nent NIPA through hydrophobic interaction becomes more substantial than that by MAPTAC. The adsorption becomes independent of MAPTAC concentration and the power becomes 0.

The mechanism of multiple-point adsorption is different from that by charged gels through the nonspecific Donnan potential (*3*). Under our experimental conditions, where a high salt concentration (100 mM) was used, the Donnan potential was completely destroyed. Adsorption by the Donnan potential is estimated to be more than three orders of magnitude smaller than what we observed. Furthermore, dependence of the Donnan potential adsorption on MAPTAC should be much weaker (less than a power of 1) than the power of 3 or 4 as observed in our case.

Although we have not created the adsorber as specific as proteins, we have shown that, by varying polymer conformation and concentration, we can change the reversible affinity for target molecules by two or three orders of magnitude. In the compact state, in particular, the gel showed a dramatic change in affinity in response to a slight change in volume. In our experiments, the number of contact was three or four. If more contact points with more diverse interactions (such as hydrogen bonding and hydrophobic interaction) were used, it is possible that the gel-target interaction could be made more specific and the affinity might show a sharper response to change in polymer density (*4*).

In our experiments, we used temperature to trigger the adsorption and release. Similar gels can be, in principle, designed in which the reversal of affinity is triggered by other physical parameters such as solvent composition, pH, light, electric or magnetic field, and osmotic or hydrostatic pressure (*5*).

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4. There have been works on molecular adsorption, in particular, on its dependence on phase states of polymers and gels. These studies mostly used nonspecific hydrophobic interaction. The affinity changes in response to polymer density changes triggered by temperature. See, for example, M. Yamato *et al.*, *Connect. Tissue* **31**, 13 (1999).
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6. The work was supported by the U.S. Department of Energy, NIH, and Sumitomo Bakelite.

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Pressure Effect on Hydrogen Isotope Fractionation Between Brucite and Water at Elevated Temperatures

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Experimental evidence for a pressure effect on isotopic partitioning at elevated temperatures demonstrates that equilibrium deuterium-protium fractionation between the mineral brucite [$Mg(OH)_2$] and pure water systematically increases by 12.4 per mil as pressure increases from 15 to 800 megapascals at 380°C. A linear relation is observed between the measured fractionation factor and the density of water (0.070 to 1.035 grams per cubic centimeter). The trend of the isotope pressure effect is the same as that of recent theoretical studies, but the magnitude is smaller. The pressure effect must be accounted for in the interpretation of isotopic data of geologic systems involving water (paleotemperature, source of fluids).

It has been commonly assumed in stable isotope geochemistry and cosmochemistry that temperature is the principal variable in determining equilibrium partitioning of the isotopes of light elements among different phases and chemical species and that pressure is of no importance. In classic statistical-mechanical calculations of reduced partition functions for geologically relevant materials, intermolecular forces and interactions of molecular species usually have been ignored. For solid phases, changes in molar volumes due to isotopic substitution are small except for hydrogen isotopes. Previous calculations indicate that pressure effects on isotopic partition function ratios of minerals are probably small ($\leq$0.5 per mil in $^{18}O/^{16}O$) at pressures up to 1000 to 2000 MPa at elevated temperatures (*1, 2*). Pressure effects on isotopic fractionation between two minerals may even cancel each other as the potential change in partition function ratio of one of these minerals is similar in magnitude to that of the other mineral. Previous experimental investigations, primarily on oxygen isotope fractionation between minerals and aqueous fluids, have revealed no significant pressure effect ($\leq$0.2 per mil) on isotopic partitioning at temperatures up to 700°C and pressures up to 2000 MPa (*3*).

