaller bodies. The low-pressure experimental data can also be used to benchmark the systematic biases that often occur

Table 4.1 Existing studies on density of liquid iron and its alloys with carbon.

Source	Composition	P-T Range	Method
Jimbo & Cramb (1993)	Fe-C liquid (0–4 wt% C)	0 GPa, 1523–1823 K	Sessile drop profile
Terasaki et al. (2010)	Fe ₃ C	3.6–9.5 GPa, 1973 K	X-ray absorption
Sanloup et al. (2011)	Fe-5.7 wt% C	2–8 GPa, 2273 K (corrected)	X-ray absorption
Shimoyama et al. (2013)	Fe-3.5 wt% C	≤6.8 GPa, 2200 K	X-ray absorption
Morard et al. (2017)	Fe-C liquid (2.5–3.0 wt% C)	6–58 GPa, 3200 K	Diffuse scattering

in the first-principles calculations, such as the tradeoffs between the accuracy and duration of the simulations. After being benchmarked against lower pressure experimental results, first-principles calculations can then be effectively and reliably carried out to explore more relevant P-T ranges for the core.

In this chapter, we first discuss recent results on the structure of the Fe-Ni-C liquids at high pressures. We then discuss the structural effects on the elastic and viscoelastic properties of Fe-Ni-C liquids, from the perspectives of laboratory experiments and computational techniques, in order to establish a systematic dataset on the density, sound velocity, viscosity, and structure of the liquids in a previously unexplored pressure-temperature-composition sector.

4.2. STRUCTURE OF FE-C AND FE-NI-C LIQUIDS

One of the most remarkable observations in physical sciences is that most substances (liquid or solid state) with a well-defined chemical composition can transform from one structure to another simply by varying thermodynamic conditions such as pressure and temperature. Physical properties of the substances on the macroscopic scale are intimately controlled by their structure at the atomistic scale. In planetary sciences, knowledge of the structural evolution of iron liquids as core-forming materials upon compression is essential for understanding the evolution and dynamics of terrestrial planets and moons, as the liquid properties are governed by the liquid structure. However, the pressure-induced structural transitions of iron liquids have not been thoroughly investigated, largely due to the subtle changes of the liquid structure and the ambiguities of the reported liquid structural data in most previous studies (Sanloup, Guyot, Gillet, Fiquet, Hemley, et al., 2000; Shen et al., 2004; Shibazaki et al., 2015).

4.2.1. Experimental Results

Based on X-ray diffraction measurements and the appearance of two distinct subpeaks of the second peak in the experimental pair distribution function (PDF), Sanloup, Guyot, Gillet, Fiquet, Hemley, et al. (2000) reported a structural change in liquid Fe from *bcc*-like to *bcc-fcc*-like local order in the vicinity of the δ - γ -liquid triple point at ~ 5 GPa. This splitting, however, was not observed in the other two measurements of liquid Fe up to 6.4 GPa (Kono et al., 2015) and 58 GPa (Shen et al., 2004). The incorporation of carbon in liquid Fe may promote the structural transition. A liquid structural transition in Fe-3.5 wt% C liquid was inferred from peak distance changes in their experimentally determined PDFs at ~ 5 GPa (Kono et al., 2015). Structural transitions in

liquids have also been inferred from changes in physical and chemical behaviors of liquid Fe alloys at high pressures. Both Fe-5.7 wt% C (Sanloup et al., 2011) and Fe-3.5 wt% C (Shimoyama et al., 2013) liquids showed marked changes in their densities at ~ 5 GPa. The structural transition in the metallic liquids was also thought to be intimately related to the observed nonlinear systematics in the metal-silicate partitioning behaviors for trace elements (i.e., Ni, Co, and W) (Sanloup et al., 2011). Compared to the studies of solid Fe-carbides (Chen et al., 2014; Fang et al., 2009; Fiquet et al., 2009; Gao et al., 2008, 2011; Li et al., 2002; Lin et al., 2004; Litasov et al., 2014; Litasov et al., 2013; Mookherjee, 2011; Mookherjee et al., 2011; Prescher et al., 2015; Sata et al., 2010; Scott et al., 2001), relatively limited experimental work has been conducted on the Fe-C or Fe-Ni-C liquids. Occurrence of structural changes in liquids Fe-alloys in the P-T-X space such as a polyamorphic transition at ~ 5 GPa inevitably makes the extrapolation of their physical properties to core conditions irrelevant. Therefore, it is crucial to probe the high P-T structure of Fe-rich alloys considered for the outer core, in order to profoundly understand their elastic and viscoelastic properties and geochemical consequences, e.g., the partitioning coefficients of elements between liquid silicates and liquid metallic phase (Sanloup et al., 2011).

