

## Quantification of cationic exchanges in the Upper Rhine valley potash basin: Coupled geochemical and modeling approach

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The Upper Rhine alluvial water table has been hugely polluted by mining brine infiltrations (Na<sup>+</sup> and Cl<sup>-</sup>). In order to constrain the geochemical consequences of such a pollution on the Rhine water table, (1) we analyzed major and trace element concentrations, as well as Sr isotope ratios in groundwater samples for evaluating the main water-rock interactions occurring in such a system, and (2) we have developed a transport reactive modeling approach able to predict the future evolution of these waters.

The geochemical data point out that a loss of Na<sup>+</sup> compared to Cl<sup>-</sup> together with a gain of Ca<sup>2+</sup> occurs in the polluted waters, by infiltrating the water table, downstream from spoil heaps. Furthermore, the Sr isotope data show that polluted waters, by infiltrating the water table, lose their Sr isotopic signature and take that of the host rock. All these data demonstrate that the main process controlling the geochemical evolution of the mining brines during their infiltration into the alluvial water table is a cation exchange at the water-rock interface, mainly controlled by the presence of a small proportion of clays (montmorillonite) in the aquifer system.

The hydrogeochemical model we developed and quantify the cation exchange mechanism is a transport reactive model where the aquifer rock is represented by an inert rock with about 1% of montmorillonite, and the pollution history from 1910 to 2005 is sub-divided into four different stages. This model allows us to fit quite precisely the present day concentrations of the cations in the upper Rhine groundwaters downstream from spoil heaps. Our simulations also indicate that several parts of the system, now less affected by the brine pollution, would be affected by a reverse cationic exchange between Na, previously stored in the aquifer rocks, and the Ca of the groundwater. Such a reverse Na exchange should become an important process, which will control the geochemical evolution of the Rhine ground waters in the next century.

## Refertilization mechanisms of mantle lithosphere beneath mid-ocean ridges

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Abyssal peridotites are commonly interpreted as polybaric melting residua of asthenospheric mantle decompressing beneath oceanic spreading centers. In these peridotites, however, mildly incompatible elements such as Na and Ti are too high for a given MgO content to be produced by melt extraction alone, and likely imply low-pressure refertilization by basaltic liquids [1]. The mechanisms and physical conditions of such refertilization are little explored. Batch addition of basalt, although compelling from a geochemical perspective, seems unlikely because it requires significant melt pooling. Focused melt percolation in the adiabatically upwelling mantle explains reactive dunite formation [2], but cannot account for the harzburgite-lherzolite trends observed in abyssal suites.

We explored the possibility of melt percolation accompanied by significant cooling, which allows for basaltic liquids to eventually 'freeze in', resulting in effective refertilization. We examined a simple 1-D scenario in which aggregate liquids resulting from polybaric fractional melting of peridotite beneath mid-ocean ridges percolate the mantle section of the overlying thermal boundary layer (TBL) and chromatographically react with residual harzburgites under constraints of local geothermal gradients. Simulations were performed using the *Adiabat\_1ph* code [3] running with *pMELTS* thermodynamic database [4], and prescribing various TBL thicknesses, geothermal gradients, and extent of melt focusing. Results indicate that the compositions of worldwide abyssal peridotites can be successfully reproduced by reactive refertilization of depleted harzburgites within the TBL. Increasing the extent of melt focusing furthers fertile lherzolite formation as well as plagioclase precipitation. The amount of sequestered melt increases with thickness of TBL and dT/dP of geotherm and decreases with extent of focusing. Our results imply that suboceanic lithospheric mantle may be much more fertile than currently thought. This has implications for the interpretation of oceanic crustal thickness as a measure of melt fraction and potential temperature.

[1] Elthon (1992) *JGR* **97**/B6, 9015-9025. [2] Asimow & Stolper (1999) *J. Pet.* **40**, 475-494. [3] Smith & Asimow (2005) *G-cubed* **6**/Q02004. [4] Ghiorso *et al.* (2002) *G-cubed* **3**/1030.