

Deep water gives up another secret

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Just as water is essential for life as we know it, so too is it critical to our planet's inner workings. In PNAS, Pan et al. (1) report results that constrain one of water's most important properties at deep-earth conditions: its dielectric constant. A host of geologic processes signal water's important role at depth. The volcanoes of the Pacific Ocean's "ring of fire" erupt explosively because the magmas carry water from the deep interior. Water influences the still-mysterious, sudden breaking and sliding of rock we sense as earthquakes. Furthermore, many concentrations of valuable metals on which our society depends are created through complex natural reaction processes mediated largely by H₂O. Indeed, without deep water, we might not have continents (2), and the plate tectonic engine controlling the outer part of the planet would probably operate quite differently (3).

Aqueous fluids in the subsurface are confined in pores and fractures in sediment and rock; as temperature rises with depth, porosity and permeability decline (4), but the solubility of rock components increases dramatically (5). Thus, the rock hosts exert strong control on the available solutes, whereas the properties of H₂O govern their concentrations and structure in solution. At depths more than several tens of kilometers (i.e., the lower continental crust and the upper mantle), the chemistry of aqueous fluids remains enigmatic because direct sampling from deep drill holes is limited to less than about 10 km, small deep-fluid inclusions trapped in minerals often have complex histories that can hinder their study, and experimental approaches have been challenging.

An alternative to direct sampling or experimental study is thermodynamic modeling of water–rock reactions, for which a key ingredient is the dielectric constant (static relative permittivity) of H₂O ($\epsilon_{\text{H}_2\text{O}}$). Seminal work by Helgeson and coworkers provided geoscientists with the tools necessary to model such systems, most significantly via the Helgeson–Kirkham–Flowers (HKF) equation of state for ions (7, 8). In this approach, the stabilizing energy of transferring an ion into H₂O (the Gibbs energy of ion solvation)

and its pressure and temperature derivatives depend chiefly on $\epsilon_{\text{H}_2\text{O}}$. The dielectric constant quantifies a solvent's ability to hold ions in solution; solvents with higher ϵ better shield ions such as Na⁺ and Cl[−] from interacting to bond with another ion or precipitate. Polar condensed phase water possesses a high dielectric constant of ~ 80 times vacuum at ambient conditions. This explains water's remarkable solvent properties relative to other geologically relevant compounds such as CO₂.

Previous determinations of $\epsilon_{\text{H}_2\text{O}}$ extend to modest pressures (1.2 GPa; 600 °C) and indicate that it declines with increasing depth and rising temperature (9). The limited pressure–temperature range has prevented extending the HKF model to mantle conditions, where H₂O participates in important geologic processes. To date, it has not proven possible to measure $\epsilon_{\text{H}_2\text{O}}$ in situ at the requisite conditions. However, Pan et al. (1) show that ab initio molecular dynamics offers a solution. They used density functional theory (DFT) to derive $\epsilon_{\text{H}_2\text{O}}$ from fluctuations in dipole moment at high density and temperature. Good agreement between simulation pressures and those from accepted equations of state gives confidence in the approach. Achieving a high level of accuracy depends on tracking water molecules over sufficiently long trajectories (times) in the simulation cells. Pan et al. (1) take advantage of the fact that at high density and temperature, diffusion and rotation of water molecules are fast compared with ambient conditions. As a result, the authors could derive $\epsilon_{\text{H}_2\text{O}}$ from simulation times of 20 ps, or about 300 times shorter than is required at ambient conditions (10).

Pan et al. (1) calculate $\epsilon_{\text{H}_2\text{O}}$ to 11 GPa and 2,000 K. They find that it increases with density along isotherms. At low pressure, their results agree with existing compilations (9). This is in contrast to the significantly lower $\epsilon_{\text{H}_2\text{O}}$ reported in a previous molecular dynamics study using the simple point charge extended (SPC/E) potential with a constant dipole moment (11). At 1,000 K, an increase in pressure from 1 to 11 GPa causes $\epsilon_{\text{H}_2\text{O}}$ to rise from ~ 15 to ~ 40 , which is only about

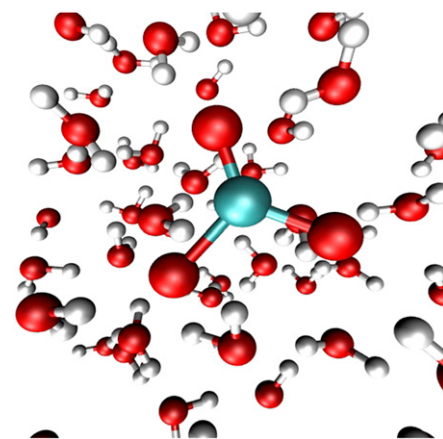


Fig. 1. Carbonate anion in H₂O. Ab initio molecular dynamics results on H₂O improve estimates of the static dielectric constant (1), which allows extension of thermodynamic models of aqueous fluids to the high pressures and temperatures of the earth's mantle. The predicted solubilities of metal and carbonate ions are higher than previously recognized. Image courtesy of Q. Wan (University of California, Davis, CA).

half that at ambient conditions. This indicates that hot, dense fluids of the upper mantle should be better solvents for ions than their shallower crustal equivalents, at equal temperature. At constant pressure, increasing temperature leads to a decline in $\epsilon_{\text{H}_2\text{O}}$, so along such a trajectory increased ion pairing should be expected.

