

## Mass Transfer of Fluids and Metals in the Deep Earth

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Mantle-derived fluids are generally considered to be involved in the transport and distribution of trace elements in the deep Earth. However, we lack a robust understanding of the processes that lead to mass transfer of fluids and metals between the mantle and the crust. In this study, we integrate a series of volatile- and S-bearing high P/T experiments with the analysis of rock samples collected from one of a series of Ni-Cu-PGE mineralized alkaline ultramafic pipes in the Ivrea-Verbano Zone (IVZ). This exhumed section of the critical crust-mantle interface shows tantalizing relationships between ultramafic fluid-rich rocks and metal-rich sulfide mineralization. Geothermometry suggests that the Valmaggia pipe was emplaced at a temperature of ~900-950°C, close to the water-saturated peridotite solidus. The high P/T experiments support this observation, based on an H<sub>2</sub>O-saturated run at 950°C and 2 GPa that yielded a mineral assemblage remarkably similar to the pipe. High H<sub>2</sub>O contents in the melt are also supported by SHRIMP-SI analysis of pyroxene that yielded 550 ppm H<sub>2</sub>O, which corresponds to ~4 wt% H<sub>2</sub>O in the melt. Whole-rock and laser ablation ICP-MS data of silicate phases from the pipe suggest that a juvenile, sulfur- and metal-bearing mantle fluid refertilized a depleted harzburgitic source at depth, causing partial melting. The evolving, volatile-rich melt then intruded the IVZ, most likely as a series of open-system feeder conduits and/or chonoliths that subsequently reached sulfide saturation and formed widespread Ni-Cu-PGE mineralization. This hypothesis is supported by isotopic data, which indicate that this alkaline pipe was emplaced slightly after the voluminous mafic magmatic event that underplated the lower crust in the IVZ during the late Carboniferous. The significant difference in epsilon Nd values between whole-rock (-3.1) and amphibole-phlogopite concentrates (respectively -1.0 and -1.6) at ca. 290 Ma indicates that multiple metasomatic events may have been responsible for the establishment of open conduits and the transfer of fluids and metals between the metasomatized lithospheric mantle and the lower crust.

## Cation adsorption, hydrogen bonding structure and dynamics at the clay-water interface: MD simulations with new models of muscovite and montmorillonite

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The structure of water films at charged clay surfaces is crucial factor in understanding and predicting the physico-chemical properties of the adsorbed aqueous species which can provide fundamental insights into mobility of contaminants in soils and subsurface environments. Concurrently, the ion-water interactions strongly depend upon both the nature of the charge-compensating ions and the clay substrate structure. Classical molecular dynamics (MD) computer simulations using CLAYFF forcefield [1] were performed for a series of monovalent cations at the surfaces of newly developed models of muscovite and montmorillonite. Atomic density profiles, near-surface atomic distribution maps and the structure and dynamics of the interfacial H-bonding network were analyzed in detail for both clay substrates. The energetics of surface complexation was quantified via the calculation of potentials of mean force for the adsorption processes. Only one stable adsorption site for cations is observed at the muscovite surface in contrast to two different adsorption sites in the case of montmorillonite. The local structural disorder of the substrate charge distribution is clearly responsible for the significant redistribution of water molecules at the interfacial region.

The lateral diffusion of H<sub>2</sub>O molecules is 35% reduced at the surface of muscovite in comparison with the bulk liquid state. The diffusion rate of aqueous species in disordered montmorillonite structure is similar to that in the ordered structure. The calculated hydrogen bond lifetimes between H<sub>2</sub>O-H<sub>2</sub>O pairs are lower than between H<sub>2</sub>O and the bridging oxygens of the muscovite surface. The simulation results are compared with available experimental data and other simulations [2,3] to provide a reliable comprehensive molecular view of the structure and aqueous ion at the clay-water surface.

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