# Geochemical cycles of Fe, Mo, U, Cu, Cr, REEs, and S during the period 3.5 - 3.2 Ga ago

HIROSHI OHMOTO, DAVID C. BEVACQUA, IAN JOHNSON AND YUMIKO WATANABE

NASA Astrobiology Institute and Dept. of Geosciences, The Pennsylvania State University, University Park, PA 16803 USA (hqo@psu.edu)

To understand the geochemical cycles of redox-sensitive elements in the Archean, we have carried out systematic investigations of a variety of rocks (mostly from drill cores) in the Pilbara Craton, Western Australia, including: (a) the ~3.46 Ga Marble Bar Chert/Jasper Formation that deposited in a deep sea; (b) submarine basalts of the 3.46-3.43 Ga Duffer and Apex Formations that were altered by deep-sea hydrothermal fluids; (c) footwall alteration zones of the ~3.25 Ga massive sulfide deposits in the Panorama district; and (d) ~3.43 Ga paleosols that developed in a >50x200 km area.

Hematite crystals are abundant in many of these rocks. Mineralogical and geochemical characteristics of the hematites and their host rocks suggest the following processes for the formation of hematite (and its precursors) in these rocks: mixing of $Fe^{2+}$-rich hydrothermal fluids and $O_2$-rich deep-sea water for hematite in (a); reactions between ferrous-rich minerals and $O_2$-rich deep-sea water for hematite in (b) and (c); high temperature reactions between ferrous-rich minerals and seawater $SO_4^{2-}$ for hematite in (c); and mixing of $Fe^{2+}$-rich soil/groundwater and atmospheric $O_2$ for hematite in (d). The hematite-rich rocks are characteristically enriched in U, Mo, Cu, Cr, and REEs, much like modern goethite/hematite-rich submarine rocks and laterites. Depletions/enrichments of these redox-sensitive elements are also common in rocks below and above the hematite-rich zones in (a) – (d), much like those observed in altered modern submarine volcanic rocks and soils.

Results of our investigations suggest that, during the ~3.5–3.2 Ga period: (1) the atmosphere and oceans were fully oxygenated, because higher than 50% of the present atmospheric $pO_2$ level was required for deep oceans to be oxygenated; (2) the land surface was fully colonized by microbes to generate abundant organic acids; (3) U, Mo, Cu, Cr, REEs, and S were leached from rocks by $O_2$- and organic acid-rich soil water and transported to the oceans; and (4) the normal seawater was rich in $SO_4^{2-}$, U, Mo, Cu and Cr, but poor in Fe and Ce. These characteristics are essentially the same as those of the modern systems, suggesting that the modern-day geochemical cycles of redox-sensitive elements were already established ~3.5 Ga ago.

---

# Importance of post-adsorption on the long-term migration of actinides

T. OHNUKI

Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki, 319-1195 Japan (ohnuki.toshihiko@jaea.go.jp)

Long-term migration of actinides should be elucidated to estimate the impact of geological disposal. In the estimation by mathematical model, retardation of the migration is assumed to be caused by the adsorption of actinides on microorganisms and minerals. If the adsorbed actinides change its chemical states after adsorption, it should affect the long-term migration of actinides. We have conducted the research on the minralization and fixation of actinides after the adsorption by microorganisms and minerals.

In the study of uranium ore deposit at Koongarra, Australia, U (VI) is mineralized to be formed saleeite on apatite, and torbernite in Fe minerals in the downstream of the secondary ore deposit [1]. These mineralization gave larger retardation factor by 100 times than that estimated adsorption of U (VI) by the soils at Koongarra. We confirmed the fixation of U (VI) by the laboratory experiments. U (VI) is changed its chemical state to more insoluble species than adsorbed one during the crystalization of amorphous iron minerals to hematite [2]. U (VI) is also mineralizaed as autunite on the surface of apatite during the dissolution of apatite [3].

In the accumulation experiments of U (VI) by *Saccharomyces cerevisiae*, the adsorbed U (VI) is mineralized to H-autunite on the cell surface [4]. Cerium (III), analogue of Am and Cm, is adsorbed by Mn oxidizing bacteria. The adsorbed Ce is moved to $MnO_2$ formed by the bacteria, and is oxidized to Ce (IV) [5]. Pu (VI) is adsorbed by *Bacillus subtilis*, and then is reduced to insoluble species of Pu (IV) after the adsorption [6].

These results indicate that post-adsorption is one of the important phenomina to retard the migration of actinides in environment.

[1] T. Murakami, T. Ohnuki, *et al. American Mineralogist,* **82**, 888–899. (1997)v [2] T. Ohnuki, *et al. J. Nucl. Sci. Tech.* **34**, pp.1153-1158. (1997). [3] T. Ohnuki, *et al. Chem. Geol.* **211**, 1–14(2004). [4] Ohnuki, T. *et al. Geochim. Cosmochim. Acta,* **69**, pp. 5307–5316, 2005 (2005). [5] T. Ohnuki, *et al.* C*hem. Geology,* **253**, pp. 23–29, 2008. [6] T. Ohnuki, *et al. Environ. Sci. Technol.* 2007, **41**, 3134–3139.