PREFACE

Earth's bulk water content likely exceeds that of all other terrestrial planets combined. Here, plate tectonics is responsible for the recycling of water between the crust and uppermost mantle. Water descends in hydrated oceanic crust, mostly in the form of hydrous minerals. Much of this water returns to the surface in the form of back-arc volcanism. But to what extent, if at all, does water recirculate deeper into the mantle below a few hundred kilometers? What are the observed fluxes, and how do they compare with potential fluxes based on the capacity of deep nominally anhydrous minerals to store water? Does some amount of Earth's primordial hydrogen or "water" remain trapped at deeper levels in the mantle? Is it possible to detect water in the deep mantle seismically or from electrical conductivity profiles? And to what extent may water be necessary for plate tectonics in the first place? These and other questions surrounding Earth's potential deep water cycle are covered in this volume through interdisciplinary studies from mineral physics, geochemistry, and geophysics. Indeed, with laboratory synthesis and physical properties measurements, seismology, and geodynamic modeling, we are beginning to understand what parameters will allow us to obtain a broader appreciation of the dynamic role that water plays in our planet.

Liquid water covers 70% of Earth's surface, but constitutes only about 0.025 wt% of the planet's mass – far less than Earth is thought to have contained during accretion and before core formation. Hydrogen loss during accretion must have been extensive, and there is compelling evidence that degassing of the mantle with greater than ninety percent efficiency has led to the formation of Earth's oceans [see e.g. *Rüpke et al.* of this volume]. However, the mass fraction of liquid water on Earth (0.025 wt% H_2O) is still on the order of ten times less than the water content of mid-ocean ridge magmas (0.2-0.3 wt% H_2O), and about half of what model "enriched mantle" sources contain (~0.04 wt% H_2O). Perhaps rather than asking from where did Earth's water originate, we should be asking to where has Earth's water gone?

It is possible that the majority of Earth's "missing water" resides in the deep mantle. Trace amounts of hydrogen have been measured in nearly all natural upper mantle-derived rocks, and evidence for dehydration and flux melting at shallow depths is well known, but the story below the asthenosphere becomes more elusive. Chapters in this volume will focus on the deeper upper mantle and transition zone at 410-660 km depth. Because of the large volume of rock associated with this part of the mantle, a small fraction of hydrogen goes a long way. Just a thousand ppm H_2O by weight, or roughly 0.1 wt% H_2O, if spread uniformly throughout the transition zone, would roughly equate in mass to the Atlantic Ocean.

The present volume is divided into five sections beginning with (I) two overview chapters where mineral physics and geochemical constraints are reviewed by *Smyth and Jacobsen*, followed by a review of seismological studies and constraints on water in the deep Earth by *Van der Lee and Wiens*. Subsequent chapters are grouped into sections dealing with (II) water storage and stability of OH-bearing phases, (III) properties of a deep hydrous mantle, (IV) observational studies from seismology and electrical conductivity, and (V) global models of the deep-Earth water cycle.

In section II, *Komabayashi* presents a complete phase diagram of hydrous peridotite in the MgO-SiO_2-H_2O system extending to lower mantle conditions. His thorough treatment of phase stability is based upon the latest high-pressure experimental results and new thermodynamic calculations. The section on storage capacity and stability continues with a look at natural samples from the upper mantle; *Mosenfelder et al.* examine the OH-signatures in mantle-derived olivine using infrared spectroscopy and high-resolution microscopy to evaluate some key differences between natural samples and those synthesized in laboratory experiments. Going deeper, *Bolfan-Casanova* *et al.* report on the storage capacity and hydration mechanisms in phases of the transition zone and lower mantle including wadsleyite, ringwoodite, silicate perovskite, and magnesiowüstite. Section II concludes with a chapter on Raman spectroscopic studies of OH-bearing minerals by *Kleppe and Jephcoat*. Their chapter features a new graphical database of Raman spectra for the most important OH-bearing and hydrous phases.

