O and H diffusion in uraninite: Implications for fluid-uraninite interactions and nuclear forensics

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Diffusion coefficients for O and H were determined from a series of uraninite-H_2O experiments between 50 and 700 °C. Under hydrous conditions there are two mechanisms of diffusion: (1) an initial extremely fast-path diffusion mechanism that overprinted the O isotopic composition of the entire crystals regardless of temperature and (2) a slower volume diffusive mechanism dominated by defect clusters that displace or eject nearest neighbour O atoms to form two interstitial sites, two partial vacancies, and by vacancy migration. Using the volume diffusion coefficients in the temperature range 300-600 °C, diffusion coefficients for O can be represented by $D = 2e^{-5}$ exp (-29489 cal/RT) cm^2/sec and for temperatures between 100-300°C the diffusion coefficients can be represented by $D = 2e^{-10}$ exp (-14934 cal./RT) cm^2/sec, where the activation energies for uraninite are 29.5 kcal/mole and 14.9 kcal/mol, respectively. Hydrogen diffusion in uraninite is controlled by similar mechanisms as O. Using the volume diffusion coefficients in the temperature range
50-700 °C, diffusion coefficients for H can be represented by $D = 9e^{-6}$ exp (-37411 cal/RT) cm^2/sec for temperatures between 450 and 700 °C and $D = 1e^{-14}$ exp (-8250 cal/RT) cm^2/sec for temperatures between 50 and 400 °C, where the activation energies for uraninite are 37.4 kcal/mole and 8.3 kcal/mol, respectively.

Exceptionally low $\delta^{18}O$ values of natural uraninites (i.e. -32‰ to -19.5‰) from unconformity-type uranium deposits in Saskatchewan, in conjunction with theoretical and experimental uraninite-water fractionation factors, suggest that primary uranium mineralization is not in O isotopic equilibrium with coeval clay and silicate minerals. The low $\delta^{18}O$ values have been attributed to O isotopic exchange with recent meteoric water ($\delta^{18}O$ = -20‰) at temperatures <50°C. Our data show that the anomalously low O isotopic composition of the uraninite can be a result of meteoric water-uraninite interaction under reducing conditions. The rather fast O and H diffusion coefficients for uraninite, especially at low temperatures, suggest that O and H diffusion studies can be used to track the route of fissile material from origin to location.

Can Fe isotopes be used to fingerprint Precambrian BIF?

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The Fe isotope composition of BIF, with $\delta^{56}Fe$ ratios ranging from -2 to +1.5 ‰, stands in marked contrast to the overwhelming majority of iron reservoirs on Earth [1]. Consequently, Fe isotopes might have potential to identify BIF protoliths in strongly altered and metamorphosed rocks (e.g. [2]). Here we report data from two groups of samples: (1) genuine BIF representing ages from 1.9 Ga to ~3.8 Ga, and (2) non-sedimentary samples. All of the genuine BIF samples studied so far have bulk-rock Fe isotope compositions that are consistent with a BIF 'fingerprint' (-0.239 ‰ < $\delta^{56}Fe$ < +1.046 ‰). However, the Fe isotope signatures of the non-chemical sedimentary samples suggest a more complicated story. A banded jasper+magnetite rock from the Abitibi Greenstone Belt has $\delta^{56}Fe$ = +1.25 ‰, and thus lies within the expected confines for a chemical sediment, as does a relatively pure metasomatic carbonate sample from the Isua Greenstone Belt (IGB; $\delta^{56}Fe$ = -0.350 ‰). Three other samples that have a mineral assemblage inconsistent with a sedimentary origin, have fractionated negative $\delta^{56}Fe$ values that range from -0.206 to -0.188 ‰, which is similar to a BIF sample from the IGB. Although the expected range of Fe isotope compositions occurs in our BIF samples, non-sedimentary samples share those values, and so it seems impossible to fingerprint BIF with Fe isotopes.

[1] Johnson & Beard (2006) *GSA Today* **16**, 4–10.
[2] Dauphas *et al.* (2004) *Science* **306**, 2077–2080.