DIAMONDS FROM THE DEEP

WINDOWS INTO SCIENTIFIC RESEARCH

Karen V. Smit and Steven B. Shirey

Diamonds Help Solve the Enigma of Earth's Deep Water

Water is carried down into Earth at subduction zones by the process of plate tectonics. Much of the water escapes close behind the subduction zone, promoting melting of the mantle and giving rise to the volcanic chains in the Pacific Ocean basin known as the Ring of Fire, and many other volcanoes elsewhere. But can water be carried even further into the mantle? How would we even know? Why is it important, and what are the effects of such deep water storage? Diamonds can give us the answers to these questions. Recent discoveries of water-containing mineral inclusions and even free water held at high pressures in diamonds tell us that water is carried into Earth's deep interior—perhaps as deep as 700 km.

Why Do Earth Scientists Want to Know the Water Content at Great Depths?

Water, Water Everywhere... Everyone can see how abundant water is at Earth's surface from our oceans. But because water can fit into mineral structures at high pressure and the volume of Earth's mantle is so large, there could be at least another ocean's worth of water stored in the minerals of the mantle. To know precisely how much water and in what form it was stored would help scientists understand where the water for our oceans came from, how much water returns to the mantle through plate tectonics, and how the stored water affects the properties of the mantle.

Water in the deep earth is not always a free fluid phase, and many minerals instead have water incorporated in the crystal structure as hydrogen bonded to oxygen. Common mantle minerals such as majorite, bridgmanite, Mg-Al spinel, and olivine (and its high-pressure equivalents wadsleyite and ringwoodite), are "nominally anhydrous," but experiments show that they have the capacity to carry and host water in such a form in their structures.

Once in the mantle, water has many important effects on the properties of the mantle. Water affects the temperature at which the mantle begins to melt, along with its physical properties such as viscosity and density. In turn, these properties influence the strength of the mantle rock (its resistance to being deformed). It therefore becomes important for our understanding of the mobility and melting of mantle rock in the deep Earth to know how much water is down there. Water-rich fluids—i.e., water solutions wherein a variety of elements, compounds, and gases may be dissolved—are also a very effective way to transport other elements between different parts of Earth. Specifically, subduction fluids can transfer elements from the surface to diamond-stable portions of Earth and may even be a critical ingredient for growing diamonds.

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How Is Water Distributed, and How Does It Get into the Deep Earth? The mantle transition zone (410–660 km) is thought to be a major sink for water in the mantle (Smyth, 1987). The two key minerals that make up the transition zone, wadsleyite and ringwoodite, have been shown experimentally to host an abundance of water, up to about 3.3 wt.% and 2.2 wt.% H_2O, respectively (Kohlstedt et al., 1996). Seismic images show that oceanic slabs—containing the water that was not released at shallower levels—are recycled into the mantle by subduction and can sit within the transition zone (van der Hilst et al., 1997). So both a delivery and storage mechanism for water exists for the mantle transition zone.

The water content in the lower mantle (below 660 km) is likely not as high as it is in the transition zone. Experiments show that the minerals in the lower mantle do not have a high water-carrying capacity (Inoue et al., 2010; Schmandt et al., 2014). When some oceanic slabs are subducted past the transition zone and into the lower mantle, it is expected that any water would be released upward into the overlying mantle. However, a lower mantle diamond from the Juína area of Brazil was found to contain brucite ($Mg(OH)_2$) in association with ferropericlase ($(Mg,Fe)O$) (Palot et al., 2016). Water in the brucite structure likely originated as a H_2O-bearing fluid film around the ferropericlase inclusion. This diamond preserved an inclusion that indicates that some water transport beyond the transition zone is possible.

Evidence for Mantle Water from Minerals Found in Superdeep Diamonds

Water as a Solidified Fluid: Samples of High-Pressure Ice. Direct observations of water-rich fluids in superdeep diamonds (see box A) are rare and have only been reported in two studies. At atmospheric pressure, H_2O occurs as a liquid, but at higher pressures (and relatively cool temperatures compared to mantle temperatures), H_2O occurs as two different forms of ice, known as Ice VI and Ice VII (figure 1).

Ice VI was found in fibrous diamonds from the Democratic Republic of the Congo with a remnant pressure of 1.9 GPa (Kagi et al., 2000), where 1 GPa is 1 gigapascal or 10,000 times atmospheric pressure. Ice VII was found in diamonds from Orapa (Botswana), Shandong (China), and Namaqualand (South Africa) at pressures ranging from 7 GPa to 28 GPa, which is equivalent to 220 to 880 km (Tschauner et al., 2018). Amazingly, once these water-rich fluids are trapped as inclusions in diamond, they retain some high pressure even after eruption to the earth's surface. As the diamond cools down to ambient conditions (25°C, 100 kPa), the trapped H_2O recrystallizes as Ice VI or Ice VII (figure 1).