Section III deals mainly with physical properties of hydrated mantle minerals. Experimental studies on the physical properties of hydrous and OH-bearing phases provides a key link between mineral physics and the observational studies and models to follow in subsequent sections. *Litasov et al.* report experimental results on the influence of water on the phase transformations related to the major seismic discontinuities at 410 and 660-km depth. *Karato* presents a critical review of the effects of hydrogen on transport properties including electrical conductivity and plastic deformation. *Jacobsen and Smyth* have measured compressional and shear wave velocities in hydrous ringwoodite ultrasonically at high pressures and model hydrous velocities in the transition zone. *Inoue et al.* report new *in-situ* high-pressure and high-temperature studies on the stability and equation of state of superhydrous phase B, a dense hydrous magnesium silicate that may play a role in transporting large amounts of water along cooler subduction geotherms. Section III concludes with a new look at the properties of pure H_2O – *Lin et al.* examine the phase diagram of H_2O as it pertains to planetary interiors and review various lines of evidence for the newly discovered triple point beyond which solid-H_2O becomes "superionic", with freely moving H^+ (protons).

Section IV highlights current methods to infer the presence and amount of hydrogen in the mantle. *Koyama et al.* interpret a region of high electrical conductivity and high seismic P wave velocities in the transition zone beneath the Mariana Islands as ~0.3 wt% more hydrous than the surrounding mantle. Next, *Courtier and Revenaugh* examine transition-zone discontinuities through *ScS* reverberations and find that observed depths and impedance contrasts are consistent with a locally hydrous transition zone beneath the eastern US. In the western US, *Song and Helmberger* study triplicated S waves and infer a possibly water-triggered low-velocity layer atop the 410-km discontinuity that has a sharp western edge. To complete the variety of seismic observations used to detect "deep protons", *Braunmiller et al.* turn to S waves converted from P waves at transition zone discontinuities and find that the transition zone beneath the Andes could be either saturated with water or dry as a desert. *Shito et al.* combine various seismic observations, specifically anomalies in P and S velocities and S-wave attenuation, to systematically map the possible distribution of water in the upper mantle. They find up to 0.1 wt% H_2O above the transition zone beneath the Philippine Sea. *Suetsugu et al.* combine P-velocity anomalies with relief on the 660-km discontinuity and deduce 1-1.5 wt% H_2O at the base of the transition zone below the Philippine Sea and western Japan. Finally, *Lawrence and Wysession* study a large attenuation anomaly imaged in the top of the lower mantle beneath China that may be related to deep water cycling. Observational inferences for water content in the mantle require special attention to associated uncertainties both in material properties and data processing, but the emerging consensus suggests that there is a detectable level of hydration heterogeneously distributed in the Earth's mantle.

The volume concludes with several models of a deep-Earth water cycle in section V. Though it's easy to get caught up in the excitement about the potential of vast quantities of water in the interior, *Rupke et al*. provide compelling arguments that Earth's mantle has efficiently degassed, with the majority of the planet's water locked in the hydrosphere and shallowest upper mantle. In the case that water does resist dehydration and cycle to deeper depths at the transition zone, properties of the 410-km discontinuity likely hold key evidence one way or the other. *Hirschmann et al.* model the influence of water on various properties of the 410-discontinity, which will help to direct seismologists towards observable features related to water, or the absence of it. Finally, *Karato et al.* present an updated "transition zone water filter model" that seeks to explain how water and associated melts in the transition zone may explain paradoxical geochemical trends in surface volcanism.

In its entirety, we hope this volume portrays the nature, current directions, and future needs in the study of Earth's deep water cycle. Earth is the only planet we know of that looses internal heat through plate tectonics. Large spatial and temporal variations in viscosity are required in a planet's mantle for plate tectonics to operate. Cycling of water between the deep upper mantle and the surface could provide viscosity contrasts; thus, water content could be the second most important factor, next to temperature, influencing the viscosity of Earth's mantle and the fate of plate tectonics. In this larger context, the study of Earth's deep water cycle is central to understanding the evolution of the planet.

At the same time, this volume comes at a crossroads in the study of water in the deep Earth. Up until about ten years ago the study of OH in nominally anhydrous minerals was more or less restricted to a few papers in the mineralogical literature that went largely unnoticed by the wider geophysical community. Since then, we have come to recognize the strong possibility that water is playing a major role in mantle dynamics. Despite recent progress on many fronts, as exemplified in this volume, there remains considerable work to be done. The effects of hydration on elastic moduli and their derivatives to temperature, seismic attenuation, and the solubility of water in the lower mantle stand out as areas especially in need of exploration. Equally vital is the need to reduce ambiguities associated with the interpretation of geophysical data used to remotely sense water in the deep upper mantle.

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