

Transition metal isotopes in rivers and the weathering environment

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Transition metal isotope geochemistry is increasingly being used to shed light on the operation of the Earth System, both on the modern Earth and in the past. One key target for this research is the marine environment, with research questions surrounding the oceanic portion of the carbon cycle, interactions between the early biosphere and its physico-chemical environment, amongst others. However, the oceanic budgets of these elements can only be understood in the context of constraints on the main input to the oceans, rivers. Here, we present and discuss an extensive dataset for the isotopes of the transition metals in rivers, including data for Cu, Zn and Mo in major world drainage basins,

An array of rivers, from a variety of tectonic and climatic settings and including large rivers like the Amazon and Brahmaputra, exhibit a range in dissolved $\delta^{65}\text{Cu}$ (relative to NIST SRM 976) of 0 to +1.6 per mil. Mo isotopes exhibit a similar range, with $\delta^{97/95}\text{Mo}$ ranging from 0 to +1.5 per mil. In both cases, heavier isotopic compositions are associated with lower total concentrations. Both Mo and Cu in the continental crust have an isotopic composition close to zero so that the measured rivers are universally heavier, implying an isotopic fractionation during weathering and transport. Zn isotopes in rivers, by contrast, have a dissolved riverine isotopic composition around +0.3 per mil (relative to Lyons JMC), little different from measurements of rocks from the crust.

Though Mo and Cu exhibit similarly heavy isotopic compositions in the dissolved phase of rivers, their systematics in particulate phases in rivers are very different for the two elements. The particulate data for Cu reveal a significant isotopically light fraction. This suggests that the riverine Cu budget is controlled by partitioning during transport of a weathered pool of Cu, between an isotopically light fraction adsorbed to particulates and a heavy dissolved fraction dominated by Cu bound to strong organic complexes. By contrast, riverine particulates contain negligible amounts of Mo, suggesting that the heavy dissolved phase must have an origin in soils, perhaps due to preferential uptake of the light isotopes onto metal oxide phases. Neither of these processes appears to be important for Zn, which appears to behave simply in the weathering environment.

A model of S solubility in basaltic melts at 1 atm

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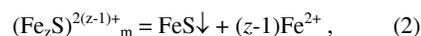
Proposed Mechanism of Sulfide Dissolution

We have developed a new technique for thermodynamic processing of experimental data on sulfide solubility in a wide range of basaltic and silica-rich compositions. The technique is based on the assumption of existence of complex sulfide species in reducing silicate melts [1], which are similar to cationic iron-sulfur clusters in gas systems [2]. We propose a new mechanism for sulfide dissolution in iron-bearing silicate liquids, which leads to formation of stable positively charged iron-sulfur complexes



Calibration of a New SCSS Model

In our model, sulfide precipitation from iron-bearing melts is described by a reaction of decomposition of the iron-sulfur clusters:



where z is a number representing the average weighted size of clusters in the melt. Following eq.2 and mass balance constraints, it can be demonstrated that sulfur content in any sulfide-saturated melt may be approximated by a general equation:

$$\ln X_S = (z-1) \ln X_{\text{FeO}} - z \ln \Sigma \text{cat} - \ln K_{\text{FeS}\downarrow}, \quad (3)$$

where X_{FeO} and Σcat are the FeO content and sum of cations in 1 mole in the melt; and $K_{\text{FeS}\downarrow}$ is the equilibrium constant of eq.2. To calibrate the dependence of z and $K_{\text{FeS}\downarrow}$ on temperature and melt composition, we used a set of 82 anhydrous 1-atm experimental glasses [3,4] and 53 natural MORB glasses (Siqueiros FZ, East Pacific Rise). The final equation includes 14 fitted parameters and can reproduce the calibration database within 10%. The new SCSS-model allows one to realistically predict sulfide saturation in magmas crystallized between 1400-1100°C.

[1] Poulson & Ohmoto (1990) *Chem. Geol.* **85**, 57-75.

[2] Koszinowski *et al.* (2002) *J. Chem. Phys.* **117**, 10039-10056.

[3] Houghton *et al.* (1974) *Econ. Geol.* **69**, 451-467.

[4] O'Neill & Mavrogenes (2002). *J. Petrol.* **43**, 1049-1087.