The values for $\epsilon_{\text{H}_2\text{O}}$ calculated by Pan et al. (1) are used to revise the HKF model and compute equilibrium constants for the dissolution of carbonate minerals (MCO₃, where M is Ca²⁺, Mg²⁺, or Fe²⁺) in H₂O at 1,000 K to 10 GPa (Fig. 1). The predicted concentrations of Mg²⁺ and CO₃^{2−} in equilibrium with magnesite (MgCO₃) increase from effectively zero (submicromolar levels) to several millimolar in otherwise pure H₂O, illustrating the role of increasing $\epsilon_{\text{H}_2\text{O}}$ with depth.

The results add to a growing body of information about the properties of dense, hot water. It appears that there are two types of local structure in liquid H₂O, the low-density water familiar at ambient conditions, and high-density water at high pressure (e.g., 12). DFT calculations reveal that increasing

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pressure induces strong dissociation of H₂O to hydronium and hydroxyl ions by a mechanism similar to that at ambient conditions (13). Meanwhile, experimental methods are improving and show promise for providing independent determinations of water properties (14, 15). However, much still needs to be done. It is becoming clear that fluids in the mantle contain enormous solute loads derived from the rock matrix (16, 17). Mutual interactions between complex polymerized

clusters enhance solubility of other components (18) and lead to a complete continuum between dry silicate melts and H₂O (6, 19). The chemical interactions between these clusters and dissolved ions remain to be sorted out. The complexities are illustrated by fluids from Earth's mantle found as small inclusions in some diamonds. Compositions of these fluid inclusions may be rich in carbonate and chlorine along with silicate and H₂O (20).

Thus, although accurate models of the thermodynamic and transport properties of mantle fluids can usefully take H₂O as the starting point, they must eventually come to grips with the likelihood that natural mantle fluids are a compositional continuum between H₂O, silicate-rock components, CO₂, and chloride salts. However, the results of Pan et al. (1) provide a fundamental step toward unlocking the secrets of Earth's deep fluids.

- 1 Pan D, Spanu L, Harrison B, Sverjensky DA, Galli G (2013) Dielectric properties of water under extreme conditions and transport of carbonates in the deep Earth. *Proc Natl Acad Sci USA* 110:6646–6650.
- 2 Campbell IH, Taylor SR (1983) No water, no granites - no oceans, no continents. *Geophys Res Lett* 10:1061–1064.
- 3 Hirth G, Kohlstedt DL (1996) Water in the oceanic upper mantle: Implications for rheology, melt extraction and the evolution of the lithosphere. *Earth Planet Sci Lett* 144:93–108.
- 4 Manning CE, Ingebritsen SE (1999) Permeability of the continental crust: Constraints from heat flow models and metamorphic systems. *Rev Geophys* 37:127–150.
- 5 Eugster HP, Baumgartner L (1987) Mineral solubilities and speciation in supercritical metamorphic fluids. *Rev Mineral* 17:367–403.
- 6 Manning CE (2004) The chemistry of subduction-zone fluids. *Earth Planet Sci Lett* 223:1–16.
- 7 Helgeson HC, Kirkham DH, Flowers GC (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. *Am J Sci* 281:1249–1516.
- 8 Tanger JC IV, Helgeson HC (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. *Am J Sci* 288:19–98.
- 9 Fernández DP, Goodwin ARH, Lemmon EW, Levelt Sengers JMH, Williams RCA (1997) A formulation for the static permittivity of water and steam at temperatures from 238 K to 873 K at pressures up to 1200 MPa, including derivatives and Debye-Huckel coefficients. *J Phys Chem Ref Data* 26:1125–1166.
- 10 Gereben O, Pusztai L (2011) On the accurate calculation of the dielectric constant from molecular dynamics simulations: The case of SPC/E and SWM4-DP water. *Chem Phys Lett* 507:80–83.
- 11 Wassermann E, Wood B, Brodholt J (1995) Molecular dynamics study of the dielectric constant of water under high pressure and temperature conditions. *Geochim Cosmochim Acta* 59:1–6.
- 12 Soper AK, Ricci MA (2000) Structures of high-density and low-density water. *Phys Rev Lett* 84(13):2881–2884.
- 13 Schwegler E, Galli G, Gygi F, Hood RQ (2001) Dissociation of water under pressure. *Phys Rev Lett* 87(26):265501.
- 14 Abramson EH, Brown JM (2004) Equation of state of water based on speeds of sound measured in the diamond-anvil cell. *Geochim Cosmochim Acta* 68:1827–1835.
- 15 Sanchez-Valle C, Mantegazzi D, Bass JD, Reusser E (2013) Equation of state, refractive index and polarizability of compressed water to 7 GPa and 673 K. *J Chem Phys* 138(5):054505.
- 16 Kessel R, Ulmer P, Pettko T, Schmidt MW, Thompson AB (2005) The water-basalt system at 4 to 6 GPa: Phase relations and second critical endpoint in a K-free eclogite at 700 to 1400 °C. *Earth Planet Sci Lett* 237:873–892.
- 17 Wohlers A, Manning CE, Thompson AB (2011) Experimental investigation of the solubility of albite and jadeite in H₂O, with paragonite plus quartz at 500 and 600 °C, and 1–2.25 GPa. *Geochim Cosmochim Acta* 75:2924–2939.
- 18 Manning CE (2007) Solubility of corundum plus kyanite in H₂O at 700 °C and 10 kbar: Evidence for Al-Si complexing at high pressure and temperature. *Geofluids* 7:258–269.
- 19 Hunt JD, Manning CE (2012) A thermodynamic model for the system SiO₂-H₂O near the upper critical end point based on quartz solubility experiments at 500–1100 °C and 5–20 kbar. *Geochim Cosmochim Acta* 86:196–213.
- 20 Klein-BenDavid O, Izraeli ES, Hauri E, Navon O (2007) Fluid inclusions in diamonds from the Diavik mine, Canada and the evolution of diamond-forming fluids. *Geochim Cosmochim Acta* 71:723–744.