Unlike minerals, which maintain a rigid structure with near-constant lattice parameters within a given temperature-pressure range, the structure and density of pure water change significantly with pressure, particularly in near-critical regions. Among the three normal modes of vibrations of water molecules, symmetric O-H and O-D stretching frequencies of H_2O and HDO, respectively, decrease significantly (red shift) with increasing pressure at a given temperature (*4*). Polyakov and Kharlashina (*2*) calculated, on the basis of thermodynamics, that the pressure effect on the reduced partition function ratio for D/H in pure water is substantial. More recently, Driesner (*5*) calculated from spectroscopic data that the reduced partition function ratio for D/H in pure water changes by as much as 20 per mil near the critical temperature of water (374°C) at low pressures ($<$100 MPa), whereas the pressure effect on the partition function ratio for $^{18}O/^{16}O$ in water would be small (on the order of 0.4 per mil) in the same temperature-pressure range. Partition function ratios for D/H in molecular water clusters in the vapor phase at elevated temperatures, calculated on the basis of molecular dynamics and ab initio methods, are significantly lower than those of isolated water molecules (*5*). On the basis of these calculations, Driesner (*5*) and Vennemann and O'Neil (*6*) argued that large discrepancies in experimental D/H fractionation factors between hydrous minerals and water could be ascribed to pressure differences in the experiments. The magnitude of the calculated pressure effect on the partition function ratio for D/H in water and the discrepancies in mineral water D/H partitioning in the literature (*6*) are too large to be ignored, and experimental verification is needed. Mineev and Grinenko (*7*) reported large pressure effects (26 to 55 per mil) in the system serpentine water at 100° to 200°C and 0.1 to 250 MPa, but details of their experiments and results are not available. Here, we report experimental results that confirm the pressure effect on D/H isotope partitioning between a hydrous mineral and water at elevated temperatures.

The isotope pressure effect in water is

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defined (*5*) as

$$\Gamma_P = (Q_D/Q_H)_{\mathrm{water},P(\mathrm{ref})}/(Q_D/Q_H)_{\mathrm{water},P} \quad (1)$$

where Q_D and Q_H are the reduced partition functions of HDO and H_2O water, respectively. The Γ_P can be determined experimentally as a change in the equilibrium isotope fractionation factor (α) between water and any other coexisting phase (A), assuming that the coexisting phase A is not influenced by pressure

$$\Gamma_P = \alpha_{A\text{-water},P}/\alpha_{A\text{-water},P(\mathrm{ref})} \quad (2)$$

where $\alpha_{A\text{-water}} = (Q_D/Q_H)_A/(Q_D/Q_H)_{\mathrm{water}}$. Then,

$$1000 \ln \Gamma_P = 1000 \ln \alpha_{A\text{-water},P} - 1000 \ln \alpha_{A\text{-water},P(\mathrm{ref})} \quad (3)$$

A series of hydrothermal experiments were conducted to determine the effect of pressure on the equilibrium D/H fractionation factor between the mineral brucite [$Mg(OH)_2$] and water at 380°C in the pressure range from 15 to 800 MPa. The temperature was chosen slightly above the critical temperature of 374°C, where the largest pressure effect is expected (*5*). Brucite is chemically and structurally a simple mineral stable over a wide temperature-pressure range with a very low solubility and a high water content (*8*). Fine-grained (0.1 to 0.5 μm) $Mg(OH)_2$ reacted with three or four isotopically different pure waters in sealed gold capsules at 380°C and at 15 to 800 MPa (*9*). Deuterium-protium isotope exchange between brucite and water was largely facilitated by dissolution and precipitation, as suggested by significant grain coarsening. Equilibrium D/H fractionation between brucite and water was calculated by the partial isotope exchange technique (*10, 11*).

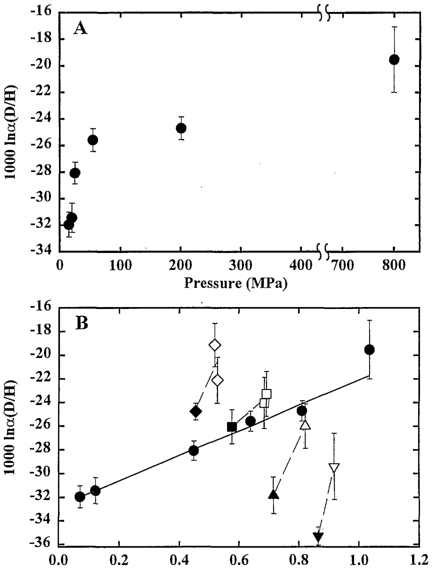

Fig. 1. (**A**) Plot of brucite–pure water equilibrium D/H fractionation factor (1000 ln α) versus pressure at 380°C. (**B**) Plot of brucite-water equilibrium D/H fractionation factor (1000 ln α) versus water density at experimental conditions. ▼▽, 200° to 205°C; ▲△, 300°C; ●, 380°C; ■□, 400° to 410°C; ◆◇ 500° to 510°C. Solid symbols, this study; open symbols, recalculated from Satake and Matsuo (*13*).