Recently, the structure change of Fe or Fe-Ni liquid alloyed with various amounts of carbon has been experimentally investigated at high pressures (Lai et al., 2017; Shibazaki et al., 2015). Based on multiangle energy-dispersive X-ray diffraction measurements, a liquid structure transition at ~ 5 GPa was inferred from the observations of peak distance changes in experimentally determined PDFs in Fe-3.5 wt% C liquids (Shibazaki et al., 2015) and Fe₉₀Ni₁₀-5 wt% C and Fe₉₀Ni₁₀-3 wt% C (Lai et al., 2017). Notably, the derived PDFs for Fe₉₀Ni₁₀-5 wt% C and Fe₉₀Ni₁₀-3 wt% C liquids up to 7.3 GPa and 1773 K show changes to the rich features of the second nearest neighbors peaks at ~ 5 GPa, which were used as primary indication of a polyamorphic liquid structural transition for both liquids (Figure 4.1) (Lai et al., 2017). Unlike Si, which is found to be substitutionally incorporated into Fe, carbon, as well as a small amount of S, is alloyed with liquid Fe through interstitial incorporation (Shibazaki & Kono, 2018). Detailed structural information of the liquids, however, could not be directly derived solely from the experimental data. A model analysis based on atomic packing motifs is consistent with the result from first-principles MD calculations, which suggest that the transition is related to the three-atom polyhedral connection of Fe-Ni atomic motifs in the high-pressure liquids at >5 GPa (Figure 4.1 and Figure 4.2) (Lai et al., 2017). Such a change in intermediate range structure has a significant effect on the properties

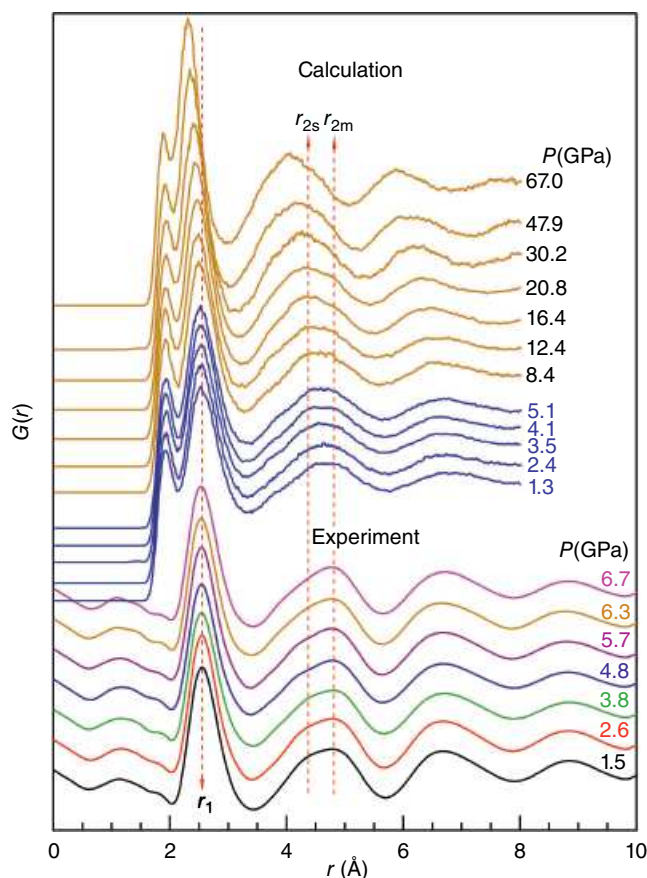


Figure 4.1 Reduced pair distribution function $G(r)$ of $\text{Fe}_{90}\text{Ni}_{10}$ -5 wt% C liquid at high pressures and temperatures by experiments up to 7 GPa (Lai et al., 2017) and molecular dynamics calculations up to 67 GPa. The dashed lines with arrows serve as guides for the r_1 and r_2 (r_{2s} , r_{2m}) positions of $G(r)$ of the $\text{Fe}_{90}\text{Ni}_{10}$ -5 wt% C liquid at low pressures. See electronic version for color representation of the figures in this book.

of the liquid because a three-atom connection (a triangle) between polyhedra could geometrically induce a structural and dynamical stability (Figure 4.2).

