The Tono Natural Analogue Project: Geochemical constraints on uranium mobility within the Tono uranium deposit, Japan

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The Tono uranium deposit in Gifu Prefecture, central Japan provides evidence that U has been effectively immobilized within the lignite-bearing lower Toki Formation for at least 10 Ma. Uranium-series isotope data indicate, however, that some re-mobilization of U has occurred within the deposit, albeit over scales of space and time that are not well constrained at present. Here we examine whether this apparent mobility could result from local variations in the geochemical environment, and from associated effects on the aqueous-speciation and solubility behavior of U.

Although U is associated with a variety of minerals in the Tono deposit, thermodynamic calculations suggest that U concentrations in contemporary porewaters are controlled by the solubility of an amorphous to incipiently crystalline $UO_2(s)$ solid that is metastable with respect to uraninite. Uranium concentrations in paleo-groundwaters inferred from the U contents of authigenic calcites are also consistent with solubility control by $UO_2(s)$. Results of a BSE/SEM study to confirm the existence of this phase are inconclusive, however.

Geochemical constraints on U mobility within the Tono deposit can be evaluated with the provisional conclusion that $UO_2(s)$ is solubility controlling. The solubility of this phase is calculated to vary by up to two orders of magnitude over a range of conditions (pH ≈ 7.5 – 10; Eh ≈ -250 — -400 mV; log $P_{CO2(g)} \approx -2.5$ — -5 bar) that we believe are representative of porewaters in the deposit, and which appear to be controlled by microbially mediated reactions leading to sulfate reduction and lignite oxidation, and by mineral-fluid equilibria involving pyrite, Fe(III)-oxyhydroxides and calcite. The calculated solubilities are especially sensitive to variations in $P_{CO2(g)}$ at a given pH because $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{2-}$ dominate the aqueous speciation of U under these conditions. Conservative estimates of the relative importance of uranyl complexing by organic acid anions and humic substances suggest that the latter could also increase $UO_2(s)$ solubilities by up to an order of magnitude at concentrations of humic substance as low as 100 ppb. These results suggest that plausible local variations in environmental conditions within the Tono deposit could induce mass transfer of U among solid and aqueous phases, and that this could explain the uranium-series isotope data if such mass transfer is accompanied by mass transport on a local-to-regional scale.

Isotopic effect on Zinc through isotopic separation using macrocyclic polyethers

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Non-mass dependent isotopic fractionation was first reported on U isotopes by Fujii et al. (1989). Since then, the non-mass dependent isotopic effect has been found for several elements including Mg, Ti, Cr, Fe, Ni, Zn, Sr, Zr, Mo, Ba, Sm, Gd, Yb through a liquid-liquid distribution, ligand exchange reaction and ion exchange chromatography separation techniques. However, the mechanism of non-mass dependent isotopic effect can not be fully explained by the “bench mark” theory proposed by Bigeleisen and Mayer (1947). However, for the further understanding of the non-mass dependent isotopic separation using various separation conditions are strongly required. In this study, isotopic effect of Zn through the chemical separation using macrocyclic compounds including series of crown ethers and cryptands was investigated. Based on the breakthrough technique on chromatography using a cryptand (2B, 2, 2) polymer, both the mass dependent and non-mass dependent isotopic fractionation could be found. The degree of non-mass dependent isotopic fractionation was largest for the solution collected by elution front. Even in the even-isotopes (^{64}Zn, ^{66}Zn, ^{68}Zn, ^{70}Zn), no linear fractionation line (mass dependent fractionation) could be found. Also non-mass dependent fractionation was observed in a liquid-liquid distribution using series of crown ethers. Nishizawa et al. (1993) reported the non-mass dependent fractionation on Zn isotopes. They demonstrated that only ^{67}Zn deviates from the mass dependent fractionation line defined by ^{64}Zn, ^{66}Zn, ^{68}Zn and ^{70}Zn isotopes. However, the Zn isotopic data obtained here shows that no linear fractionation line could be defined from even-isotopes, indicating that non-mass dependent fractionation could not be explained by simple odd-even effect. The data obtained here suggests that the isotopic effect could be due to changing in energy level of orbital electron caused by coupling of nuclear and orbital electron. We would like to discuss the mechanism of non-mass dependent isotopic effect on Zn.

References

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