The fate of carbonate in oceanic crust subducted into Earth’s mantle

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The H/C ratio in earth’s exosphere is higher than it is in the source region of primitive basalts, suggesting an enriched carbon reservoir in the mantle[1]. A plausible explanation is that subduction of carbon may have enriched the mantle in recycled carbon over time. Average basaltic crust contains ~2 wt.% CO2 [2], and modeling of slab devolatilisation suggests that subducted carbonate may survive to be transported deeper into the mantle [3]. Carbonated oceanic crust should melt in the transition zone along most subduction geotherms due to a deep trough in the carbonated basalt solidus, and mineral inclusions in superdeep diamonds testify to carbonate melt in their formation [4]. Along cool subduction geotherms carbonate may subduct into the lower mantle, potentially enriching the deep mantle in carbon. Here we report on laser-heated diamond anvil cell experiments in the CaO-MgO-SiO2-CO2 and FeO-MgO-SiO2-CO2 systems at lower mantle pressures where we investigate the stability of carbonate in oceanic crust, and test for decarbonation and diamond forming reactions involving carbonate and coexisting free silica. We find that carbonate reacts with silica to form bridgmanite ± Ca-perovskite + CO2 at pressures in the range of ~50 to 70 GPa. These decarbonation reactions form an impenetrable barrier to subduction of carbonate into the deeper lower mantle, however, slabs may carry solid CO2 (Phase V) into the deeper lower mantle. We also identify reactions where carbonate or CO2 dissociate to form diamond plus oxygen. We suggest that the deep lower mantle may become enriched in carbon in the form of diamond over time due to subduction of carbonate and solid CO2, and its eventual dissociation to form diamond plus oxygen. Release of oxygen during diamond formation may also provide a mechanism for locally oxidizing the deep mantle.

S-isotope study of Archean shallow-crust recycling in the Earth's mantle

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Archean supracrustal rocks (i.e. chemical sediments and metavolcanics) preserve sulfur Mass Independent Fractionations (MIF) that originate from photochemical reactions occurring in atmosphere before the great oxygenation event, 2.45 Ga. Reduced and oxidized aerosols were produced by photochemistry and respectively carry $^{33}\text{S}$ enrichment ($\Delta^{33}\text{S} > 0$‰) and depletion ($\Delta^{33}\text{S} < 0$‰). The relative abundance of the minor isotope of sulfur ($^{36}\text{S}$) was also affected by MIF in such a way that compact negative correlation exists between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. For much of Archean sediments, $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -1$, while slight variation of this slope have been attributed to minor change in the chemical composition of the atmosphere affecting global MIF source mechanism. On another hand, $^{36}\text{S}$ abundance is also affected by microbial cycling and in this specific case, $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -7$. Accordingly, $\Delta^{33}\text{S}-\Delta^{36}\text{S}$ co-variations can be used to discriminate distinct sedimentary pool.

This contribution aims to test the robustness of MIF array of specific exospheric sulfur pools along their journey from the surface to the mantle. We examine the $\Delta^{36}\text{S}$ in addition to $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ signatures measured in-situ with secondary ion mass spectrometer, in sub lithospheric peridotitic and eclogitic sulfides from Kaapvaal (Jwaneng and Kimberley Pool) and Siberian craton (Mir and Udachnaya).

Unlike peridotitic sulfides, eclogitic sulfides from both localities display significant MIF attesting from the presence of surficial sulfur in their source. More interestingly, the magnitude of the anomalies as well as $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio, differ from one locality to the other. Siberian eclogites match the composition of Eoarchean sulfate ($\Delta^{36}\text{S}/\Delta^{33}\text{S} = -3$ and $\Delta^{33}\text{S} < 0$‰). Sample from Jwaneng follow the MIF array previously reported in Archean chemical sediment ($\Delta^{36}\text{S}/\Delta^{33}\text{S} = -1$) while sulfide from Kimberley pool match the composition of some meso-Archean sediments in good agreement with isochron age reported in the literature for the sulfide from this locality.

