Chapter 1

Introduction

To attempt to understand our planet's origin and subsequent evolution, we must look below the thin skin of the Earth's surface into its deep interior. Comprising over 99% of our planet's mass, the Earth's mantle and core have been actively redistributing heat and matter for the last four and a half billion years, as they respond to and help shape conditions at the surface. The evolutionary path traced by the Earth's interior is strongly linked to the behavior of the rocky material from which it is made. Understanding the physical properties of mantle rocks over a wide range of extreme conditions is therefore crucial to the goal of building a coherent picture of the Earth, both as it is today and as it once was in the distant past. Peering into the deep Earth is no easy task, as it requires that we probe through thousands of kilometers of opaque rock to a region that is both visually and physically inaccessible—instead, we must rely on more indirect methods. In this thesis, I present experimental and theoretical work which helps to expand our understanding of the thermodynamic properties of rocky material at extreme temperatures and pressures, relevant to both the modern-day mantle and to the mantle as it was early in Earth's history.

The Earth is composed primarily of a large thick shell of solid silicate rocks surrounding a liquid iron core. The core is just under half the Earth's radius, leaving almost 85% of the

volume to the Earth's mantle. The mantle is in turn split between the upper and lower mantle, where the distinction reflects the different mineral assemblages that comprise each region. The Earth's lower mantle is composed primarily of a mixture of roughly 80% $(Mg, Fe)(Si, Al)O_3$ perovskite and the remaining 20% is mostly $(Mg, Fe)O$ ferropericlase. As perovskite dominates the largest volumetric region of the Earth, this mineral likely represents the single most common material in the entire Earth. It also lies in a particularly dynamic region that is actively convecting, carrying heat up and out of the Earth's interior. If we could choose to understand only a single material in the hopes of shedding light on the evolutionary processes that shaped the Earth, silicate perovskite would undoubtedly be the best choice.

Our understanding of the Earth's mantle depends on direct seismic observations of how waves propagate at depth, combined with our knowledge of how terrestrial rocks behave at extreme conditions. Constraining the high-pressure thermal properties of mantle minerals is therefore one of the outstanding challenges in mineral physics, and helps to inform us about the structure and evolution of the deep Earth. The core-mantle boundary region is marked by numerous seismically observed heterogeneities spanning a wide range of length scales, the largest of which are the Large Low Shear Velocity Provinces (LLSVPs) that lie beneath Africa and the Pacific. These ~1000 km-tall structures are made visible by their distinct shear and bulk sound speeds, density contrasts, and seismically sharp boundaries, which are generally interpreted as evidence of combined thermal and compositional differences from the bulk mantle. Likely compositionally distinct and lying at the base of the Earth's mantle, these large intriguing structures prompt many questions. How could such a

vast compositional heterogeneity remain chemically isolated from the convecting mantle? What is the cause of their extreme topographic relief and how does this relate to their apparent longevity? What process is capable of forming such large compositionally distinct reservoirs and implanting them at the base of the mantle?

There are a number of geodynamic theories that potentially explain how such vast chemical reservoirs could resist mixing with the bulk mantle, a situation further complicated by the large vertical length scales involved. These theories generally fall into two broad categories: dynamically lifted passive piles and self-supporting metastable domes (*Tan and Gurnis*, 2007). Passive piles are made of material that is everywhere denser than the ambient mantle, causing it to pool on the core-mantle boundary (CMB), where externally imposed forces like down-going slabs dynamically sweep the piles upward giving them their observed morphology. Metastable domes, on the other hand, are less dense than average mantle at the CMB, causing them to internally convect and propping themselves up with a height determined by the height of neutral buoyancy. As these behaviors are a consequence of the material properties of the pile, they can be directly tested by experiments that determine the compression behavior of mantle minerals at high pressures and temperatures.

In Chapters 2 and 3, I report the results of laser-heated diamond anvil cell experiments that are analyzed to constrain the thermal properties of $(\mathrm{Mg}, \mathrm{Fe})\mathrm{SiO}_3$ perovskite, the dominant phase in the Earth's lower mantle and therefore a large likely component of LLSVPs. Unlike previous equation of state studies, we investigate the effect of iron (13%) on both the ambient and thermal properties of perovskite in a quasi-hydrostatic neon pressure medium.

We further employ a simplified mixture model in order to estimate the physical properties of perovskite for a wide range of iron compositions and compare these values to bulk mantle properties at a range of P-T conditions. Using the apparent contrast in density and bulk modulus relative to average lower mantle values, we assess the relative likelihood of passive pile and metastable dome theories for perovskite-dominated LLSVPs.