Hydrous fluids have previously been found trapped as thin films around shallower lithospheric diamonds (again, see box A; Nimis et al., 2016). But the presence of Ice VII in superdeep diamonds confirms the presence of a free fluid phase at pressures corresponding to the transition zone and lower mantle. As discussed with the finding of hydrous ringwoodite (below), these H_2O-rich fluids could represent the fluid-rich diamond-forming environment, or they could be indicative of the ambient water content of the deep Earth. A likely scenario is that H_2O-rich fluids are introduced into the deep Earth through subduction, consistent with the compositions of many superdeep diamonds that indicate an affinity with subducted oceanic slabs. This suggests that these fluid-rich regions of the transition zone occur locally around subducted slabs. Only further work on other superdeep inclusion-bearing diamonds from worldwide localities will show if this is the case, or how widespread such water contents are. But the highly diverse nature of the host diamonds that have been studied already suggests that these ices may be much more common than thought—we just need to look more carefully.

Water Isn't Always a Free Fluid Phase: Examples of Mineral-Hosted Water. Ringwoodite is a high-pressure form of olivine (Mg_2SiO_4) that occurs in the lower half of the mantle transition zone, where it comprises around 60% of the total mineralogy. We know this from experimental work that simulates the high-pressure conditions deep within Earth. Until 2014, ringwoodite had only been found in highly shocked meteorites. This is because at surface pressures, ringwoodite—even when confined to its diamond host—is notoriously unstable and reverts to olivine at lower pressure.

Unchanged ringwoodite from deep in Earth was found for the first time as a 30 μm inclusion trapped within a diamond from Juína, Brazil (figure 2; see also Pearson et al., 2014). Even more remarkable was that this tiny ringwoodite grain was able to provide the first direct measurement of the water content of the most common mineral in the mantle transition zone. Water content was measured using nondestructive infrared spectroscopy (IR) while the inclusion was still trapped at high remnant pressure within the diamond. When the scientists attempted to remove the inclusion from the diamond for additional measurements, it self-destructed by exploding!

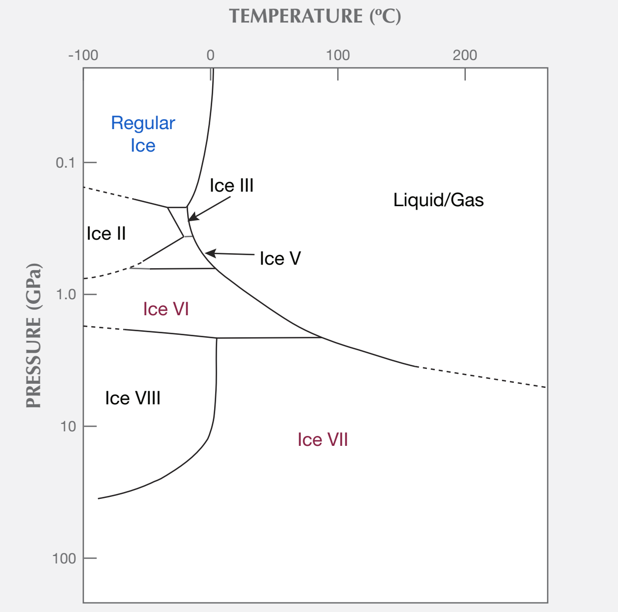

Figure 1. Phase diagram showing the stability fields of H_2O as liquid and ice at high pressures (modified from Lobban et al., 1998). Superdeep diamonds form at temperatures between 1300 and 1500°C (beyond scale of diagram) where H_2O occurs as a liquid. As the diamond cools at the earth's surface, H_2O trapped within the diamond retains its original high pressure and recrystallizes as the high-pressure form of solid H_2O known as Ice VII.

By comparing the intensity of the water peaks in the IR spectrum with those from synthetic ringwoodite with known amounts of water, the natural ringwoodite inclusion was estimated to contain around 1.4 wt.% H_2O. This value could represent either a locally water-enriched portion of the mantle transition zone, perhaps associated with the fluids that formed the diamonds, or the water content of the mantle transition zone as a whole. It is interesting to note that if this water content is applied to the whole mantle transition zone, the total water content would be approximately 2.5 times the volume of water in Earth's oceans (Nestola and Smyth, 2015).

The Tip of the Iceberg: Much Further Work Is Needed. Wadsleyite, another potential water carrier, has not yet been observed as an inclusion in diamond. This is the high-pressure