This study confirms that surficial sulfur has been efficiently transferred to the lithospheric mantle. More interestingly, it shows that peculiar sedimentary pools are still preserved in the cratonic keels.
Anomalous behavior of the compressibility and thermal conductivity of Fe, Al-bearing bridgmanite

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For iron-containing minerals under high pressure, it is important to understand the effect of pressure-induced spin-crossover of iron on its physical properties: spin-crossover of iron changes its ionic radius and number of peripheral electrons, thus this may change the thermodynamic and physical properties of materials bearing iron. The most abundant mineral in the Earth’s lower mantle is MgSiO$_3$ bridgmanite containing a certain amount of iron and aluminum. There are two recent experimental studies on the thermal conductivity of iron and aluminum-bearing bridgmanite [1][2], but their results are inconsistent. Moreover, the effect of spin-crossover of iron in bridgmanite on its thermal conductivity is yet unknown.

Here we report the lattice thermal conductivity of Al-rich Fe, Al-bearing bridgmanite with chemical compositions of Mg$_{0.793}$Fe$_{0.075}$Al$_{0.217}$Si$_{0.914}$O$_3$ and Mg$_{0.718}$Fe$_{0.123}$Al$_{0.281}$Si$_{0.878}$O$_3$ measured up to 180 GPa and 74 GPa respectively, at 300 K using the pulsed light heating thermoreflectance technique in a diamond anvil cell. Also we experimentaly determined the compressibility of the above bridgmanite samples up to ~60 GPa at 300 K investigated by the synchrotron XRD measurements at BL10XU, SPring-8. Both compressibility and thermal conductivity of Mg$_{0.793}$Fe$_{0.075}$Al$_{0.217}$Si$_{0.914}$O$_3$ and Mg$_{0.718}$Fe$_{0.123}$Al$_{0.281}$Si$_{0.878}$O$_3$ bridgmanite showed abnormal change in the pressure range of around 20 to 40 GPa, probably due to the spin transition of ferric iron.

**Equations of state and phase diagram of SiO$_2$ to lower mantle conditions**

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Silica is thought to be present in the Earth’s lower mantle in subducting plates. It is known to undergo a phase transition from stishovite to the CaCl$_2$-type structure at $\sim$50–80 GPa, but the exact location and slope of the phase boundary in pressure-temperature space is unresolved. There have been many previous studies on the equation of state of stishovite, but they span a limited range of pressures and temperatures, and there has been no thermal equation of state of CaCl$_2$-type SiO$_2$ measured under static conditions. We have investigated the phase diagram and equations of state of silica at 21–89 GPa and up to $\sim$3300 K using synchrotron X-ray diffraction in a laser-heated diamond anvil cell. The phase boundary between stishovite and CaCl$_2$-type SiO$_2$ can be approximately described as $T = 64.6(49)P - 2830(350)$, with temperature $T$ in Kelvin and pressure $P$ in GPa. The stishovite data imply $K_0' = 5.24(9)$ and a quasi-anharmonic $T^2$ dependence of $-6.0(4) \times 10^{-6}$ GPa*cm$^3$/mol/K$^2$ for a fixed $q = 1$, $\gamma_0 = 1.71$, and $K_0 = 302$ GPa, while for the CaCl$_2$-type phase $K_0 = 341(4)$ GPa, $K_0' = 3.20(16)$, and $\gamma_0 = 2.14(4)$ with other parameters equal to their values for stishovite. The behaviors of the $a$ and $c$ axes of stishovite with pressure and temperature were also fit, indicating a much more compressible $c$ axis with a lower thermal expansion as compared to the $a$ axis. The phase transition between stishovite and CaCl$_2$-type silica should occur at pressures of 68–78 GPa in the Earth, depending on the temperature in subducting slabs. Silica is denser than surrounding mantle material up to pressures of 58–68 GPa, with uncertainty due to temperature effects; at higher pressures than this, SiO$_2$ becomes gravitationally buoyant in the lower mantle.
Oxygen isotopes in Kankan super-deep diamond inclusions reveal variable slab-mantle interaction

