Modelling Li isotope signatures of waters altering a basaltic glass in under-saturated conditions

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In order to use lithium isotopes as tracers of silicate weathering, it is necessary to constrain the Li isotope fractionation caused by weathering processes (especially, mineral dissolution and secondary phase formation) as a function of environmental parameters.

Preferential uptake of ^{6}Li during the formation of clay minerals was quantified by several studies (e.g. [1]). Concerning leaching, experiments with a Li-rich basaltic glass in under-saturated conditions have shown that the δ^7Li values of the leachates are lower than the fresh basaltic glass value during the early stages [2]. This was explained by a 2-step model: (1) Li is released in solution by diffusion, which leads to the formation of a leached layer. As ^{6}Li is lighter than ^{7}Li, the ratio of the diffusion coefficients of both isotopes (a=D_7/D_6) is lower than 1. Thus, the solution is enriched in ^{6}Li and the leached layer in ^{7}Li. (2) The dissolution of the leached layer tends to increase the solution δ^7Li value. D_7/D_6 is also found to correlate with temperature.

In order to model natural data, D_7/D_6, but also the relative contribution of diffusion and dissolution rates has to be estimated. At T < 20°C, D_7/D_6 is nil. However, it can be significant for hydrothermal fluids. Using diffusion and dissolution rates at high T°, the model shows that the high dissolution rate masks the kinetic effect due to diffusion. In any case, the only way to produce δ^7Li values in solution greater than that of the fresh mineral is to preferentially incorporate ^{6}Li into the secondary phases formed during the alteration.

[1] Vigier *et al.* (2008) *GCA* **72**, 780–792. [2] Verney-Carron *et al.* (2011) *GCA* (in press)

The Pb age of the Earth from Neoarchean galenas

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Pb isotopes have provided the earliest estimates for the age of the Earth [1-3] and still provide important absolute age constraints on Earth's formation. Recent age determinations using the Pb isotope composition of the bulk silicate Earth range from 50 to 150 Ma after solar system formation [4-8]. Variation in present-day Pb isotope compositions in the silicate Earth, however, contribute to the uncertainty in these age determinations. Here we use the Pb isotope composition of galenas in volcanogenic massive sulfide (VMS) deposits in the Superior Province, Canada to determine the Pb age of the Earth. All deposits are Neoarchean (~2.7 Ga) and are derived from juvenile, mantle-derived volcanic rocks, as evidenced by their Nd and Hf isotopic compositions. Pb isotopes in the galenas are time invariant and thus provide a snapshot of the Neoarchean mantle from which they are ultimately derived.

A plausible scenario for Earth's Pb evolution is that it began with a low μ in the solar nebula and increased progressively during accretion to the current value of ~ 8 for the silicate Earth [4-8]. Using a low average μ from 4.56 to 4.52 Ga (< 0.7) with an increase to its current high μ at 4.52 Ga, the galena Pb trend is nearly coincident with the 2.7 Ga Geochron. With these parameters there is no Pb paradox at 2.7 Ga. The timing of this process, however, is dependent on the early stage of Pb evolution on Earth: If μ was lower during Earth's formation, the bulk of Pb loss occurred earlier; if μ was higher, integrated Pb loss occurred later, but with maximum of ~4.48 Ga. Our estimate for the Pb age of the Earth of ~4.52 Ga is older than the range of ages based on the present-day silicate Earth. This age most likely dates Pb loss to the core [4-8] or to space during accretion [9], and may have been finally punctuated by a moon forming impact.

[1] Holmes (1946) *Nature* **157**, 680–684. [2] Houtermans (1946) *Naturwissenschaften* **33**, 185–186. [3] Patterson (1956) *GCA* **10**, 230–237. [4] Allegré *et al.* (1995) *GCA* **10**, 1445–1456. [5] Galer & Goldstein (1996) *AGU Monogr.* ***95***, 75–98. [6] Halliday (2004) *Nature* **427**, 505–509. [7] Wood & Halliday (2005) *Nature* **437**, 1345–1348. [8] Allègre *et al.* (2008) *EPSL* **267**, 386–398. [9] Albarède *et al.* (2011) *MinMag*, this volume.