The experimentally determined hydrogen isotope fractionation factors between brucite and pure water, expressed as 1000 ln $\alpha_{\text{brucite-water}}$, increased systematically from −31.9 ± 0.9 per mil at 15 MPa to −19.5 ± 2.5 per mil at 800 MPa, all at 380°C (supplementary material is available at www.sciencemag.org/feature/data/1043206.shl). The fractionation factor increased markedly with pressure in the low-pressure range (≤100 MPa) but less so in the high-pressure range (Fig. 1A). The observed change (12.4 per mil) is far beyond the analytical errors (±0.8 to ±2.5 per mil, 1σ). A linear relation is observed between the D/H fractionation factor and the density of pure water at 380°C (*12*) (Fig. 1B).

Several investigators have determined D/H fractionation factors between brucite and water over a wide range of temperature (*13, 14*). Our results at 200°C and 2.1 MPa, 300°C and 10 MPa, 400°C and 50 MPa, and 500°C and 80 MPa are systematically lower than those of Satake and Matsuo (*13*) obtained at the same temperatures but at higher pressure (100 MPa) (Fig. 1B). It appears that pressure affects the brucite-water hydrogen isotope fractionation over the entire temperature range from 200° to 500°C. Calculations by Polyakov and Kharlashina (*2*) and Polyakov (*15*) show that the partition function ratio for D/H in brucite increases about by 6 per mil linearly with pressure, and not with the density of water, from 0 to 800 MPa at 380°C. Thus, the pressure effect on brucite can account for half the observed pressure effect in our experiments. Comparison of our experimental results and Driesner's calculations (*5*) on the pressure effect on the partition function ratio for D/H in water shows that the direction and pattern of the pressure effect are the same, but the magnitude of the effect obtained from the experiments is about a factor of 3 smaller than that calculated by Driesner at 376° to 380°C (Fig. 2). At the other temperatures, the results of calculations and experimental studies appear to agree. It is likely that the observed changes in the equilibrium D/H fractionation factor between brucite and water are due largely to changes in the partition function ratio of water, rather than in that of brucite, induced by changes in pressure. However, further theoretical and experimental studies are needed.

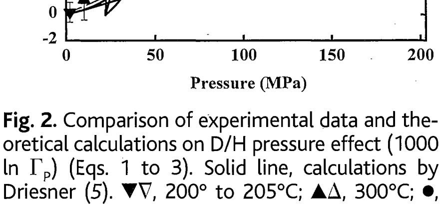

Fig. 2. Comparison of experimental data and theoretical calculations on D/H pressure effect (1000 ln Γ_P) (Eqs. 1 to 3). Solid line, calculations by Driesner (*5*). ▼▽, 200° to 205°C; ▲△, 300°C; ●, 380°C; ■□, 400° to 410°C; ◆◇ 500° to 510°C. Solid symbols, this study; open symbol, recalculated from Satake and Matsuo (*13*). No experiment was conducted at a reference pressure of Driesner (0 and 22.0 MPa below and above 374°C), and experimental data are shown for comparison with the calculations.

D/H fractionations of several mineral-water systems have been studied by different investigators, and fractionation factors obtained at higher pressures are generally much greater (10 to 36 per mil) than those at lower pressures (*11, 16*). These discrepancies in many mineral water D/H fractionations can be reconciled only to a modest extent (about one-quarter to one-half of the deviations) by the pressure effect, and it is likely that the discrepancies are more likely related to experimental and analytical problems. Gross discrepancies (on the order of 2 per mil at 350° to 700°C) observed in mineral (calcite, quartz, and albite)-water oxygen isotope fractionation factors between those experimentally determined at high pressures and others obtained from calculated reduced partition function ratios of minerals and water (*17*) also may be due to a pressure effect.

Potential geochemical implications of the large pressure isotope effect determined in this study can be significant in many low-pressure (≤100 MPa) geologic environments with a wide range of temperature (≤100° to ≥1000°C) encountered in the upper crust of the Earth (for

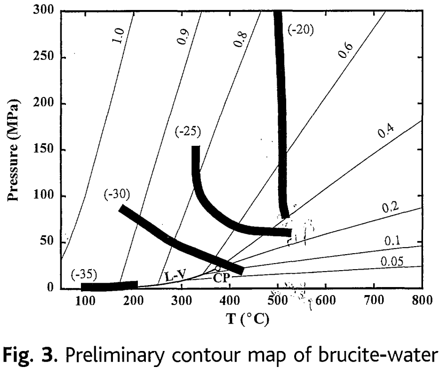

Fig. 3. Preliminary contour map of brucite-water D/H fractionation factor (1000 ln α) in pressure-temperature space with isochores of pure water (g/cm³). Data source: this study, unpublished Oak Ridge National Laboratory data, and recalculated from Satake and Matsuo (*13*). L-V, pure water liquid-vapor boundary; CP, critical point of pure water (374°C and 22.0 MPa).

