

First inference of molecular Hydrogen in mantle pyroxene and isotopic consequences

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Hydrogen plays a key role in the evolution, dynamics and habitability of the Earth. It was primarily incorporated into the Earth's interior during its accretion and then evolved through degassing and recycling. Hydrogen is a ubiquitous trace component of nominally anhydrous minerals (NAMs) in the upper mantle, estimated to amount to 0.5–1 times the total mass of the oceans. So far, hydrogen was known to exist in NAMs in the form of OH, with storage capacity varying with depth. However, studies of cratonic mantle xenoliths indicate that fO_2 ranges from FMQ -2 to -4.5, conditions under which a substantial amount of hydrogen may be present in a reduced form (H_2). Experimental data suggest that H_2 could be present in NAMs, however it is difficult to detect due to its low infrared extinction coefficient. We show that molecular hydrogen (H_2) coexists with OH in natural omphacite in eclogite xenoliths from the Siberian craton (4-5 GPa, 1100 °C), suggesting that H_2 plays a role in water recycling to deep mantle.

Hydrogen isotope ratios (δD values) in our samples increases with decreasing water content; contrary to previous inferences that δD decreases during subduction dehydration. The presence of H_2 can explain the extremely negative values due to the positive fractionation between fluids and H_2 and these counter-intuitive relationships can be explained by the coexistence of OH and H_2 in minerals. This better explains the relations between δD estimates for MORB-source convective upper mantle (about -50‰) and glass inclusions in phenocrysts from plume basalts (down to -218‰) that were previously attributed to a primitive deep reservoir or to contamination by recycled partially dehydrated oceanic crust.

Since molecular H_2 is most likely to be the dominant form of hydrogen in the reduced deep mantle, it follows that H isotopic fractionation should be controlled by equilibria involving H_2 -bearing minerals rather than H_2O - or OH-bearing minerals. This

must be taken into account when interpreting hydrogen isotopic distribution in the mantle, as well as partitioning and isotopic exchange of hydrogen between the hydrosphere and the deep mantle.