

Water, carbon and noble gases in Earth's interior

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Evidence for the storage of volatiles in Earth's interior comes from magmatic degassing, the observation of traces of water in nominally anhydrous mantle minerals, and the occurrence of carbonates in mantle xenoliths. Geochemical evidence suggests that a significant fraction of Earth's bulk argon and xenon may reside in the mantle.

Carbon probably substitutes as C^{4+} for Si^{4+} in most silicates. Due to the large misfit between C^{4+} and the silicon sites in silicates, the carbon solubility in mantle minerals is generally very low, implying that most carbon in the mantle is present either as carbonate or perhaps in the form of graphite or diamond. Water, on the other hand, may be dissolved in silicates by a variety of mechanisms. The direct substitution of proton pairs for Mg^{2+} occurs in olivine and wadsleyite. Coupled substitutions of $H^+ + Al^{3+}$ for Si^{4+} or $2 Mg^{2+}$ appear to dominate in pyroxenes. While water solubilities in wadsleyite and ringwoodite reach several wt. %, the solubility of water in the perovskite and magnesiowustite phases of the lower mantle is very low.

Compared to carbon and water, little is known about noble gases in mantle minerals. We present new experimental data suggesting that argon is quite soluble in aluminous magnesium silicate perovskite, the dominant mineral of the lower mantle. Solubilities reach several 100 ppm by weight or more and they appear to be correlated with oxygen vacancies. These numbers are comparable to the expected solubilities in depolymerized silicate melts in the deep mantle, implying that argon is compatible in perovskite. The storage capacity of perovskite for argon is orders of magnitude larger than the total amount of ^{40}Ar produced by radioactive decay of ^{40}K over the entire history of the Earth.

While water is probably enriched in the transition zone of Earth's mantle, the lower mantle is probably the main reservoir for argon and possibly other noble gases. The distribution of carbon may be rather inhomogeneous, as it is related to accessory minerals.

Both water and carbon dioxide may contribute to partial melting in the mantle. However, CO_2 -rich near solidus melts are carbonatitic in composition, while hydrous melts at low melt fraction may only contain a few wt. % of water. Therefore, to produce a comparable melt fraction, much higher bulk CO_2 contents would be required.

Oxidative adsorption of iron(II) at the hematite-water interface

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The redox transformation of iron oxides in aqueous solutions is of great importance due to its major role in the cycling of iron. Experimental work in our group on the reductive transformation of hematite ($\alpha-Fe_2O_3$) has revealed the coupling between oxidative adsorption of iron(II) at one surface and internal reductive dissolution of iron(III) at another through bulk charge transport. In this paper, we seek to shed light on the mechanisms of reductive transformation using molecular-computational techniques. Focusing on the (001) hematite surface, atomistic and quantum-mechanical calculations are employed to compute the rates of electron-transfer reactions between adsorbed iron(II) and surface sites, and of subsequent electron diffusion within the hematite surface.

One important aspect of this approach is determining the relative affinity for forming inner- versus outer-sphere iron(II) complexes. The preference for inner- versus outer-sphere adsorption will impact the rates of electron transfer between adsorbed and surface iron. Therefore, free energy profiles for iron(II) adsorption from aqueous solution on the neutral (001) hematite surface are obtained from constrained molecular dynamics simulations. The calculations reveal the presence of both an inner-sphere iron(II) adsorption site, which corresponds to an iron lattice site, and a shallow outer-sphere free energy minimum. However, adsorption of iron(II) as an inner-sphere complex is calculated to be endothermic, for the surface conditions considered in this work, and electron transfer is predicted to be more facile from the outer-sphere position despite a weaker electronic coupling.

Interestingly, the main free energy barrier separating the outer- and inner-sphere positions is similar in size to the free energy barrier for water exchange around an aqueous iron(II), thus highlighting the coupling between water exchange dynamics and adsorption kinetics. It is therefore critical to be able to accurately determine the rate of water exchange around aqueous ions. However, in cases where the exchange rate is slow on the timescale of a typical molecular dynamics simulation, this requires the use of rare-event techniques. In this talk, we discuss the ability of two such methods, namely reactive flux and transition path sampling, for probing the rate and mechanism of water exchange around aqueous iron(II).