The evolutionary theories of how such chemical piles could have been generated in the first place is another important line of inquiry, one that connects us with the deep history of our planet. As is often the case, finding answers to the question of "why?" are even more challenging than the question of "what?". Generally speaking, the mechanistic hypotheses for the generation of LLSVPs fall either into the camp of slow accumulative processes or the remnant of a primordial event. The favored class of long-timescale explanation is that these chemical piles represent the residue of billions of years oceanic crust generation and subduction as a consequence of plate tectonics (*Tackley*, 2011). Oceanic crust is chemically dense relative to the ambient mantle and order of magnitude estimates of the total amount of crust generated over the Earth's lifetime are sufficient to explain the inferred volumes of these reservoirs (*Xie and Tackley*, 2004). The major poorly constrained aspect of the problem is how efficiently the basaltic component of oceanic plates can be de-laminated and segregated from the bulk of the plate to avoid being carried back upward by convective mantle flow. In contrast to this slow and gradual formation mechanism, the leading primordial remnant theories propose a link between the generation of these chemical reservoirs and the evolutionary processes that operated in the magma ocean present early in Earth's history. The magma ocean theory states that the large accretional energies

delivered to the Earth in the form of giant impacts resulted in melting of significant portions of the mantle (discussed in greater detail below). The cooling of the mantle from this initially molten state is accompanied by complex crystallization processes that have the potential to generate and gravitationally segregate the bulk mantle into multiple chemically separated constituents. Great uncertainty exists about the cooling pathways available to the early molten Earth, but likely potential processes that could generate chemically distinct reservoirs include fractional crystallization (*Solomatov and Stevenson*, 1993) and the longer-lived evolution of an insulated and isolated basal magma ocean (*Labrosse et al.*, 2007). Though our understanding of magma ocean processes are fraught with uncertainty, it is an attractive focus of study due to its potential for fundamentally altering the course of deep Earth evolution.

As magma ocean evolution likely represents one of the primary forces that shaped the early development of the mantle, understanding the behavior of silicate liquids at mantle pressures is crucial to reconstructing the early evolution of Earth and other terrestrial planets. While molten silicates play a minor role in the deep mantle today, their material properties directly determined the Earth's evolutionary path as it cooled from a nearly whole-mantle magma ocean to its present-day solid state. Earth's early history was marked by a series a giant and traumatic events. Giant impacts of large planetary embryos were responsible for setting the initial thermal state of the mantle. Since the gravitational energy of accretion for the Earth exceeds the threshold for complete melting by many orders of magnitude (*Stevenson*, 2007), the degree of melting actually experienced was determined by a balance between accretion and cooling timescales, which depend on how effectively energy

was delivered to great depth by large impacts. Based on accretion simulations (e.g., *Chambers*, 2004), we expect that the Earth suffered a series of a few to ten giant impacts during formation, the largest of which probably formed the moon. A recent numerical investigation into the moon-forming impact suggests that the entire mantle is likely to have melted (*Nakajima and Stevenson*, 2012); at the same time, new He and Xe isotopic evidence indicates that the Earth must have experienced at least two magma ocean periods in its history while simultaneously maintaining some primordial unmixed reservoirs (*Mukhopadhyay*, 2012; *Mukhopadhyay et al.*, 2012). These isotopic studies underscore the potential links that exist between very early Earth processes and the structures that we can seismically observe today residing in the deep mantle.

Our understanding of magma ocean crystallization and evolution is currently undergoing significant changes, linked directly to new insights on the behavior of silicate melts. Recent experimental and theoretical works (*Mosenfelder et al.*, 2007; *Stixrude et al.*, 2009) show that the thermal properties of silicate liquids upon compression differ significantly from our previous understanding, causing adiabatic thermal profiles that are much steeper than previously assumed—steeper even than the solidus (or melting curve for simple systems) at the base of the mantle. The cooling liquid adiabat adopted by the rapidly convecting magma ocean therefore likely first encounters the solidus at mid mantle depths, rather than at the base of the mantle, indicating a complex center-outwards style of crystallization rather than the classic bottom-up solidification that has dominated our thinking in magma ocean studies (e.g., *Solomatov and Stevenson*, 1993).

Considering these recent advancements in our general understanding of high-pressure

silicate liquids and the serious qualitative implications they have for magma ocean evolution, it is clear that we need to take a deeper mechanistic look into the compression behavior of silicate melts. In Chapter 4, I present the development of a general simplified model for oxide liquids. The **C**oordinated **HA**rd **S**phere **M**odel (CHASM) provides a simplified framework for predicting the behavior of oxide and silicate liquids at high pressures and temperatures. This model builds upon the analytic hard sphere liquid model, applied to silicates by *Jing and Karato* (2011), which captures the dominant entropy source for liquids, stemming from structural freedom due to lack of long-range order. On top of the basic hard sphere model backbone, CHASM incorporates an explicit accounting of the variable oxygen coordination states available to each cation in the liquid. The addition of a range of coordination states that are populated according to free energy minimization is crucial to representing gradual coordination evolution, which is the primary compression mechanism of silicate and oxide melts. In addition to presenting the general model framework, we also show how the CHASM approach can be adapted to any chemical system of interest by training its parameters on the energy compression curves for a variety of different crystal structures. We demonstrate this training method and the subsequent calculated results for the MgO system, showing strong agreement with first-principles calculations over a wide range of pressures and temperatures.

Throughout this thesis, I have endeavored to demonstrate the tight links that exist between our knowledge of the thermodynamic properties of rocky materials and our understanding of the Earth's interior. Using a mixture of experimental and theoretical techniques, I have studied the high-pressure and -temperature properties of silicate perovskite and gen-

eral oxide-silicate melts. Together, these represent the dominant phases of the Earth's mantle, now and in the distant past. Through the work presented in this thesis, I have added to our understanding of the behavior of these important phases under extreme conditions, and thus contributed to our growing knowledge of the deep Earth.