## Compositional controls on hydrogen generation during serpentinization

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At the Earth's surface peridotites and pyroxenites are inevitably unstable in the presence water causing the formation of serpentine, brucite or talc, magnetite and, most notably hydrogen. We compute equilibrium mineral assemblages, mineral compositions and the fluid/gas chemistry during serpentinization of an array of olivine- and/or pyroxene-rich rocks under near surface conditions from 25-400 °C and 50 MPa at a water-to-rock mass ratio of one. Our results indicate that the optimal temperature for hydrogen generation during serpentinization of olivine (Ol, Fo90)rich peridotite and dunite is at about 300-330°C. At this temperature we predict that rocks having an Ol -orthopyroxene (Opx) mass ratio > 1 generate more hydrogen during serpentinization than rocks having an Ol - Opx mass ratio < 1. There is a direct link between the fayalite content of olivine, its stability relative to water, temperature, and redox conditions. Favalite-rich olivine is stable to significantly lower temperatures in the presence of water than fayalite-poor olivine. Accordingly, the most reducing conditions during serpentinization of fayalite-rich olivine develop at temperatures lower than 330 °C. Notwithstanding the lower temperatures, rocks having abundant fayalite-rich olivine are predicted to generate significantly more H2,aq during serpentinization than typical forsterite-rich (Fo90) mantle rocks.

Our modeling results indicate that serpentinization of Ferich ultramafic rocks might represent one of the most reducing environments at or close to the Earth's surface. The results also suggest that serpentinization on Mars, where Fe contents of olivine in peridotites are higher than in terrestrial counterparts, will generate higher levels of  $H_2$ .

## Partitioning of F between nominally fluorine-free minerals and basaltic melts: Implications for the global cycle of halogens

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We present preliminary experimentally determined partition coefficients for fluorine (F) between nominally fluorine-free minerals and corresponding basaltic melts in the systems CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>+F, Na<sub>2</sub>O-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>+F, and in natural compositions at pressures up to 2.5 GPa and temperatures between 1285°C and 1445°C. F is incompatible in olivine, whereas the F in orthopyroxene is slightly more compatible. Our preliminary partition coefficients agree well with our analyses of F in natural olivines and orthopyroxenes from spinel peridodites and oceanic basalts, both indicating that F is much more compatible in olivine and orthopyroxene than hydrogen. Based on high-resolution TEM images of one of the samples, we argue that the F incorporation into the olivine structure is mass balanced via oxygen defects.

Hence, fluorine, and to a lesser extend chlorine, may be effectively stored in nominally fluorine-free mantle minerals such as olivine and orthopyroxene. By considering their high modal proportions in the upper mantle, both phases are the major hosts for F in the Earth's mantle, and must be taken into account when calculating the Earth's budget of halogens or global cycles of halogens in the deeper Earth. It, therefore, seems that other F-bearing minerals such as amphibole or phosphates are not required in order to balance the F concentrations between crust and mantle.

Applying our new partition coefficients to primitive olivine hosted melt inclusion data from mid-ocean ridge basalt (MORB) and from primary melt inclusions from ocean island basalts (OIB), we suggest slightly higher fluorine contents in OIB than in MORB.