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Secondary phase formation on depleted uranium metal in soil

E.R. TRUEMAN¹, S. BLACK¹, D. READ²
AND M.E. HODSON¹

¹ School of Human and Environmental Science, University of Reading (e.r.trueman@reading.ac.uk)

² Enterpris Ltd, University of Reading and University of Aberdeen

The fate of Depleted Uranium (DU) in the environment is currently not well known, despite the fact that contamination exists in many diverse environments. Deployment of DU has been undertaken in former war zones such as in Kosovo and Iraq, as well as on proving grounds in countries such as the United States and the Great Britain, following weapons testing [1,2]. Therefore, a need has arisen for studies on the corrosion and secondary alteration phases of DU under different geochemical conditions in order to better understand mobility of DU in the environment.

We reported preliminary results at Goldschmidt 2003 of experiments examining the alteration of DU metal in 3 different solutions [3]. Phases found in these experiments were schoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}]$ and studtite $(\text{UO}_4 \cdot 4\text{H}_2\text{O})$ in ultra high quality (UHQ) water; uranyl phosphate hydrate $[(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$ in a calcium phosphate solution; and becquerelite $[\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8]$ in a silicate-rich solution. Corrosion rates varied between each solution, with rates of 0.25mg per day in UHQ, 8.84mg per day in the silicate-rich solution, and no measurable corrosion in the calcium phosphate solution. It is thought that the phosphate forms a protective layer over the metal thus preventing corrosion.

To further investigate the above, experiments have been conducted using soil columns containing two types of soil from UK firing ranges: a sandy soil with a pH of 7.5 and loamy clay with pH 4.9. Annual rainfall was simulated to artificially weather discs of DU metal cut from an unfired CHARM 3 penetrator, placed 5cm down a 20cm soil column. Solution data were collected and replicate columns removed every six weeks for soil sampling and examination of the DU disc by XRD.

Preliminary results show that the discs in the loamy clay columns corrode at a faster rate than those in the sand. This could be explained by the lower pH of the clay compared to the sand. Discs in the sand have shown little alteration other than the formation of UO_2 and metaschoepite, while oxide phases, metaschoepite and uranyl phosphate hydrate have formed on those in clay. Uranium migration through the columns has been slow, reaching only a few cms below the discs after four months.

References

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U-Th disequilibrium dating of geological samples approaching secular equilibrium

M.B. ANDERSEN, C.H. STIRLING, E-K. POTTER
AND A. N. HALLIDAY

Dept. Earth Sciences, ETH, 8092 Zürich, Switzerland
(andersen@erdw.ethz.ch; stirling@erdw.ethz.ch;
potter@erdw.ethz.ch; halliday@erdw.ethz.ch)

U-Th disequilibrium dating has been of major importance for paleoclimate research and has, for example, been used to calibrate the ^{14}C chronometer and provide independent constraints on the timing and character of marine $\delta^{18}\text{O}$ glacial-interglacial stages.

Over the last decade, analytical developments in U-Th disequilibrium dating by multiple-collector mass spectrometry (TIMS and MC-ICPMS) have emphasized high precision measurements using small sample sizes; it is now possible to routinely measure both $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ with 1-2 per mil uncertainties (2σ) using only a few tens of nanograms of uranium. These levels of precision have allowed climate models to be rigorously tested, particularly through the last ~140 ka, spanning the last glacial-interglacial cycle. However, in older samples the age uncertainties associated with these methods are often too large to resolve adjacent climate episodes and improved analytical precision is needed. Because sample size is not a limiting factor for many U-series studies, we have focussed our efforts on significantly improving analytical precision by increasing sample size.

Using a NuPlasma MC-ICPMS we have developed new methods for measuring both $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ with an external reproducibility better than 0.5 ‰ (2σ). With these levels of precision, ~300 ka samples can be dated with analytical errors of <1500 years, compared with age uncertainties of ~2000-10,000 years reported by earlier workers. We are currently applying these methods to old carbonate samples, including ~300-600 ka corals from Henderson Island, south Pacific [1] thereby providing important information on sea-level and climate change before the last glacial-interglacial cycle.

Reference

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