

## Biological fractionation of molybdenum isotopes: Lake Mývatn, Iceland

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Molybdenum (Mo) is an essential enzyme cofactor in nearly all organisms and has been known to be of biological importance for some time [1]. Such biochemical ubiquity may come as a surprise given the relative scarcity of Mo at the Earth's surface. However, its unreactive, conservative behaviour in oxygenated, aqueous solutions makes it the most abundant transition metal in the oceans.

Laboratory based studies have shown that certain soil bacteria and cyanobacteria all favour light isotopes during Mo assimilation, thus causing measurable fractionations [2]. This study aims to bridge the gap between these laboratory experiments and the natural environment. Lake Mývatn is an ideal location to investigate these processes. Located on young, porous lava of the Icelandic rift zone it is almost exclusively sourced by groundwater flow and has only one riverine output, making it a perfect natural "box-model". Groundwater and outlet samples were analysed for Mo isotopes over the course of one growing season.

There are two distinctive groundwater inputs;  $\delta^{98}\text{Mo}_{\text{hot}}$ : 0.57 ‰ and  $\delta^{98}\text{Mo}_{\text{cold}}$ : 0.35 ‰ (0.1 2s.d.). The Mo concentration of the lake waters is described by simple, proportional mixing of these inputs. However, the Mo isotope value of the lake is heavier than the mixed inputs, consistent with a preferential uptake of light Mo isotopes by *Anabaena* (cyanobacteria), known to bloom in the lake in the summer months. Over the course of the year the outlet varied systematically between  $\delta^{98}\text{Mo}$  0.36 ‰ and  $\delta^{98}\text{Mo}$  0.66 ‰ with a signal predicted by a concentration driven model and biological fractionation of between - 0.2 ‰ and - 0.4 ‰. These results represent the first measurements of biological fractionation of Mo in the natural environment and have implications for our understanding of Mo systematics and its potential as a proxy in a geological context.

[1] Howarth & Cole (1985) *Science* 229. 653-655. [2] Zerkle, Scheiderich, Maescam, Liermann & Brantley (2011) *Geobiology* 9 (1): 94-106

## XAFS analysis of C-S-H formed by cement-bentonite interaction

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The analysis of long-term alteration of engineered barriers to be used for the disposal of TRU waste predicted precipitation of calcium silicate hydrate (C-S-H) minerals in the bentonite along the interface with the cement. In order to quantitatively measure the C-S-H predicted to form as a secondary mineral in the bentonite, the authors used XAFS analysis technique. The XAFS analysis which provides information around the concerned element regardless of the crystallinity of the mineral was assumed to be an effective mean to analyze poorly crystallized C-S-H. The local structural environment of calcium in the C-S-H with different Ca/Si ratio was also evaluated based on the EXAFS spectra in this study.

A test piece prepared by contacting a compacted bentonite and a hardened cement paste was immersed in the simulated fresh, reducing and high pH (FRHP) groundwater. The calcium K-edge XAFS measurement was conducted for the compacted bentonite. A synthetic C-S-H with high Ca/Si ratio was prepared and dissolved to generate low Ca/Si ratio C-S-H. These C-S-H minerals were subjected to the XAFS analysis.

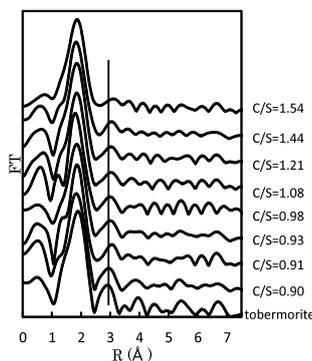


Fig.1 Radial structure function of C-S-H

The XAFS measurement allowed for evaluation of the variation of the quantity of the C-S-H in the bentonite. No significant difference was observed in the EXAFS spectra and conditions around the calcium among C-S-H minerals with different Ca/Si ratio. Conditions around the calcium in the C-S-H were similar to those in the tobermorite (Fig. 1).

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