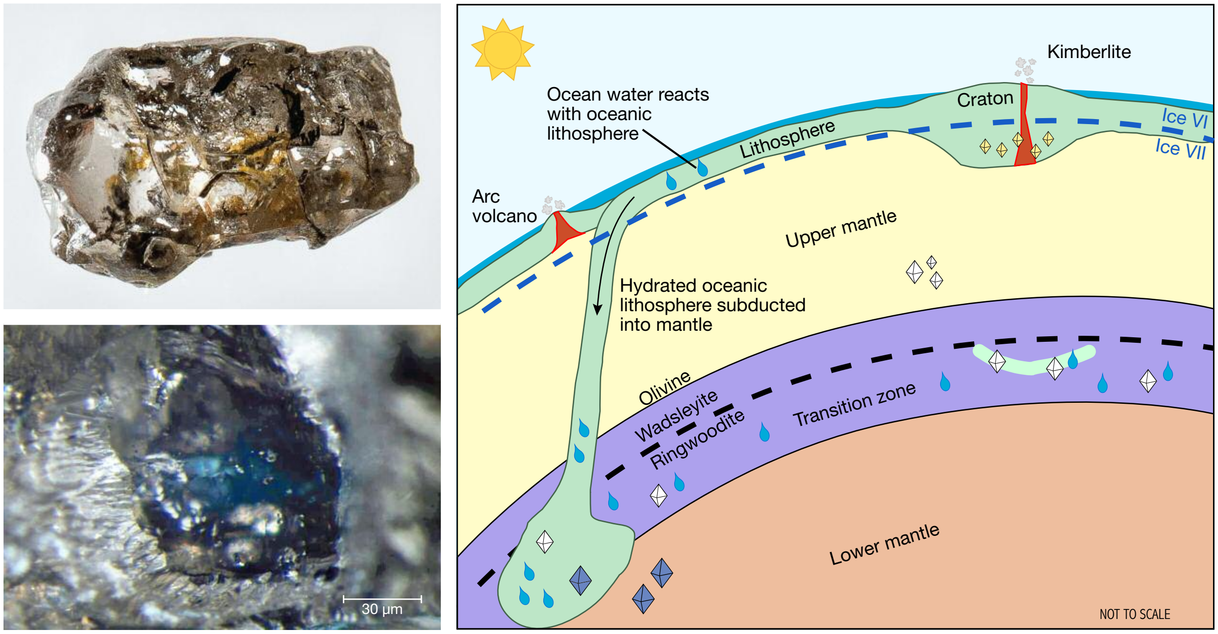

Figure 2. Ringwoodite is the high-pressure form of the mineral olivine (Mg_2SiO_4) that occurs between 520 and 660 km below the surface of the earth in the transition zone. The first terrestrial observation of this mineral was in a diamond from Juína, Brazil (top left). Water content in this 30 µm inclusion (bottom left) is around 1.4 wt.%, indicating that the global transition zone could contain at least 2.5 times the amount of water as Earth's oceans. The majority of diamonds come from the cratonic lithosphere (indicated here as yellow diamonds). Superdeep diamonds (indicated here as white and blue diamonds) are rarer and originate from greater depths, often from the transition zone, which extends between 410 and 660 km.

phase of olivine that is found between 410 and 520 km, just slightly shallower than ringwoodite (figure 2). Finding wadsleyite, along with more occurrences of ringwoodite, and analyzing their water contents will give a better understanding of the mantle transition zone's average water-carrying capacity. Expectations are that wadsleyite will carry at least

BOX A: DIAMOND IN THE EARTH'S MANTLE

Natural Diamond Formation. Natural diamonds typically form 150–200 km below the surface of the earth. Diamond formation does not occur everywhere at these depths, but only below the oldest continents that have been stable for billions of years; these areas are known as *cratons*. This is because these old cratons all have thick continental roots with cool temperature profiles conducive to diamond formation. Diamonds that form within these continental roots are known as *lithospheric diamonds* and are carried up to the surface of the earth by rare volcanic eruptions known as *kimberlites*. Other diamonds form much deeper in the earth, below these continental roots. So-called *superdeep diamonds* form at depths greater than 200 km in areas of the mantle known as the *transition zone* (410 to 660 km below the earth's surface) and *lower mantle* (> 660 km). After formation they are transported to shallower depths in the mantle, likely through mantle convection cells, and then also brought to the surface by kimberlite eruptions.

Inclusions in Superdeep Diamonds Are Direct Samples of the Deep Earth. Diamonds often trap tiny pieces of their surrounding rocks as they grow. These trapped inclusions are the only direct samples we have to study the composition of the deep earth. In the absence of mineral inclusions in diamond, the way to study the earth's composition at depth is through experimental work: subjecting minerals to high pressures in the lab to see what their properties are. This experimental work has given us a good understanding of the mineral phase transitions in the deep earth, but inclusion-bearing diamond remains an unparalleled tool to uncover the earth's properties at depth.

as much water as ringwoodite. Will water in these minerals turn out to be ubiquitous? Is the earth even wetter than we thought?

Further evidence for water in mineral inclusions in many more superdeep diamonds must be sought. An easy way to start is through nondestructive infrared spectroscopy of diamonds and their inclusions, specifically looking for water and ice peaks (see Kagi et al., 2000 for example spectra). Even some lithospheric diamonds are thought to form from water-rich fluids (Stachel and Luth, 2015; Smit et al., 2016), yet observation of water in these diamonds is incredibly rare (Nimis et al., 2016). Could it be that these high-pressure ices are much more common than we thought? Could the discovery of Ice VII in Earth's diamonds revolutionize our thinking about ice storage at high pressure in other planets of our size range, such as Mars or Venus? In any case, these secrets will be revealed by more work on diamonds.

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