

**$^{238}\text{U}/^{235}\text{U}$  RATIOS OF ANAGRAMS: ANGRITES AND GRANITES.** F.L.H. Tissot<sup>1</sup> and 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:** Significant  $^{238}\text{U}/^{235}\text{U}$  variations have been documented in meteoritic [e.g. 1-4] and terrestrial [5] samples, which can affect Pb-Pb ages. In most cases, the cause of these variations is not understood. Here, we report an extensive study of the U isotopic composition of planetary crustal rocks. Determination of  $^{238}\text{U}/^{235}\text{U}$  ratio in angrites is critical to establish their age: an important anchor in early solar system chronology [6,7]. The extent to which the protolith of terrestrial granites affects their U isotopic composition is unknown. We report high-precision U isotope measurements of angrites and terrestrial granites to address these two outstanding questions in solar system chronology and crustal differentiation.

**Sample preparation and methods:** U separation and purification was conducted on U/Teva specific resin (Eichrom®) following the procedure detailed in [8]. Each sample was subjected to the procedure twice to ensure complete purification.

Measurements were performed on a ThermoFinnigan Neptune MC-ICP-MS at the Origins Lab of the University of Chicago using an Aridus II desolvating nebulizer. Enhanced signal stability was achieved by placing a spray chamber between the Aridus II and the ICPMS. Quantification and correction of mass fractionation occurring during chemical separation and mass spectrometry was done 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 below 0.01 % of the signal measured. Tailing of the major  $^{238}\text{U}$  beam onto  $^{236}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$  was estimated to be, respectively, 0.6 ppm, 0.25 ppm and 0.1 ppm and was corrected for. Tailing on  $^{235}\text{U}$  was found to have virtually no influence on the results, unlike tailing on  $^{236}\text{U}$  and  $^{234}\text{U}$ .

All samples (except the angrites) were double-spiked prior to digestion using IRMM-3636. Spiking after digestion, but before column chemistry, was found to have no effect on the results. The amount of spike added is such that the ratio  $U_{\text{spike}}/U_{\text{sample}}$  is ~3 % for each sample. The procedural blank was estimated to represent 0.02-0.05 ng U. When not given as absolute values, ratios are reported in  $\delta^{238}\text{U}$  relative to the U standard CRM-112a (also named SRM960, NBL112-a or CRM-145).

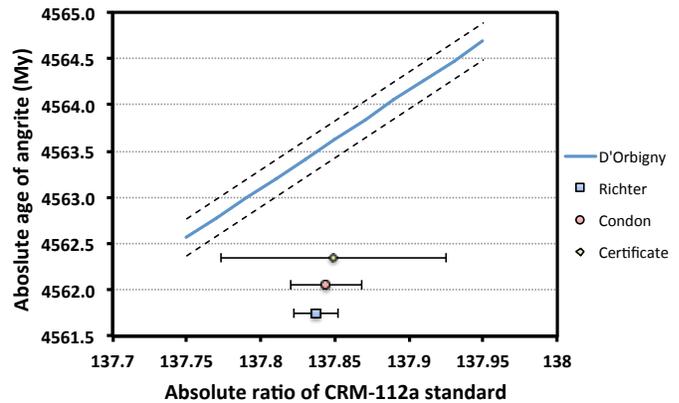
$$\delta^{238}\text{U} = \left[ \left( \frac{^{238}\text{U}/^{235}\text{U}}{\text{sample}} \right) / \left( \frac{^{238}\text{U}/^{235}\text{U}}{\text{CRM-112a}} \right) - 1 \right] \times 10^3.$$

**Results and Discussion:** Uncertainties on the measurements are evaluated by examining the dispersion of bracketing standard measurements and is ±

0.03-0.06 ‰ ( $2\sigma$ ) depending on the session during which the samples were analyzed.

