Geochemical and isotopic properties of micro-metallic aggregates in the Oklo natural reactor

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The Oklo-Okelobond-Bangombé uranium deposits, the Republic of Gabon, known as natural fission reactors are useful natural analogues for radioactive waste disposal in geological media, because large-scale fission reactions occurred spontaneously 2.0 Ga ago. Our major concern is to understand the geochemical behavior of fission products geneated in the reactors. Since Tc, Ru, Rh and Pd are highly produced by fission, their long-term behaviors are important for the radioactive waste disposal.

It has been known from the microscopic observation of artificial spent fuel that fissiogenic Ru, Rh and Pd formed aggregates [1]. Similar aggregates were also found in the Oklo reactors [2, 3]. We found a number of metallic aggregates sized 10 to 40 µm in the Oklo reactor zone 13. EPMA analyses showed that the aggregates consist mainly of Ru, Rh, Pd, Te, Pb, Bi, As, Sb and S. Isotopic analyses with a sensitive high resolution ion micro-probe (SHRIMP) revealed that Ru, Pd and Te in the aggregates are pure fissiogenic origin.

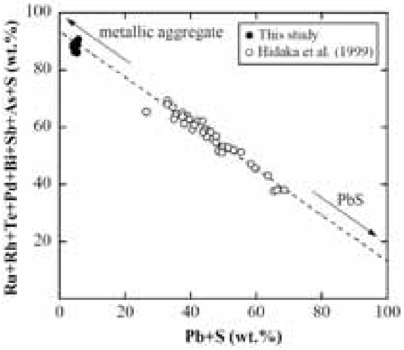

Figure 1: Two components diagram of metallic aggregates in SD37-S2/CD at the Oklo reactor 13.

Figure shows a correlation diagram between (Ru+Rh+Te+Pd+Bi+Sb+As+S) and (Pb+S) components of the aggregates found in SD37-S2 borehole at the Oklo reactor 13. Interestingly, almost all of the data points are plotted on a single line, suggesting that fissiogenic Ru, Rh, Te and Pd formed aggregates after mixing with microcrystal of galena in the reactor.

[1] Kleykamp (1985) *J. Nucl. Mat.* **131**, 221-246.
[2] Gauthier-Lafaye *et al.* (1996) *GCA* **60**, 4831-4852.
[3] Hidaka *et al.* (1999) *Chem. Geol.* **155**, 323-333.

Effects of nanoparticle aggregation on metal sorption, desorption and speciation

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Iron oxyhydroxide nanoparticles play an important role in the mobility of aqueous metal species through both sorption and desorption processes. However, the natural and often rapid aggregation of such nanophases in aqueous systems can lead to changes in their structure, available surface area, porosity, and reactivity that may modify the mechanisms by which metal ions are retained and therefore the long-term potential of metal sequestration in the solid phase.

Batch and spectroscopic methods were used to investigate the uptake, release, and speciation of metals onto and within nanoscale iron oxyhydroxides exposed to conditions which induce nanoparticle aggregation and growth. Aqueous Cu(II) or Zn(II) was added to a suspension of synthetic 5-nm iron oxyhydroxide nanoparticles either prior to or following aggregation induced through increases in pH, ionic strength, or temperature and allowed to adsorb for a period of 24 hours. Samples were analyzed both after initial metal uptake and following a desorption step induced by lowering the pH back below the macroscopic absorption edge for the specific metal.

Analysis of filtered supernatants combined with EXAFS studies of the solid aggregates suggest that the desorption step removes the weakly-held (i.e. surface-bound) metal fraction but retains strongly-held metals that appear to be more structurally incorporated within the nanoparticle aggregates. Separate long-term desorption studies with continuous monitoring of metal concentrations were also conducted to assess the slow exchange of the strongly-bound fraction of metals from the aggregates back into solution over time.

Results show the relative effects of different aggregation methods on metal uptake and subsequent release, with temperature/time most effective at retaining metals in the solid phase and pH-based aggregation less so, while ionic strength-based aggregation had little effect relative to unaggregated particles. These findings have implications for the removal of hazardous metals from the aqueous phase and the design of remediation strategies targeting contaminated environments such as mine-impacted regions.