Isotopic tracing of lithium sources in the Seine River, Paris (France)

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Li isotopes have recently been used for tracing chemical erosion of silicate lithologies in present-day river basins and in the past, through oceanic records. Silicate weathering is a significant sink of atmospheric CO_2, but classical methods are insufficient for determining alteration rates and control laws with sufficient precision to be used in modeling of geochemical cycles and climate at large scale.

Most of the published studies show that dissolved lithium mainly come from silicate lithologies, even in mixed lithology basins (e.g. Kisakurek *et al.* 2005). However, recently a couple of sudies have also shown that anthropogenic input might impact the Li isotopic composition of natural waters. Indeed, some rain waters display unusually high δ^7Li and fertilizers may also be highly enriched in ^{7}Li (Millot *et al.* 2010). Analyses of commercial solutions show that their δ^7Li are particularly high relative to the range estimated for natural systems (Tomascak, 2004).

In order to estimate the order of magnitude of Li contamination of natural waters from anthropogenic sources, the Seine River in Paris, the largest urban area in France, has been sampled at various seasons. Li isotopes were measured in the filtered fractions (<0.2µm) by MC-ICP-MS, after the Li separation procedure described in Vigier *et al.* (2009).

The δ^7Li measured in the dissolved fractions of the Seine River range between 8.6‰ and 14.2‰. This range is within that determined for rivers located far from human activity. However, these values are low when compared to the published values for carbonate and evaporite lithologies (~30‰). This may mean that, even in a basin dominated by this kind of lithology, dissolved Li mainly comes from minor silicate phases. This is consistent with the low Li levels in carbonates. Another possibility is that anthropogenic inputs are significant and have on average a low δ^7Li in the Paris area. Some streams draining rooves and roads display a wide range of δ^7Li (from 25‰ to -17‰), with an average of 7‰. A positive correlation between δ^7Li and discharge in the Seine waters does suggest a role of anthropogenic components, such as for Zn (Chen *et al.* 2008). More investigation is needed in order to better determine the isotope composition of each potential endmember.

FTIR study of OH-OD exchange in Fe-free ringwoodite-wadsleyite samples

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Mantle ringwoodite and wadsleyite may incorporate large amount of H in their structure (up to several wt % H_2O). A good knowledge of hydrogen diffusion in these mineral phases and its relationship with their electrical conductivity is critical to estimate the real amount of water present in the transition zone. We synthesized ringwoodite and wadsleyite in multi-anvil presses up to 21 GPa and 1100 °C from forsterite powder surrounded by a small amount of brucite. The grain size of the ringwoodite samples ranged between 30 and 70 μm, while wadsleyite samples had grains sizes smaller than 20 μm. The samples incorporated moderate amount of water in the range of 0.1 to 0.2 wt% H_2O as confirmed by FTIR analyses performed on double face polished thin slices of few hundred microns.

In order to measure H diffusion rate in ringwoodite, we annealed a 106 μm thick slice for up to 80 hours in a OD enriched atmosphere at 400°C and we followed step by step the OH-OD exchange by FTIR. The main OH band in ringwoodite, the OH broad band at 3120 cm^{-1}, decreased rapidly but no equivalent OD band was produced. It suggests that, in ringwoodite, the mobility of H linked to this defect, is high and the removing of hydrogen from the crystals are not limited by D self-diffusion (ringwoodite was not destabilized even after 80 hours annealing, as confirmed by Raman and FTIR analyses). The effective diffusion coefficient through the thin section is of the order of $2\ 10^{-14}\ m^2s^{-1}$, and the corresponding intra-crystalline diffusion coefficient is around $3\ 10^{-15}\ m^2s^{-1}$ assuming an average grain size of 40 μm. These results are ten times faster than the diffusion coefficient in wadsleyite extrapolated at 400°C from the experiments of Hae *et al.* 2006 performed in wadsleyite [1].

[1] Hae *et al.* (2006) *Earth Planet Sci Let* **247**, 141–148.