4.2.2. Computational Results

First-principles MD simulation shows that short-range order of carbon atoms in Fe-C liquids changes significantly with carbon concentration (0 to 5 wt% carbon), varying from simple carbon solution in iron to carbon forming local sites like the distorted prismatic sites in Fe_3C (Sobolev & Mirzoev, 2013). MD simulations indicate that liquid structure and transition are not affected by replacing Fe with 10 at% Ni in the $\text{Fe}_{90}\text{Ni}_{10}$ -5 wt% C liquid (Lai et al., 2017). For the $\text{Fe}_{90}\text{Ni}_{10}$ -5 wt% C liquid, the short-range structure in the pressure range from 0–67 GPa (Figure 4.2) shows the coordination number in the Fe/Ni-Fe/Ni subsystem around 12, indicative of a nearly close-packed structure. The coordination number in the

C-Fe/Ni subsystem increases from 6.5 to 8.5, indicating an approximately octahedral to cubic transition. The Fe/Ni-Fe/Ni bond length is significantly compressed as compared to the C-Fe/Ni bond. The mixing of Fe, Ni, and C are not ideal, which is based on their pair distribution functions. The preferential clustering between the atoms is pressure dependent. Such subtle miscibility changes with pressure between the elements are possibly related to changes in the local chemical and structural environment but may particularly influence other physical properties. Based on the analysis of the partial configurationally decomposed distribution function, the intermediate-range structures of both Fe/Ni-Fe/Ni and C-Fe/Ni subsystems change substantially, which can be characterized by a significant increase of three-atom shared polyhedra. The computational results suggest a close correlation between the structural change and an increased bulk modulus, decreased diffusion coefficient, and increased shear viscosity from the polyamorphic transition. Both miscibility and clustering of the liquid component elements are structural characteristics that appear to have a significant impact on the physical properties of the liquid.

The synergy between experiments and calculations provides critical structural information about the liquids for the interpretation and understanding of the intrinsic nature of the pressure-induced structural rearrangements of the liquids and the resultant effects on the liquid properties. The structural changes of liquid iron alloys upon compression, as exemplified by the Fe-Ni-C liquids in this study and others, can have a significant effect on the liquid properties, such as viscosity, sound velocity, and density. The liquid structure change may also influence the partitioning behaviors of major or trace elements and isotopic fractionation between metal and silicates during planetary core formations. Knowledge of the equation of the state and polyamorphic transitions in core-forming liquid iron alloys is thus crucial for our understanding of the chemical evolution of terrestrial planets and moons.

4.3. RELATIONSHIP BETWEEN PROPERTY AND STRUCTURE AND GEOPHYSICAL IMPLICATIONS

Incorporation of light elements such as carbon into liquid Fe is known to have significant effect on the macroscopic properties of the liquids, which are dictated by their atomic-scale structures at high pressures (Shibazaki & Kono, 2018). Light elements are known to reduce the densities of their alloys with liquid Fe at high pressures (Morard et al., 2014; Nishida et al., 2008; Nishida et al., 2016; Sanloup et al., 2004; Shimoyama et al., 2013; Tateyama et al., 2011; Terasaki et al., 2010). For Fe-C liquids, the densities of Fe-5.7 wt% C (Sanloup et al., 2011) and Fe-3.5 wt% C (Shimoyama et al., 2013) both showed marked changes at ~5 GPa (Figure 4.3), which is the pressure at which both experiments and computations