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Inclusions in super-deep diamonds provide a unique window to the sublithospheric mantle (e.g. [1-4]). Here we present oxygen isotopes for Kankan majoritic garnet and former bridgmanite inclusions. The clustering of Kankan majorites around a $\delta^{18}O$ of $+9$‰ is nearly identical to those reported from Jagersfontein [1]. This elevated and nearly constant $\delta^{18}O$ signal indicates homogenization of partial melts from the uppermost part of altered basaltic slabs. Conversely, $\delta^{18}O$ values in Juina majorites are highly variable [2] due to crystallization from small, discrete melt pockets in a heterogeneous eclogitic source. While all these majorites have eclogitic/pyroxenitic Cr$_2$O$_3$ and CaO contents, charge-balance for Si$^{VI}$ is achieved very differently, with Jagersfontein [3], Kankan [4], and Juina [2] majorites transitioning from eclogitic Na$^{VIII}$/Si$^{VI}$ to peridotitic-pyroxyenic [5] Mg$^{VIII}$/Si$^{VI}$ substitutions. We interpret this shift as the result of homogenized eclogitic partial melts infiltrating and reacting with adjacent pyrolitic mantle at Kankan and Jagersfontein. Increases in Mg# and Cr$_2$O$_3$ with reductions in $\delta^{18}O$ support this reaction. This model is in agreement with recent experiments in which majorites and diamonds form from a reaction of slab-derived carbonatite with reduced pyrolite at 300-700 km depth [6].

The Kankan diamonds also provide an opportunity to establish the chemical environment of the lower mantle. Four inclusions of MgSiO$_3$, inferred to be former bridgmanite [4], provide the first-measured $\delta^{18}O$ values for lower mantle samples. These values suggest derivation from primitive mantle, or unaltered subducted oceanic lithospheric mantle. The Kankan super-deep inclusions thus provide a cross-section of deep mantle that highlights slab-pyrolite reactions in the asthenosphere and primitive compositions in the lower mantle.

The lowermost mantle is driven to Earth’s surface by mantle plumes, providing a volcanic record of its structure and composition. Plumes consist of a head and tail, which melt to form large igneous provinces (LIPs) and ocean island basalts (OIBs), respectively. Recent analyses have shown that such sites of volcanism exhibit tungsten (W) isotope heterogeneity that was created in the first ~60 million years of our solar system’s evolution. Moreover, the isotopic signature found in LIPs differs to that found in OIBs, revealing that the melt products of plume heads must be dominated by a different ancient mantle reservoir to that of plume tails. However, existing geodynamical studies show that plume heads and tails sample the same deep-mantle source region, and, therefore, cannot account for any systematic differences in composition. Here we propose an isotopic model that can account for the W signature of LIPs and OIBs and present a suite of numerical simulations that highlight the conditions under which such a model is dynamically feasible. Our simulations demonstrate that the W isotope systematics of LIPs and OIBs can, under certain conditions, arise as a dynamical consequence of plumes forming in a heterogeneous, thermo-chemical boundary layer. We also show that ultra low-velocity zones (ULVZs), which sit on the core-mantle boundary (CMB), likely contribute to the chemical diversity observed in OIBs but not LIPs. This study places geochemical observations from Earth’s surface in a geodynamically consistent framework and illuminates their relationship with seismically imaged features of the deep mantle.
First-principles simulations of pyrite-type FeO$_2$H and its isochemical melts at high pressure

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Recent laser-heated diamond-anvil cell experiments suggest that the pyrite-structured iron peroxide with varying hydrogen concentration (FeO$_2$H$_x$) is stable up to 2,600 K and 133 GPa while exhibiting thermoelastic properties consistent with ultralow velocity zones (ULVZs). As a result, subducted FeO$_2$H$_x$ has been invoked to be a plausible cause of ULVZs. However, the temperature near the core-mantle boundary is expected to reach 4000 K at 136 GPa. Under such extreme conditions, the stability of FeO$_2$H$_x$ remains unkown.