#### 1) Angrites:

A problem that arises when converting  $\delta^{238}\text{U}$  values into absolute ratios is the choice of the ratio of the U standard CRM-112a. References [9], [10] and the New Brunswick Certificate report three different values (identical within error bars), respectively,  $137.837 \pm 0.015$ ,  $137.844 \pm 0.024$  and  $137.849 \pm 0.076$  ( $2\sigma$ ). For the sake of comparison, we use the value from [9], previously used by [6]. Using the highest value instead of the lowest one will increase all absolute ages by 0.13 My: ~1/2 of the uncertainty ( $2\sigma$ ) reported herein. See Fig 1.



**Fig. 1.** Age of the angrite D'Orbigny as a function of the assumed absolute ratio of the standard CRM-112a. The three dots represent the values recommended by (from bottom to top) references [9], [10] and New Brunswick Certificate.

Figure 2 shows the measured  $^{238}\text{U}/^{235}\text{U}$  isotopic ratios of five angrites, corresponding to a global average of  $137.775 \pm 0.024$  ( $2\sigma$ ). This is in very good agreement with the value of  $137.776 \pm 0.026$  reported by [7] in the same samples.

Using a  $^{238}\text{U}/^{235}\text{U}$  ratio of 137.837 for CRM-112a, we obtained a corrected Pb-Pb age of  $4563.49 \pm 0.20$  My ( $2\sigma$ ) for D'Orbigny (in good agreement with the age reported by [7]), and  $4566.44 \pm 0.30$  My ( $2\sigma$ ) for AdoR. The non corrected ages were taken from [11]. Note that the uncertainty does not include uncertainties on the certified value of the standard as in early solar system chronology, one is most often interested in relative ages rather than absolute ages.

The angrites analyzed here were U elution cuts recovered from a previous column chemistry meant to

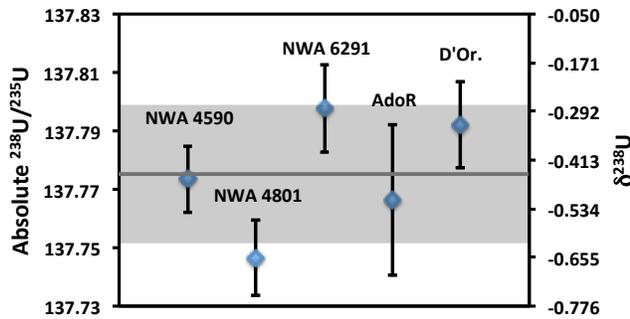


Fig. 2. U isotopic ratio of five angrites.  $\delta^{238}\text{U}$  values (left axis) are relative to CRM-112a. Absolute values (right axis) assume a ratio of 137.837 for CRM-112a (from [8]). The grey line represents the average ratio of the five samples and the shaded area the associated uncertainty.

purify Fe. It is possible that some fractionation and/or loss of U occurred during the chemistry. Work is currently under way to analyze samples prepared from rock powder.

## 2) Geostandards and Lachlan Fold Belt granites:

### a) Sample digestion

Sample mass varied from 3 mg to 1.6 g. All samples were treated with two 24 h attacks in HF/HNO<sub>3</sub> 2:1 followed by two 24 h attacks in aqua regia (HCl/HNO<sub>3</sub> 2:1) on hot plates. Between the two steps, all granites and geostandards susceptible of hosting chemically resistant phases were placed in Parr Bombs for 5 days in HF/HNO<sub>3</sub> 2:1 at 180 °C, to ensure complete dissolution of these phases. Samples were then dried down and taken back in concentrated HNO<sub>3</sub> and put back on hot plate for 24 h, before dilution to 3 M HNO<sub>3</sub>.

### b) Geostandards

A large range of geostandards were analyzed, covering most of Earth rocktypes (e.g., basalts, andesites, granites, coals, shales, seawater, individual minerals).