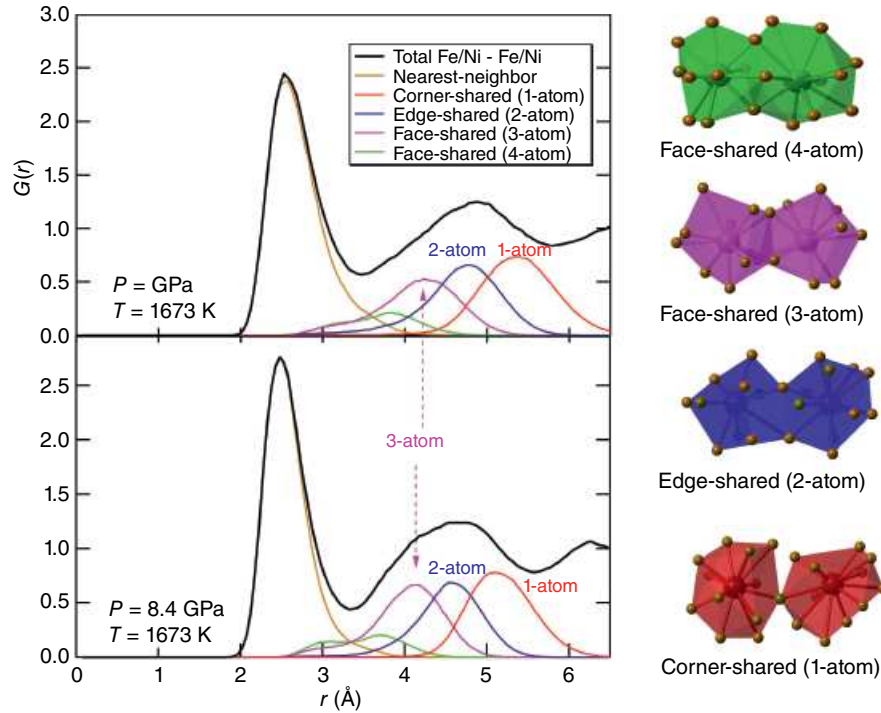


Figure 4.2 The total pair distribution functions (PDFs) of the Fe/Ni-Fe/Ni pair in the $\text{Fe}_{91}\text{Ni}_9$ -5 wt% C liquid and the decomposed PDFs for the second nearest neighbor shells at (a) 1.3 GPa, 1673 K and (b) 8.4 GPa, 1673 K from MD simulations, modified after Lai et al. (2017). The color-coded polyhedra are 1-atom corner-shared (red), 2-atom edge-shared (blue), 3-atom face-shared (magenta), and 4-atom distorted face-shared (green) connections of Fe/Ni atom with their second nearest neighbors. See electronic version for color representation of the figures in this book.

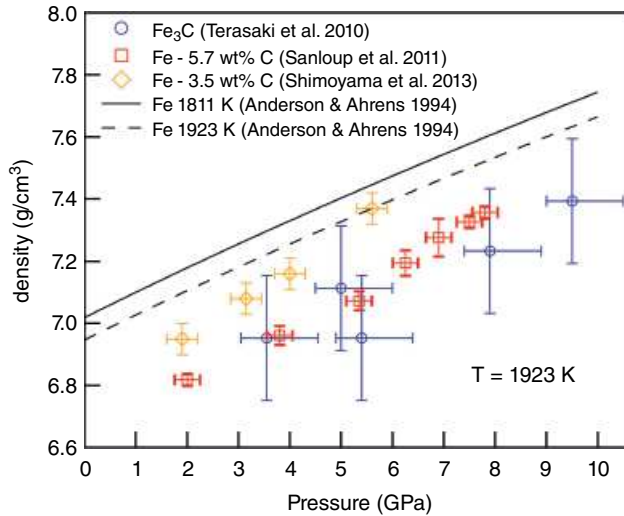


Figure 4.3 The effect of carbon alloying with Fe on the density of Fe-C liquids, in comparison with density of liquid Fe (W. W. Anderson & Ahrens, 1994). See electronic version for color representation of the figures in this book.

inferred a liquid structural transition (Lai et al., 2017; Shibazaki et al., 2015). Effect of the liquid atomic structure on the properties is also reflected on the equation of

the state in a subtle manner. Two separate piece-wise fittings of the data of pressure as a function of volume of $\text{Fe}_{90}\text{Ni}_{10}$ -5 wt% C liquid at pressures from 0 to 5 GPa and 5 to 67 GPa result in a better overall fitting statistic than fitting of the data in whole pressure range from 1 to 67 GPa, consistent with the liquid-liquid polyamorphic transition at a volume of $\sim 11 \text{ \AA}^3/\text{atom}$ around ~ 5 GPa. Furthermore, the residual fluctuation from the fitting of a single Birch-Murnaghan equation of state are closely correlated with the coordination number of three-atom shared polyhedra truncates in the pressure range, which suggests that there is a direct correlation between the intermediate-range structure of the liquid and fluctuations in its equation of state. This correlation is further highlighted by the fact that a greater number of three-atom shared polyhedra at higher pressures is correlated to a higher bulk modulus at smaller volumes based on the result of the piece-wise fitting of Birch-Murnaghan equation of state.