Here, we perform first-principles molecular dynamics simulations on the hydrogen-rich end member of FeO$_2$H$_x$ system, FeO$_2$H. We focus on the melting temperature of this material and also study the thermodynamic and structural properties of its corresponding melt. Our preliminary results show that FeO$_2$H solid is ~2% denser than the isochemical melt at 3000 K and 136 GPa. The density difference decreases gradually with pressure and a crossover is predicted to occur around 220 GPa. Our structural analysis suggests that the distribution of hydrogen atoms in the melt differs dramatically from that in the solid. In the melt, the H-bridges (linking two FeO$_6$ octahedral corners in the solid) become connected with each other forming longer -H-O-H-O- chains via two (even three) hydrogen coordinated oxygens and also tending to avoid Fe atoms. It is remarkable that more than one-third of the oxygen in the molten FeO$_2$H is not bonded with any hydrogen representing regions of hydrogen depletion. The calculated mean coordination values in most cases gradually increase with increasing pressure with abundance of various coordination species (e.g., non-octahedral Fe-O coordination polyhedra) being sensitive to both pressure and temperature.
Elasticity of polycrystalline $\beta$-Mg$_2$SiO$_4$ containing 0.73 wt.% H$_2$O to 10 GPa and 600 K by ultrasonic interferometry technique combined with synchrotron X-radiation

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Abstract
The acoustic wave velocities of wadsleyite ($\beta$-Mg$_2$SiO$_4$) containing 0.73 wt.% (7300 ppm) of H$_2$O have been determined to 10 GPa and temperatures to 600 K. Finite strain analysis of elastic bulk ($K$) and shear ($G$) moduli yielded $K_0 = K_s = 152.2(9)$ GPa, $G_o = 98.1(3)$ GPa and $(\partial K_s/\partial P)_T = 4.47(14)$, and $(\partial G/\partial P)_T = 1.43(5)$ for the bulk and shear moduli and their pressure derivatives respectively. Compared to the anhydrous phase, hydration of the wadsleyite leads to a decrease in the bulk and shear moduli by 12.5% and 3.9%, respectively. The temperature derivatives of the elastic moduli obtained by linear fitting are: $(\partial K_s/\partial T)_P = -1.55(1) \times 10^{-2}$ GPa/K and $(\partial G/\partial T)_P = -1.39(7) \times 10^{-2}$ GPa/K. The new data show that hydration of wadsleyite by 0.73 wt.% decreases both $(\partial K_s/\partial T)_P$ and $(\partial G/\partial T)_P$, in magnitude by 9.4–11% and 10–13%, respectively, when compared with current reported $(\partial K_s/\partial T)_P$ and $(\partial G/\partial T)_P$ ranges and predict a 45% orthosilicate content for the Earth’s upper mantle. In contrast, the effect of Fe substitution in wadsleyite up to $X_{Fe} = 0.9$ show no measurable effect on the temperature derivatives of the elastic bulk and shear moduli.
The Ground State of FeO\textsubscript{2} under Lower-Mantle Conditions

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From the oxygen-rich atmosphere to the iron-rich core, the iron-oxygen (Fe-O) system spreads the entire pressure-temperature-composition range of our planet, iron oxides are important materials of Earth’s interior, and play an important role in geological and biological processes. It is believed that under different pressures and temperatures, from the Earth’s surface to the core, the electronic properties, oxidation states, spin states and magnetism of different iron oxides are distinctive. Recently, a pyrite-structured FeO\textsubscript{2} which has the lowest Fe/O compositional range to date \cite{1} with a formal oxidation state of +4 was synthesized under the deep lower-mantle conditions. Here, we employed first-principle electronic structure calculations using different density functionals to investigate the electronic ground state at high pressures. For calculations using functionals including correction to the self-interaction, (i.e. Fock exchange), FeO\textsubscript{2} is found to be a ferromagnetic insulator with a formal oxidation state close to +2 at lower-mantle conditions. The Mossbauer isomer shift and high spin to low spin transition pressure are predicted. The theoretical information will help to characterize the electronic state of this novel material by experiments.

