

## Mineral formation and evolution from a first-principles perspective

SANDRO JAHN

GFZ German Research Centre for Geosciences,  
Telegrafenberg, 14473 Potsdam, Germany  
(correspondence: jahn@gfz-potsdam.de)

The formation and evolution of minerals is driven by thermodynamics or, more specifically, by the tendency of a usually complex chemical system to reach the lowest energy state at the existing pressure and temperature conditions. Much of what we know about the mineralogy of the Earth's interior stems either from laboratory experiments or from natural samples that at least partly preserved the structure and chemical composition they obtained during their formation. In recent years, computational mineralogy has become a powerful complementary approach to constrain the stability of minerals and their chemistry in the wide range of conditions of the Earth's interior. First-principles simulations that are based on quantum mechanics are especially suited in this respect as they are predictive, accurate and versatile.

In this talk, I will focus on two aspects of mineral evolution: (1) the partitioning of trace elements and isotopes between minerals, melts and fluids and (2) the phase behavior of mantle minerals at high pressures and temperatures. With a number of examples from recent case studies I will illustrate how the most likely incorporation mechanisms of minor elements into minerals are obtained from the simulations and which influence the molecular structure of the fluid or melt has on the partition coefficients. I will present efficient schemes to compute Gibbs free energy differences or element exchange coefficients and conclude with explicit simulations of mineral phase transformations, which sometimes lead to the discovery of previously unknown stable or metastable crystalline phases. All calculations presented here accompany or are accompanied by experimental or analytical work and it is important to stress the new synergies that arise from such collaborations.

## Reactive transport modeling of chromium isotope fractionation during Cr(VI) reduction under saturated flow conditions

JAMIESON-HANES, J.H.<sup>1</sup>, AMOS, R.T.<sup>1</sup>, GIBSON, B.D.<sup>1</sup>, PTACEK, C.J.<sup>1</sup> AND BLOWES, D.W.<sup>1</sup>

<sup>1</sup>Dept. of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, Canada  
(jhjamies@uwaterloo.ca, ramos@uwaterloo.ca, bgibson@uwaterloo.ca, ptacek@uwaterloo.ca, blowes@uwaterloo.ca)

Hexavalent chromium (Cr(VI)) is a very mobile groundwater contaminant most often derived from industrial processes such as tanning and electroplating, but also from naturally occurring geological sources. Reduction of Cr(VI) to the sparingly soluble Cr(III) is a common method of groundwater remediation, and is accompanied by a significant isotope fractionation. During reduction the remaining Cr(VI) pool becomes enriched in the <sup>53</sup>Cr/<sup>52</sup>Cr ratio; the degree of this enrichment depends on the reductant, the mechanism of Cr removal, and is potentially influenced by transport processes [1].

Several laboratory experiments were conducted using organic carbon and zero-valent iron to treat Cr(VI) under both static and saturated flow conditions. In addition to traditional aqueous geochemical measurements, MC-ICP-MS analyses were made to determine the Cr isotope composition of the dissolved Cr(VI). Results from the analogous batch and column experiments exhibited different Cr isotope trends, suggesting that transport processes may play a role in the overall fractionation factor. The experiments were simulated using the reactive transport model MIN3P in order to further explore the influence of transport. Modeling results indicated that the interpretation of Cr isotope fractionation during reduction can be complex, particularly where multiple removal mechanisms may exist. Overall, the simulations were able to provide further insight into the isotope fractionation associated with the Cr removal processes.

[1] Jamieson-Hanes (2012) *Environ. Sci. Technol.* **46**, 6783-6789.