example, sedimentary basins, geothermal systems, island arcs, oceanic ridges, and contact aureoles). Various hydrous minerals (clays, zeolites, micas, talc, serpentine, chlorite, epidotes, and amphiboles) form under these conditions as primary or alteration minerals, and their isotopic compositions have been used to infer the source of fluids or the temperature of mineral formation (isotope geothermometer). Many mineral water D/H fractionation factors in the literature, which were usually determined at a constant, high pressure (typically ≥100 MPa), are rather insensitive to temperature (*6*). However, pressure changes alone can shift mineral water D/H fractionation factors as shown for the system brucite water (Fig. 3). Thus, if not taken into account, pressure variations could lead to large errors in the isotopic composition of the fluid calculated to be in equilibrium with the mineral (≥10 per mil in δD) or in the estimated temperature of mineral formation (≥100°C in calculated temperatures).

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9. Typically, 10 to 25 mg of brucite and 25 to 300 mg of water were sealed in gold capsules. Three or four gold capsules, identical except for hydrogen isotope composition of water within the capsule, were loaded into an autoclave, cold-seal apparatus, or piston cylinder depending on the pressure-temperature conditions of interest. Temperature and pressure were controlled within ±2°C and ±1 MPa, respectively, except for low-pressure (15 to 25 MPa) experiments, for which pressure was calculated from the volume of the vessel and pressure-temperature-volume properties of pure water to an error of ±0.2 to 1 MPa. In a piston cylinder experiment at 800 MPa, a pressure uncertainty is ±20 MPa. At the end of experiments, the vessels were quenched to <50°C within 5 to 30 min, and the gold capsules were weighed to check for leakage. The brucite run products were washed with deionized water and dried. After drying in vacuum overnight at 150°C, water was extracted from brucite by heating to 900°C for an hour in a vacuum. The water extracted was converted to H_2 by passing over hot uranium metal at 750°C [J. Bigeleisen, M. L. Perlman, H. C. Prosser, *Anal. Chem.* **24**, 1356 (1952)].
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A Laboratory Model for Convection in Earth's Core Driven by a Thermally Heterogeneous Mantle

Ikuro Sumita* and Peter Olson

Thermal convection experiments in a rapidly rotating hemispherical shell suggest a model in which the convection in Earth's liquid outer core is controlled by a thermally heterogeneous mantle. Experiments show that heterogeneous boundary heating induces an eastward flow in the core, which, at a sufficiently large magnitude, develops into a large-scale spiral with a sharp front. The front separates the warm and cold regions in the core and includes a narrow jet flowing from the core-mantle boundary to the inner-core boundary. The existence of this front in the core may explain the Pacific quiet zone in the secular variation of the geomagnetic field and the longitudinally heterogeneous structure of the solid inner core.

The temperature profile in Earth's outer core is estimated to be nearly adiabatic (*1*) as a consequence of its highly turbulent state. The total heat flux from the core to the mantle is estimated to be comparable to (within a factor of 2) the heat conducted down the core adiabat (*1, 2*). These conditions lead to an unusual thermal regime in which the turbulent convective heat transfer amounts to less than one-half of the total heat transfer from the core. The situation is further complicated by a heterogeneous heat-flow boundary condition due to the large-scale pattern of mantle convection. As a consequence, the convective part of the heat transfer in the core is likely to exhibit extremely large lateral variations, perhaps of more than an order of magnitude (*3*).

The importance of a thermally heterogeneous core-mantle boundary (CMB) for convection in the core has been recognized (*4*). Theoretical studies have investigated the flow driven by boundary heterogeneity, but mostly in the cases in which the heat-flux variation is relatively small (*5*). These studies have shown that, under some conditions, the convective pattern in the core can be locked to the CMB heterogeneity. In the core, we expect a generally convective state modulated by a large lateral variation in convective heat flux. In our study, we modeled this regime using laboratory experiments in a rapidly rotating spherical shell (*6*). Such experiments realize conditions closer to those of Earth by an order of magnitude, as compared to numerical models (*7*), and also include the fine-scale structures that tend to be smoothed out in numerical models.

A hemispherical shell (Fig. 1) was filled with water and rotated at 206 rotations per minute, providing an Ekman number of $E = 4.7 \times 10^{-6}$. Radial gravity was simulated by the combined effects of Earth's gravity and centrifugal acceleration. The outer copper sphere, the model CMB, was maintained at room temperature. The inner copper sphere, the inner-core boundary (ICB), was maintained be-

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