

Lithium isotope signatures of hydrothermally altered basalts (Hengill, Iceland)

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Hydrothermal fluids are highly enriched in Li relative to seawater and represent a large input in the ocean Li budget. However, their Li isotope signatures, exhibiting a range of values significantly different from seawater and fresh MORB, and relatively homogeneous ($\delta^7\text{Li} \sim 9\text{‰}$), are still difficult to interpret. The principal reason is our lack of knowledge concerning Li isotope fractionation during high-temperature weathering.

In this study, a series of samples were collected in the Hellisheidi area (SW Iceland), at various depths (from 350 to 1400 m). Samples consist of well drill cutting and are hyaloclastites, with minor amounts of calcite, and secondary phases (primarily smectites and zeolites). Temperatures of the fluids are well constrained and increase with depth (150-300°C).

Major elements and Li contents were analysed by ICP-AES and ICP-MS and $\delta^7\text{Li}$ by MC-ICP-MS ($2\sigma < 0.3\text{‰}$). $\delta^7\text{Li}$ range from 1.9 to 2.6‰ from 350 m to 1000 m depth, and are close to the fresh MORB value ($\sim 4\text{‰}$) at greater depths. An inverse correlation between $\delta^7\text{Li}$ and Al suggests a major role of Al-rich secondary phases. However, considering constrained isotope fractionation factors [1], $\delta^7\text{Li}$ and Li data cannot be fitted by clay precipitation only. Instead, a model with a path dependent dissolution/precipitation process and including recent experimental results for Li isotope fractionation during basalt glass leaching [2] can reconcile major element, Li content and $\delta^7\text{Li}$ data.

[1] Vigier *et al.* (2008) *GCA* **72**, 780-792. [2] Verney-Carron *et al.* (2010) *EGU*, Vienne.

Flux of CO₂ from a flooded bituminous coal mine, Allegheny County PA, USA

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A discharge from an abandoned bituminous coal mine in Allegheny County, Pennsylvania provides an opportunity to assess the interaction of high P_{CO_2} waters with variably permeable sedimentary strata including coal, limestone, sandstone aquifers and shale aquitards. Coal mine drainage settings differ from other natural high- CO_2 systems because they are relatively short-lived and are not hydrothermal in origin.

Circumneutral (pH 6-7), net alkaline ($\sim 200 \text{ mg L}^{-1}$ as CaCO_3), iron- ($\sim 50 \text{ mg L}^{-1}$) and sulfate-rich ($\sim 500 \text{ mg L}^{-1}$) water flows out of the Ocean No. 2 mine. At the portal, dissolved CO_2 measured directly in the discharge water is 400-500 times greater than atmospheric concentrations. CO_2 is rapidly exsolved as it flows over a 10 m waterfall and is near atmospheric pressures before the drainage enters the Youghiogheny River. The greatest flux of CO_2 occurs between the portal and the waterfall ($\sim 2 \text{ m}$) and over the waterfall.

Molecular biological analyses, direct counts, FISH, and culturing of the microbial population within the iron oxide deposits beneath the waterfall indicates the presence of a wide variety of metabolic groups, including iron- and sulfur-oxidizing and reducing bacteria.

The high P_{CO_2} waters reflect dissolution-precipitation reactions of carbonate, silicate and sulfide minerals, as well as microbial interactions under various redox conditions. The Sr isotopic composition of the high CO_2 discharge ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7121$) is within the range of nearby mine discharges (0.7121 to 0.7126). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of associated limestones (0.7106 to 0.7111) and shales (0.7158 to 0.7298) suggest involvement of both cation exchange reactions of acidic waters with clay minerals as well as carbonate dissolution.

Ongoing work at this site will assess potential surface and subsurface mineralogical, biogeochemical and water quality effects of CO_2 and sulfate release which could be analogous to CO_2 - SO_2 co-injection into geologic formations.