

**DEVELOPMENT OF HIGH PRECISION  $^{238}\text{U}/^{235}\text{U}$  RATIO MEASUREMENTS FOR COSMOCHEMICAL APPLICATIONS.** F. Tissot<sup>1</sup>, N. Dauphas<sup>1</sup>, <sup>1</sup>Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL (ftissot@uchicago.edu).

**Introduction:** Observations of variations in the  $^{238}\text{U}/^{235}\text{U}$  ratio at the 0.1 % level in both terrestrial [1] and meteoritic samples [e.g. 2-5], challenged the assumption of a constant  $^{238}\text{U}/^{235}\text{U}$  ratio throughout the solar system (SS). The light isotopic compositions measured in some CAIs could be due to the presence of live  $^{247}\text{Cm}$  in the early SS as this short-lived radionuclide decays into  $^{235}\text{U}$  with a half-life  $t_{1/2}=15.6$  Myr. The most immediate consequence of these variations is that the isotopic composition of uranium has to be measured in each CAI to get accurate Pb-Pb ages [5,6]. Given the scale of the variations, achieving high precision measurements is necessary to fully resolve compositional differences between samples and to be able to use the potential of the U isotopic system in terrestrial and extraterrestrial samples.

**Column chemistry:** Extraction from the matrix elements and purification of U is done using the U/Teva resin® (Eichrom). Distribution coefficients of the resin as a function of molarity have been measured for U and fifteen other elements (Na, Mg, Al, Ca, Sc, Ti, Fe, Ni, Y, Zr, Sn, La, Yb, Hf and Th) with three acids ( $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{HCl} + 0.1$  M Oxalic acid) (Fig. 1). Horwitz et al. [7] had previously documented distribution coefficients on U/Teva in  $\text{HNO}_3$  and  $\text{HCl}$  medium. Although the results of the two studies are very similar, in detail there are differences that may be due to the fact that [7] utilized multi-element stock solutions directly, possibly containing trace HF, while here all standards were converted to  $\text{HNO}_3$ ,  $\text{HCl}$  or  $\text{HCl} + \text{Oxalic acid}$  prior to use. The elution procedure is adapted from [1] and briefly summarized hereafter. The resin is cleaned with 20 ml of 0.05 M  $\text{HCl}$ . It is then conditioned with 6 ml of 3 M  $\text{HNO}_3$ . The sample is loaded in 3 M  $\text{HNO}_3$  and most elements except Th and U are removed with 40 ml of 3 M  $\text{HNO}_3$ . The resin is then converted to  $\text{HCl}$  with 6 ml of 11 M  $\text{HCl}$ . Thorium is eluted in 20 ml of 5 M  $\text{HCl} + 0.1$  M Oxalic acid. Finally, the resin is rinsed of the oxalic acid with 10 ml of 5 M  $\text{HCl}$  before elution of U in 25 ml of 0.05 M  $\text{HCl}$ . This procedure is done twice to ensure complete purification of the sample. More than 99% of the U is recovered during the last step.

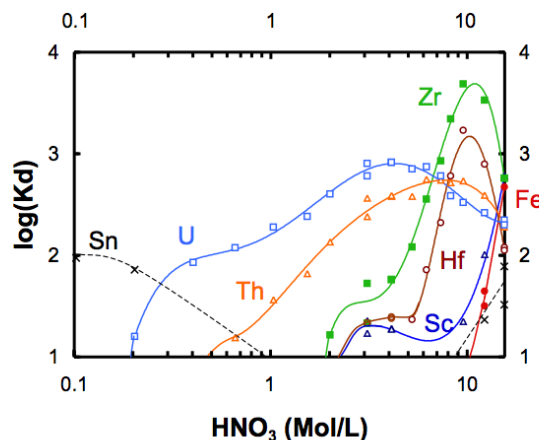


Fig. 1. Distribution coefficients ( $K_d$ ) of selected elements on U/Teva resin in logarithmic scale as a function of molarity in  $\text{HNO}_3$ .