\cite{1} Hu et al., (2016) Nature 534, 241
**Water storage capacity of Earth’s mantle and its temporal evolution**

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Hydroxyl point defects can be incorporated into mantle silicates, potentially constituting the Earth’s largest water reservoir [1]. Converting the water storage capacity of minerals on the atomic scale to the water budget of the Earth’s interior, however, remains a grand challenge. Here, we present a numerical model for the water storage capacity of a pyrolitic mantle under water-saturated conditions. Pressure \((P)\) and temperature \((T)\) dependence of water storage capacity are quantified for olivine, pyroxene, garnet and their high-pressure polymorphs combining experimental data in the literature with thermodynamic models of water solubility and partitioning that are exponential functions of \(P\) and \(T\) [2]. These storage capacities are integrated through the phase assemblages at the relevant \(P-T\) conditions along a series of adiabats computed using the HeFESTo code [3]. We estimate that the total water storage capacity of the Earth’s mantle is 1.43 ocean masses (OM) at present day with a mantle potential temperature \(T_p = 1600\) K. 0.16 OM are present in the upper mantle, 0.80 OM in the transition zone, and \(0.47^{\pm1.2\%} \text{ to } 0.47\%\) OM in the lower mantle. Based on the strong \(T\) dependence of water storage capacities, our results put a tighter constraint on the water content of the present-day mantle (1-2 OM) compared with previous estimates (few to tens of oceans) [4]. The water in the transition zone is estimated to be less than 0.3 wt.% for the current average mantle temperature and less than 0.1 wt% for a hotter mantle, which fits into the geophysical observations from electromagnetic induction [5]. The total storage capacity was 0.55 OM for an Archean mantle with \(T_p = 1900\) K. A much smaller water storage capacity is expected for the Archean mantle, which has a profound influence on water exchange between surface and interior throughout the evolution of the planet.

Understanding the (mis)behavior of water contents in nominally anhydrous mantle minerals

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In magmatic systems, water behaves as an incompatible species and therefore should be depleted in mantle peridotites during melting and enriched during metasomatism. Although some previous studies of nominally anhydrous mineral (NAM) water contents in peridotites have observed correlations with indices of metasomatism or melt extraction, in detail, these correlations are often inconsistent with predicted trends deriving from either process. For example, correlations between NAM water content and indices of metasomatism are often only observed in some minerals within a given suite of xenoliths even if all minerals have been affected by metasomatic processes. Similarly, correlations between NAM water content and indices of melt extraction result in significantly higher water contents than predicted by melting models using experimental constraints on water partitioning. Finally, although growth of hydrous minerals requires higher water activity than in anhydrous peridotites, no significant differences are observed in either NAM water content or water activity between hydrous and anhydrous xenoliths from individual localities or within a global compilation of mantle xenoliths.

We propose that the high diffusivity of water in mantle peridotites allows for equilibration of water activity in the mantle over geologic time, with water-rich (metasomatized) regions losing water over time, and water-poor (melt-depleted) regions gaining water via diffusion. This homogenizes water activity and obscures initial correlations between NAM water content and indices of metasomatism or melt extraction, explaining the inconsistencies described above. As a result of diffusive equilibration of water, variability in NAM water content in mantle peridotites is significantly reduced relative to the variability of similarly incompatible elements (e.g., Ce) in the same peridotites. For example, whereas the concentration of water in mantle-derived clinopyroxene spans ~1 order of magnitude, Ce concentrations in the same samples spans ~4 orders of magnitude. This difference in behavior explains why H2O/Ce ratios in mantle peridotites are highly variable relative to those of basalts, and why H2O/Ce strongly correlates with Ce concentration but not with cpx water content.