

Chromium isotope fractionation during reduction of Cr(VI) under saturated flow conditions

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Chromium (VI) is a pervasive groundwater contaminant that poses a considerable threat to human health. Remediation techniques have focused on the reduction of the highly mobile Cr(VI) to the sparingly soluble Cr(III) species. Reduction has been shown to produce significant Cr isotope fractionation, characterized by an enrichment in the ⁵³Cr/⁵²Cr ratio in the remaining Cr(VI) pool [1]. Chromium isotopes are promising indicators of Cr(VI) reduction in groundwater; however, the influence of transport on fractionation has not been fully examined.

A laboratory column experiment was conducted to evaluate isotopic fractionation of Cr during Cr(VI) reduction under controlled flow conditions. Simulated groundwater containing 20 mg L⁻¹ Cr(VI) was pumped through a saturated column containing quartz sand with 10% (v/v) organic carbon. Isotope measurements were performed on both effluent and profile samples. Dissolved Cr(VI) concentrations decreased while $\delta^{53}\text{Cr}$ increased, indicating that reduction of Cr(VI) occurred. Solid-phase analysis by scanning electron microscopy (SEM) and X-ray absorption near edge structure (XANES) spectroscopy confirmed the presence of Cr(III) on the surface of the organic carbon. The $\delta^{53}\text{Cr}$ data followed a linear regression equation yielding a fractionation factor (α) of 0.9979, whereas previous studies of batch experiments under similar geochemical conditions demonstrated Rayleigh-type isotope fractionation. Both the results of the solid-phase Cr and isotope analyses suggest a combination of Cr(VI) reduction mechanisms, including reduction in solution, and sorption prior to reduction [2]. The linear characteristic of the current $\delta^{53}\text{Cr}$ data may reflect the contribution of transport on Cr isotope fractionation.

[1] Ellis *et al.* (2002) *Science*, **295**, 2060-2062; [2] Park *et al.* (2005) *Water Res.*, **39**, 533-540.

Mechanisms of reaction driven porosity and permeability generation

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The evolution of the Earth's lithosphere is, to a major extent, affected by reactions in which magmatic or metamorphic rocks consume fluid components such as H₂O and CO₂. Examples include serpentinization of the oceanic lithosphere and weathering of continental rocks. The progress of such reactions, as well as many other replacement processes that depend on the presence of a fluid phase, requires that porosity is maintained to keep fluid in contact with reactive solid surfaces.

As most volatilization reactions lead to a reduction in rock density, and thus an increase in the volume of solid, the initial pore volume will tend to become filled with new mineral phases during such processes, in the absence of porosity-generating processes. However, observations at scales ranging from nanometer to outcrop scales, indicate that a variety of porosity generating processes are operating. For example, replacement reactions mediated by dissolution-reprecipitation mechanisms have been observed to produce micro-porous products in a variety of systems [1], while reactions associated with a significant volume increase often lead to fracturing [2]. However, the detailed mechanisms of these porosity-producing processes have been poorly understood.

In this contribution, we review examples of reaction driven fracturing, and propose a new model for how stress is generated at reacting olivine surfaces during serpentinization. This model emphasizes the role of interface coupled dissolution-reprecipitation processes in producing the surface roughness required to generate stress concentration and associated fracturing at the reactive surface. This process results in the hierarchical fracture network [3] represented by the characteristic mesh-structure of partly serpentinized olivine grains. Similar patterns are also observed in a variety of other systems.

[1] Putnis, A. (2009) *Reviews in Mineralogy*, **70**, 87-124.
[2] Jamtveit, B., Putnis, C., Malthe-Sørensen, A., (2009) *Contributions to Mineralogy and Petrology*, **157**, 127-133.
[3] Iyer, K., Jamtveit, B., Mathiesen, J., Malthe-Sørensen, A., and Feder, J., (2008) *Earth and Planetary Science Letters*, **267**, 503-516.