**Methods:** Measurements were performed on a ThermoFinnigan Neptune MC-ICP-MS at the Origins Lab of the University of Chicago using an Aridus desolvating nebulizer. Mass fractionation during chemistry and spectrometry was quantified and corrected for using a  $^{233}\text{U}/^{236}\text{U}$  double spike (IRMM-3636, containing ~49.51 % of  $^{236}\text{U}$  and ~50.46 % of  $^{233}\text{U}$ ). A further correction was applied by bracketing samples with standard measurements. The procedural blank was generally below 0.01 % of the signal measured. Tailing of  $^{238}\text{U}$  on  $^{236}\text{U}$  was estimated to be  $0.6 \pm 0.1$  ppm and was corrected for. This value agrees with the value of 0.5 ppm reported by [1].

To ensure measurement accuracy and precision, various geostandards were analyzed: granites GA and AC-E, basalts BCR-2 and BE-N, and shale SGR-1b. Digestion was done on ~100 mg for granites and shale and ~300 mg for basalts. Two 24 h attacks in  $\text{HF}/\text{HNO}_3$  2:1 on hot plates were followed by a 5 days  $\text{HF}/\text{HNO}_3$  2:1 Parr Bomb step for granites to dissolve refractory phases such as zircons. The basalts and a shale were subjected to two 24 h Aqua Regia ( $\text{HCl}/\text{HNO}_3$  2:1) steps on hot plate instead. Samples were then entirely dried down before being taken back in concentrated  $\text{HNO}_3$  and put back on hot plate for 24 h, before dilution to 3 M  $\text{HNO}_3$ . All samples were double-spiked prior to digestion using the  $^{233}\text{U}/^{236}\text{U}$  spike IRMM-3636. The amount of spike added is so that the ratio  $U_{\text{spike}}/U_{\text{sample}}$  is ~3% for each sample. The procedural blank was estimated to represent 0.03 ng U.

All values are reported in  $\delta^{238}\text{U} = \left[ \frac{(^{238}\text{U}/^{235}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{235}\text{U})_{\text{CRM-112a}}} - 1 \right] \times 10^3$ .

### Results and Discussion:

The measured isotopic compositions relative to CRM-112a are: -0.26‰ for AC-E, -0.25‰ for GA, -0.30‰ for BE-N, -0.23‰ for BCR-2 and -0.17‰ for SGR-1b. Uncertainty on the measurements is  $\pm 0.04$  ‰ and is evaluated by examining the dispersion of bracketing standard measurements. These results are shown in Fig. 2. Some samples were also measured by [1] and there is good agreement on the  $\delta^{238}\text{U}$  values between the two studies. Igneous rocks show little variations with an isotopic  $^{238}\text{U}/^{235}\text{U} \sim 0.15$  ‰ above the one of seawater (from [1]), while the measured shale has an isotopic composition  $\sim 0.24$  ‰ heavier than seawater.

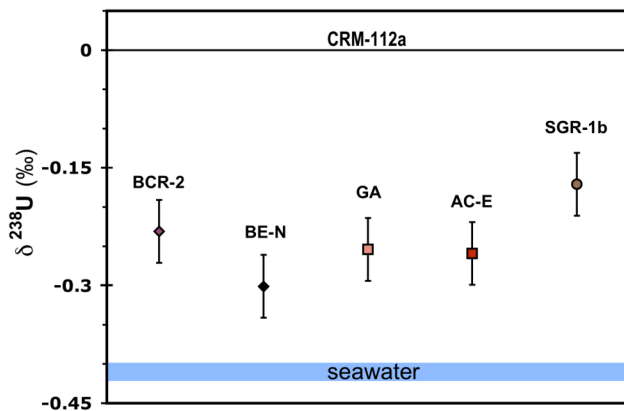


Fig. 2. Isotopic compositions of five geostandards.  $\delta^{238}\text{U}=0$  is relative to CRM-112a U standard. The blue line represents the seawater composition reported by [1].

**References:** [1] Weyer, S. et al (2008) *GCA*, 72, 345-359. [2] Stirling, C.H. et al (2005) *GCA*, 69, 1059-1071. [3] Stirling, C.H. et al (2006) *EPSL*, 251, 386-397. [4] Brennecka, G.A. et al (2010) *Science*, 327, 449-451. [5] Amelin, Y. et al (2010) *EPSL*, 300, 343-350. [6] Bouvier, A. and Wadhwa, M. (2010) *Nature Geosci.*, 3, 637-641. [7] Horwitz, E.P. et al (1992) *ACA*, 266, 25-37.