

Chromium isotopic fractionation during Cr(VI) reduction in groundwaters

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Among heavy metals at trace concentration, chromium is an essential micronutrient element necessary to humans and other organism's life in its trivalent form Cr(III) at the proper concentration, but in its hexavalent oxidation state Cr(VI) becomes toxic and suspected carcinogen. The concentration of natural Cr in soils and waters is largely determined by the weathering and erosion of the parental material. Soils derived from igneous rocks can be expected to contain higher levels of Cr compared with sedimentary rocks. The two common oxidation forms of Cr in the environment are Cr(III) and Cr(VI). The two species are different in physicochemical properties and chemical and biochemical reactivity. Cr(III) has a very low solubility and a strong tendency to be adsorbed on surfaces. Cr(VI) forms anionic oxy-compounds and it is highly soluble. The most common species in natural waters is CrO₄²⁻. The Cr speciation in aqueous solutions depends on several factors, including Eh and pH but also the occurrence of competing ions, complexing agents and others.

The ⁵³δ Cr was measured in industrial Cr sources and in groundwaters interacting with ophiolitic rocks in the La Spezia Province (Italy). Cr speciation analysis reveals that in waters the dissolved Cr is essentially present in the Cr(VI) form. Due to the absence of anthropogenic Cr sources, the relatively high Cr(VI) concentration can be attributed to natural pollution.

The isotopic data suggest that Cr released from industrial sources is isotopically close to the natural value, with an average ⁵³δ Cr = 0.34 +/- 0.43 (2-σ). Most of the groundwater Cr(VI) analyses are characterized by variable enrichment in heavy Cr isotopes, with a consequent positive ⁵³δ Cr value. In particular, the higher ⁵³δ Cr values are found in samples with the lowest Cr(VI) concentration. Despite preliminary, these data indicate that lighter isotopes were preferentially removed from these waters, suggesting that along the flow path, Cr(VI) reduction was actively occurring. The data indicate that the Cr-isotopic fractionation associated with the Cr(VI) reduction follows a Rayleigh-type process.

Lithium isotopic fractionation in pegmatites

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In order to fully utilize Li isotopes as tracers of magmatic processes it will be necessary to both characterize the Li isotopic compositions of different geological reservoirs, and quantify the magnitude of isotopic fractionations for various conditions/compositions. The continental crust appears to have lighter Li isotopic composition than the upper mantle, from which it was derived [1, 2]. Given that Li isotopes do not fractionate during high-T magmatism, juvenile crust and the mantle should have identical Li isotopic compositions. The isotopically light continental crust, therefore, is likely a result of secondary processes, e.g., weathering, metamorphism and low-T intracrustal melting. Recent studies have demonstrated large Li isotopic fractionation during surface weathering and metamorphic dehydration, but few data exist for Li isotopic fractionation during relatively low-T magmatism.

We measured Li concentrations and ^{δ7}Li of coexisting quartz, muscovite, plagioclase and spodumene from the well-characterized Tin Mountain pegmatite, Black Hills, South Dakota. This pegmatite crystallized from the wall zone inwards, as temperatures decreased from >600 to <500°C [3]. Muscovite, plagioclase and spodumene in all zones display a narrow range in ^{δ7}Li (+7.9 to +11.4‰), whereas quartz is more variable (+14.7 to +21.3‰). On average, quartz is the heaviest mineral (+18.1 ± 2.1‰ (1σ)) and has relatively low Li concentrations (~82 ppm), while spodumene, muscovite and plagioclase are lighter (+9.4 ± 1.2‰ (1σ)) with Li concentrations decreasing from spodumene to muscovite (~6420 ppm) to plagioclase (~570 ppm). The +6‰ difference between quartz and other minerals can be explained by the preference for heavy ⁷Li in higher bond-energy sites. Therefore, tetrahedrally coordinated Li in quartz is expected to host more ⁷Li than 6-fold sites in the coexisting minerals.

The isotopically heavy pegmatite body (~ +10‰) is distinct from the surrounding Black Hills metasedimentary rocks (+2 ± 1‰, n=3) and Harney Peak granites (+5 ± 1‰, n=2), consistent with ⁷Li enrichment accompanying extensive crystal-liquid fractionation.

References:

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