High precision Uranium isotope analysis in urine by MC-ICP-MS and the detection of historic exposure to depleted Uranium

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The detection of anthropogenic uranium in urine may indicate a significant environmental exposure many years or decades earlier. Development of a sensitive bioassay for such exposure may help to clarify whether depleted uranium inhalation exposure in the military theater (or elsewhere) has any connection to Gulf War Illness or other health implications. We developed and applied a method of urinary uranium isotope analysis thought to be able to detect mg-level inhalation exposures at least 15 years prior, involving analysis of ~0.5-5 ng of uranium. The method involves concentration of uranium by co-precipitation, destruction of all organic matrix components and purification by ion exchange, followed by mixed faraday-ion counter detector analysis of isotope composition by MC-ICP-MS, including measurement of ^{236}U with a detection limit of a few fg. The method was rigorously tested by (1) parallel analysis by simpler SF-ICP-MS methods, (2) analysis of ~50 blind urine samples doped with small amounts of DU and/or ^{236}U, and analysis of many hundreds of veterans' samples with average uranium concentrations of <5 ng/liter. It was also applied to a cohort of civilians that lived in the vicinity of a munitions plant in Albany NY that undoubtedly had an inhalation exposure to DU prior to 1982 as verified by an accompanying envrionmental study. None of the UK military veterans tested were found to have any DU from potential exposure in 1991; however a significant proportion of the cohort living near the Albany NY munitions factory have DU in their urine. The value of this bioassay to health studies is in offering a way to prove an historic environmental exposure thought not to be detectable previously. The chemical/mass spectrometric method and our applications will be discussed.

T–t evolution of fast diffusion pathways in alkali feldspars

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TEM shows that straight, smooth 'film' exsolution lamellae common in alkali feldspars from granites are usually *semicoherent*, with regularly spaced misfit dislocations. The dislocation cores have usually been enlarged by dissolution to produce 'nanotunnels' [1]. Nanotunnels form narrow loops in two directions, forming an orthogonal mesh on both surfaces of lamellae. The opposite sides of individual loops are often connected by short 'pull-apart' cracks. Together, these sub-μm features could provide the main pathways for Ar-loss from granitic alkali feldspars below ~400°C over geological time.

The *T* at which coherent exsolution begins depends on the bulk ternary composition, and will range from ~600°C in the most Ab-rich (~Ab_{30}) to <300°C in the most Or-rich (~Ab_5) granitic feldspars. Lamellae coarsen at rates that depend on composition and cooling rate. A perthite with a 1 μm lamellar spacing will typically take 10^5-10^7 years to form, the longest times being in Or-rich feldspars, which intersect the coherent solvus at lowest *T*. Dislocations develop as exsolution lamellae coarsen and the crystal structure stiffens. At some low *T*, at present unknown, coherency strain energy exceeds the total energy of dislocation arrays and dislocations begin to nucleate with a periodicity that depends on lamellar thickness. They do not form on thin lamellae, common in Or-rich feldspars.

We have used TEM to study the effects of heating on feldspars from the Shap granite, bulk $Ab_{30}Or_{70}$. Twins and tweed patterns persist for long *t* up to the melting point and nanotunnels are resilient, becoming irregular in shape only at >900°C. In contrast, chemical homogenization (Na↔K interdiffusion) of <200 nm lamella is complete after <4h at 900°C with partial homogenization seen after just a few hours at 700°C. Pull-aparts persist but become discontinuous. Crack-like features, up to 1 μm long, can develop adjacent to nanotunnels but in the orthoclase matrix, and closure of these leads to disc-shaped slots, some of which lie in arrays. It is clear that microtextures of K-feldspars evolve during step heating experiments and that features develop which would not have been present during slow geological cooling.

[1] Fitz Gerald *et al*. (2006) *Am. Min.* **92**, 772-783.