

Nanoparticulate Fe(III)-precipitates forming by Fe(II) oxidation in water

A. VOEGELIN*, S. SCHWARZ, S.J. HUG AND R. KAEGI

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland
(*correspondence: andreas.voegelin@eawag.ch)

The oxidation of dissolved Fe(II) at oxic/anoxic boundaries leads to the precipitation of nanoparticulate Fe(III)-phases that profoundly impact the biogeochemical cycling of Fe and the fate of other major and trace elements in environmental systems. Despite the importance of Fe(III)-precipitates as immobilizing sorbents or colloidal carriers for contaminants and nutrients, numerous questions relating to their formation, their structural diversity and resulting differences in reactivity remain to be resolved.

Own recent work on Fe(III)-precipitates formed in aerated Fe(II)-containing aqueous solutions at pH 7 indicated the importance of Fe(III)-phosphates [1, 2]: At molar dissolved P/Fe (II) ratios >0.5, we observed exclusive formation of amorphous Fe(III)-phosphates that also incorporated substantial amounts of Ca. At P/Fe(II) <0.5, we concluded from X-ray absorption spectroscopy data that Fe(III)-phosphate formed until P was depleted, followed by the formation of other Fe(III)-phases (Si-rich hydrous ferric oxide at Si/Fe > 0.5, 2-line ferrihydrite at Si/Fe ~0.2-0.5, or lepidocrocite at Si/Fe <0.2) [1]. Electron microscopy data suggested that the different Fe(III)-phases became mixed in nanoparticles with diameters of a few 10-100 nm [2].

In continuing work, we aim (i) to resolve the composition and structure of Fe(III)-phosphates and the mode of cation and anion incorporation (Ca versus Mg, phosphate versus arsenate), (ii) to evaluate the transformation of different types of fresh precipitates during aging, and (iii) to assess how the different types of fresh Fe(III)-precipitates and their aging products affect other major and trace elements in aquatic systems. This work is based on controlled laboratory experiments in synthetic aqueous solutions, complemented by studies on real systems such as diagenetic Fe accumulations in lake sediments or As-removal units for drinking water treatment.

[1] Voegelin *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 164–186. [2] Kaegi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 5798–5816.

The partitioning of volatile elements between metal and silicate at high pressures and temperatures

A.K. VOGEL^{1*}, D.C. RUBIE¹, D.J. FROST¹
AND H. PALME²

¹Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

(*correspondence: antje-kathrin.vogel@uni-bayreuth.de)

²Forschungsinstitut und Naturmuseum Senckenberg, D-60325 Frankfurt, Germany

Volatile elements are depleted in the Earth's mantle and in nearly all other solid objects of the inner solar system (Moon, Mars, meteorites), most probably because they failed to condense at high temperatures. In some cases evaporation before or during accretion may also have occurred. Many of these elements were additionally affected by core formation. To disentangle primary depletion and depletion by core formation and to provide additional clues for the processes of core formation we studied the metal - silicate partitioning behaviour of the volatile siderophile elements Sn, Pb, P, Cu and Ge, covering a range of 650 K in condensation temperatures.

Experiments were performed over a pressure and temperature range of 10.5 GPa to 23 GPa and 2273 K to 2673 K respectively using a multianvil apparatus. The oxygen fugacity varied from -2.0 to -2.4 log units relative to the iron-wüstite-buffer. The starting materials consisted of 3 parts (by weight) silicate (peridotitic composition) and 1 part (by weight) metal, with the latter consisting of 95 wt% Fe, and 1 wt% of P₂O₅, Cu, GeO₂, SnO and Pb₃O₄ respectively. To consider the effect of S one experiment was performed with 10wt% S added as FeS to the metal phase of the starting material. Analyses of the metal phases were performed with an EPMA, the compositions of the silicate phases were analyzed by LA-ICP-MS.

The volatile elements Sn and Pb are similarly depleted in the Earth's mantle, which requires similar effective partition coefficients ($D^{\text{met/sil}}$) during core formation. However, at low pressures the partition coefficients of Sn and Pb differ by up to two orders of magnitude. Our results show that the liquid metal - liquid silicate partition coefficients of Sn and Pb converge with increasing pressure, indicating that equilibration pressures of at least 30 GPa were necessary to avoid fractionating them in the Earth's mantle.

We found that 10 wt.% S in the metal phase has hardly any influence on the $D^{\text{met/sil}}$ of Pb but lowers the value for Sn by about 0.6 orders of magnitude.