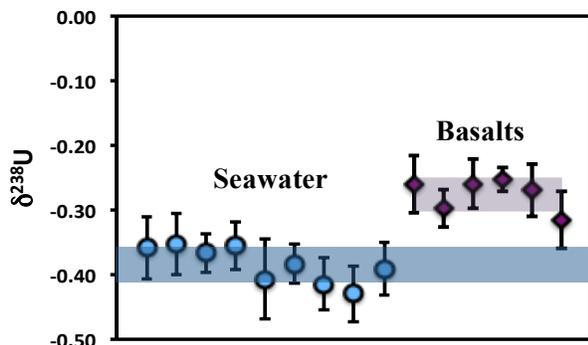


Fig. 3. Isotopic compositions of some geostandards.  $\delta^{238}\text{U}=0$  is relative to CRM-112a. The blue line represents the average seawater composition, and the purple line the average composition of basalts. Basalts samples from left to right: Arhco-1, BE-N, BCR-1, BCR-2 spiked before digestion, BCR-2 spiked after digestion, BHVO-2.

When comparison to literature was possible [5,12], good agreement was found. From these measurements we recommend average values of  $-0.385 \pm 0.024$  ‰ for seawater,  $-0.276 \pm 0.024$  ‰ for basalts (Fig 3.),  $-0.303 \pm 0.032$  ‰ for granites, and  $-0.286 \pm 0.020$  ‰ for igneous rocks in general. All values are given relative to CRM-112a.

### c) Lachlan Fold Belt granites

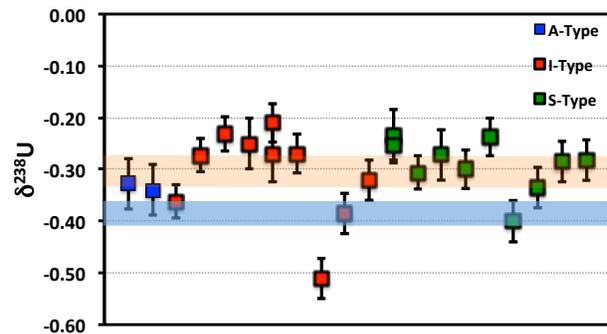


Fig. 4. Isotopic compositions of Lachlan Fold Belt granites.  $\delta^{238}\text{U}=0$  is relative to CRM-112a U standard. The blue line represents the seawater composition and the orange line the average granitic composition.

Lachlan Fold Belt granites were chosen as they were used to define the two types of granites: I-type and S-type [13, 14]. I stands for “igneous” or “intra-crustal” origin of the protolith rock and S for “sedimentary” or “supracrustal”. Distinction between the two types is made based on various chemical, petrographic and isotopic parameters (e.g. ASI,  $\delta^{18}\text{O}$ , ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ). Despite differences in their source rock, no significant variations in the  $^{238}\text{U}/^{235}\text{U}$  isotopic composition are observed between I-type and S-type granites.

**References:** [1] Stirling, C.H. et al (2005) *GCA*, 69, 1059-1071. [2] Stirling, C.H. et al (2006) *EPSL*, 251, 386-397. [3] Brennecka, G.A. et al (2010) *Science*, 327, 449-451. [4] Amelin, Y. et al (2010) *EPSL*, 300, 343-350. [5] Weyer, S. et al (2008) *GCA*, 72, 345-359. [6] Kaltenbach, A. et al (2011) *Goldschmidt Conf. Abst.* [7] Brennecka, G.A. et al (2011) *Goldschmidt Conf. Abst.* [8] Tissot, F. et al (2011) LPSC # 1082. [9] Richter, S. et al (2010) *Int. J. Mass. Spec.* 295, 94-97. [10] Condon, D.J. et al (2010) *GCA*, 74, 7127-7143. [11] Amelin, Y. (2008) *GCA*, 72, 221-232. [12] Stirling, C.H. et al (2007) *EPSL* 264, 208-225. [13] Chappell, B.W. et al (1974) *Pacific Geol.*, 8, 173-174. [14] Chappell, B.W. et al (2001) *Austr. J. Earth Sci.*, 48, 489-499