Water contents in anhydrous minerals from the upper-mantle (peridotites and eclogites)

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Water has a strong influence on the chemical and physical properties of silicate minerals, fluids, and melts in the lithosphere. The reactions occurring during the dehydration of a down-going slab, the quantity of water being kept by the slab and that expelled to the overlying mantle wedge, how water is stored in these various components, and in what form it can be released, are important factors in understanding the water budget of the mantle. Nominally anhydrous minerals may represent an important site for storing water (or more exactly hydrogen) in subducted slabs and in the mantle above slabs at depths where hydrous minerals may not be stable. This study attempts to estimate the water content of various parts of the upper mantle focusing on its primary phases, olivine, pyroxene and garnet. Here, samples from subducted basalts and mantle xenoliths are examined.

The water contents in pyroxenes and olivines from spinel peridotite xenoliths from Mexico and Simcoe (Washington State, USA) are negatively correlated with oxygen fugacity measured on the spinels. This can be related to the inferred mechanism of hydrogen incorporation in most nominally anhydrous minerals, which is thought to be based on the ferrous-ferric equilibrium. As subduction zones appear to be characterized by high oxygen fugacities, the low water content of mantle-wedge pyroxenes was interpreted as being the result of oxidation of the mantle above subduction zones by slab-derived metasomatic fluids or melts.

Preliminary results on eclogites from high-pressure terranes of the Alps yield contents of the structurally-bond water in clinopyroxenes (omphacites) and garnets of 200-425 ppm and 0-40 ppm respectively. No relation has been found yet with pressure or temperature of equilibration (range of 2.6 to 4 GPa and 700-900°C). This study will include an evaluation of the influence of decompression and cooling metamorphism on water content of nominally anhydrous minerals.

Hydrogen isotope geochemistry of nominally anhydrous minerals

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Mantle derived materials span a range of ~100 ‰ in hydrogen isotopic composition. Nominally anhydrous minerals from mantle xenoliths are the most deuterium depleted of all mantle materials, with δD values 50 ‰ lower than average mid ocean ridge basalt. These variations suggest large hydrogen fractionations within the mantle but available data are limited to large, high quality samples needed for conventional measurement techniques. We have recently developed a continuous-flow technique for measuring hydrogen isotopic composition in small (5-50 mg) samples of mantle pyroxenes, making it possible to analyze many more mantle samples.

Pyroxenes from a lherzolite xenolith from the continental interior have δD values of -113‰ ± 3 (cpx) and -127‰ ± 10 (opx), in agreement with prior measurements of the same samples, supporting the conclusion that nominally anhydrous minerals in the upper mantle are a reservoir of low δD hydrogen.

Our initial measurements are of a lherzolite from the Central American arc. The hydrogen isotopic composition of clinopyroxene is -92 ± 6 ‰, and orthopyroxene is -65‰. This xenolith is deuterium enriched by 30-50‰ relative to xenoliths from the continental interior and is similar to mid-ocean ridge basalts. These are the first measurements of nominally anhydrous mantle minerals from an arc environment.

Models of hydrogen fractionation during mantle processes create a framework for interpreting isotopic results and will be used to guide further sampling. In subduction zones the δD of subducting material can be calculated using experimental and predicted fractionation factors. Altered oceanic basalt with initial δD of -40 ‰ has hydrogen remaining in nominally anhydrous minerals with a δD of -110 ‰ following dehydration. Though the number of samples analyzed is very small, our data show there is hydrogen isotopic variation in nominally anhydrous minerals and potential for using hydrogen isotopes to describe the mantle water cycle.