

U AND Th DECAY CHAINS: APPLICATION TO REGOLITH CHRONOLOGY

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Dating based on the natural decay of U and Th is the most widely used technique among the methods used for the chronology of Earth and planetary materials. Increasing application of this technique in the field of low temperature geochemistry during the last decade is facilitated by the significant improvement of analytical instruments and chemical separation procedures. The main advantage provided by U and Th decay chains is the large number of parent-daughter pairs available for the timing of surface processes within a variety of time intervals. The method also gives an opportunity to crosscheck the obtained age data, which often results in relatively high precision and increased confidence in the calculated ages. In fact the uncertainty associated with the correction for initial concentration of daughter nuclides in the analysed samples remains the largest source of error. This introduces a requirement to separate mineral phases, which concentrate parent and do not concentrate daughter nuclides, in order to minimise this error and take full advantage of the method. For the purpose of dating the processes associated with regolith formation, expected to be in the age range between several hundred m.y. and several k.y., this translates into a requirement of identifying mineral phases that concentrate U and that do not concentrate Th and Pb. In other words, precise dating of regolith materials will remain impossible until every detail of retention and migration mechanisms of these three elements in the regolith is well understood.

The level of current understanding of migration of U, Th and their daughters in the regolith is at best extremely uneven. The chemical behaviour of U and to the lesser degree of Th and Pb in solution is constrained with a comparatively high degree of detail (Chabaux *et al.* 2003 and references therein). Fractionation of these elements during weathering is largely controlled by the differences in their chemical properties, which are in turn determined by the classical thermodynamic parameters of aqueous solutions. Uranium thermodynamic data indicate that under surface conditions predominant species stable in the presence of H₂O are either in (IV) or (VI) oxidation states. Under the reducing conditions U(IV) is extremely insoluble and tends to precipitate as uraninite. Solubility increases, however, at low pH in the presence of fluoride by formation of fluoride complexes, and above pH 7-8 by formation of hydroxyl complexes. In oxidic conditions U(VI) is considerably more soluble in water as UO₂²⁺ and formation of complexes with carbonate, phosphate, fluoride, etc., increases its solubility even further. Th and Pb are only found in nature in tetravalent and divalent form respectively. Both are considered to be extremely insoluble. However, their mobility can be significantly enhanced by complexation with both inorganic and organic ligands. Described chemical properties of U, Th and Pb suggest that in general U is most soluble under surface conditions and that any precipitate from the water will be enriched in U relative to Th and Pb. This also means that any material formed by the deposition from surface or groundwaters is potentially datable by U-Th based methods. Our limited experience, however, very often contradicts this prediction. For example, results of opaline silica dating indicate that the opal veins formed from hydrothermal solutions related to volcanic activity (i.e., Nevada, USA and Mexico) have an expected high degree of enrichment in U relative to both Th and Pb. However, some Australian opals deposited from groundwater show significant proportions of common Pb. Thorium in these opals remains at the low level predicted by theory and therefore eliminating interpretation of higher Pb content as a result of mixing of silica with some other minerals such as clays. An explanation for this apparent decoupling of Th and Pb must therefore consider the potential physical-chemical conditions, such as pH or presence of certain anions in the groundwater, which favour preferential increased solubility of Pb.

In addition to the chemical behaviour of U, Th and Pb in solution, sorption of these elements onto mineral surfaces has to be considered, since it can become the limiting factor for the element mobility (Chabaux *et al.* 2003 and references therein). In general U sorption on Fe-oxides and silica gels is high. It is lower in clays, micas and opals. Illite and montmorillonite have higher retention of U than kaolinite. For Fe-oxides decreasing U retention is reported from amorphous Fe-oxyhydroxides to goethite and to haematite. Murphy *et al.* (1999) proposed that the crystallisation of amorphous Fe-hydroxides can result in a partial release of U. The pH of solution as well as the presence of organic and inorganic ligands has a strong influence on retention capacity of U by the minerals. Th adsorption on Fe-hydroxides is higher than that of U, although, it is also influenced by the composition and pH of the groundwater. A number of goethite samples tested at Curtin University for potential use in geochronology, showed U concentrations from several ppm to tens of

ppm, with Th content always several times higher than U. Manganese oxides often concentrate hundreds of parts per million of U, Th and Pb with the relative proportion of these elements being similar to those in goethite. These relationships can limit the usefulness of these minerals for dating, unless some 3D reconstructions (Ludwig 2003) can be applied to the analysed samples. This possibility has to be investigated in the future. In addition, the proposed U release during crystallisation of amorphous Fe-hydroxides, may prove to be significant for the geochronology of ferruginous parts of weathering profiles. A study of U migration near the U deposits (e.g., Jerden *et al.* 2003) suggests that U is accumulated as a phosphate at the boundaries of Fe and Mn-oxides and hydroxides. If this is proved to be a general feature of profiles away from U-deposits and a mechanism to retain U expelled from crystallising Fe-hydroxides, these phosphates can potentially be dated and the ages will reflect the transformation from amorphous to crystalline Fe-hydroxides.

Analysis of both successful applications and difficulties in the application of U-Th decay schemes in regolith chronology highlights the urgent necessity to investigate migration and fixation mechanisms of U, Th and Pb in the regolith profiles. The identification of U bearing minerals and their stability within the profiles would be the first priority of such investigation.

REFERENCES

- JERDEN J.L., SINHA A.K. & ZELAZNY L. 2003. Natural immobilisation of uranium by phosphate mineralisation in an oxidizing saprolite-soil profile: chemical weathering of Colies Hill uranium deposit, Virginia. *Chemical Geology* **199**, 129-157.
- CHABAUX F., RIOTTE J. & DEQUINCEY O. 2003. U-Th-Ra fractionation during weathering and river transport. *Reviews in Mineralogy* **52**, 533-576.
- LUDWIG K.R. 2003. Mathematical-statistical treatment of data and errors for $^{230}\text{Th}/\text{U}$ geochronology. *Reviews in Mineralogy* **52**, 631-656