On the other hand, incorporation of light elements such as C in the liquid Fe may increase or decrease the V_p (Shibazaki & Kono, 2018). Substitutional incorporation of Si in liquid Fe as characterized by the shortening r_1 and r_2 distances in the PDFs may increase the V_p . In contrast, the expansion of r_1 and r_2 distances by the interstitial incorporation of C and a small amount of S may

decrease the V_p of the liquids (Shibazaki & Kono, 2018). Due to the challenges of experiments on liquids, most experiments on liquid properties and structure were conducted at low pressures (<10 GPa) and the above structure V_p relationship may not be valid at higher pressure conditions. Indeed, V_p of liquid Fe-16 at% C was reported to be higher than that of pure liquid Fe (Nakajima et al., 2015), contradictory to the empirical relationship determined at lower pressures (Shibazaki & Kono, 2018).

The distinct effect of C on the r_1 and r_2 distances of liquid Fe and the structural evolution with pressure may also control other physical and chemical properties of liquid Fe. Viscosity of liquid Fe alloys at high pressure is another important physical property that is closely related to the internal dynamics of the outer core. Estimates of the viscosity of Earth's outer core varies in the orders of magnitude, particularly between observation and theory (Secco, 1995). Laboratory measurements indicated that the interstitial incorporation C into liquid Fe has little effect on the viscosity at <5 GPa (Terasaki et al., 2006). The structural evolution of the Fe-Ni-C liquids as explained by the increased fraction of three-atom cluster connections at ~5 GPa may significantly affect the viscosity of the liquids, which still awaits further experimental verification. For small terrestrial planets or moons, i.e. Mercury, Ganymede, and Moons, the structural change of the Fe-C liquids may occur at depths in the liquid portion of their cores. The resultant changes in liquid properties such as density and viscosity may lead to distinct layered stratifications and convection in the liquid cores.

The structural change of the Fe-Ni-C liquids may also influence chemical properties such as partitioning behaviors of major or trace elements and isotopic fractionation between metal and silicates during the formation of planetary cores. The nonlinear systematics in the metal-silicate partitioning behavior for trace elements (i.e., Ni, Co, and W) were also assumed to result from the polymorphic transition, which was inferred from a liquid compressibility change in the Fe-C liquid (Sanloup et al., 2011) and is consistent with the experimental and computational study on the structural change of Fe-C liquid at ~5 GPa (Lai et al., 2017; Shibazaki et al., 2015). The structural change may also render the distinct geochemical imprints (i.e., iron and carbon isotopes) of the bulk silicate Earth left behind by the core formation: bulk silicate Earth carbon is isotopically distinct (−5 ‰) from that in other terrestrial planets or planetary bodies (i.e., Mars and Vesta) and primitive undifferentiated meteorites (chondrites) (−20 ± 5 ‰) (Wood et al., 2013). The knowledge of the structural changes and potential polymorphic transitions in core-forming liquid iron alloys is thus crucial for our understanding of the chemical evolution of terrestrial planets and moons (Lai et al., 2017).

4.4. CONCLUSIONS

An outer core compositional model requires reliable material properties of iron-nickel liquids alloyed with lighter elements under core conditions. Probing the high P-T behavior of the iron-rich liquids through synergies between laboratory experiments and theoretical calculations could help improve our understanding of the physics and chemistry of the core, particularly of the liquid outer core. This approach provides a tractable methodology and offers a new and practical interplay between experiments and first-principles-based modeling for studying the liquid properties under outer core conditions that are difficult to reach with the current static high-P capabilities. A key component of this methodology is that all details of the structural and electronic information are fully accessible from the computations while experiments are used to validate the computed properties under experimentally accessible conditions. The new data from this methodology would add additional constraints on core composition and shed new light on the deep interiors of the Earth, as well as terrestrial planets and moons. Such a method can be particularly of value in determining if there are unanticipated changes in the large pressure range encountered in the Earth's outer core similar to the polymorphic transition around ~5 GPa or changes of intermediate structure and clustering involving light elements such as C. Recent studies based on such methodology show promising results.

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