

**ON THE  $^{238}\text{U}/^{235}\text{U}$  PALEOREDOX PROXY: A WORD OF CAUTION WITH BLACK SHALES AND THE NEED FOR SEQUENTIAL LEACHING OF CARBONATES.** F. L. H Tissot<sup>1</sup>, B. M. Go<sup>1</sup>, N. Dauphas<sup>1</sup>, D. Asael<sup>2</sup>, C. T. Reinhard<sup>3,4</sup>, O. Rouxel<sup>5</sup>, T. W. Lyons<sup>4</sup>, E. Ponzevera<sup>5</sup>, C. Liorzou<sup>6</sup> and S. Chéron<sup>5</sup>, <sup>1</sup>Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago, IL ([ftissot@uchicago.edu](mailto:ftissot@uchicago.edu)), <sup>2</sup>Department of Geology, Université de Liège, <sup>3</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, <sup>4</sup>Department of Earth Sciences, University of California, Riverside, CA, <sup>5</sup>IFREMER, Centre de Brest, Plouzané, France, <sup>6</sup>Université de Brest, IUEM, Plouzané, France

### Introduction:

In the past several years, there has been a growing interest in the emerging U stable isotope systematic as it could prove a useful tracer of the redox state of the global ocean through time. However, important questions remain to be addressed before the full potential of this proxy can be exploited. In this abstract we show 1) how detrital contamination can be dealt with to avoid data misinterpretation, and 2) that bulk carbonates can record the  $\delta^{238}\text{U}$  value of the seawater they form from.

### Background:

The sub-permil variations observed in the  $^{238}\text{U}/^{235}\text{U}$  ratio of sediments deposited under different redox conditions [1, 2] are best explained as being a result of the Nuclear Field Shift effect [3]: a volume-dependent shift that leads to a preferential incorporation of the heavy isotope of U ( $^{238}\text{U}$ ) into reduced sediments (*e.g.* black shales). In the modern ocean U occurs mostly in two valence states: soluble  $\text{U}^{\text{VI}}$  and insoluble  $\text{U}^{\text{IV}}$ . Because U has a long residence time in the modern ocean (~400 kyr, [4]) and behaves conservatively, it is homogeneously distributed in the ocean both in concentration and in isotopic composition. Lastly, U in the ocean has one main source: the riverine input, and three main sinks: carbonates and anoxic and suboxic sediments. Incorporation of U in anoxic sediment is accompanied by a strong isotopic fractionation relative to seawater  $\Delta\text{U}_{\text{Sw-Anox}} \approx -0.5\text{‰}$ , whereas for suboxic sediments  $\Delta\text{U}_{\text{Sw-Sub}} \approx -0.2\text{‰}$  [2]. Carbonates seem to record directly the seawater U isotopic composition [2, 5]. Knowledge of the seawater isotopic composition at a given time can thus be interpreted in terms of extent of anoxia in the ocean using a simple two or three end-member model [6, 7].

One major inconvenience with using a sediment to assess the seawater U isotopic composition is that one has to assume a constant fractionation  $\Delta\text{U}_{\text{Sw-Sediment}}$ , an assumption that may not always be warranted. Though some recent effort has been done in this direction on a variety of modern surface carbonates [5], the precision of the measurements was relatively poor, and those results need confirmation. Furthermore, Romaniello *et al.* showed that in the first 60 cm below the seawater-sediment interface, some remobilization of U occurs, leading to a potential fractionation of the stable isotop-

ic composition eventually recorded in the sediment. Finally, for all samples, detrital contamination is a crucial concern that needs to be dealt with properly, as we show below.

### Case Study – The Paleoproterozoic Shunga Event and detrital contamination:

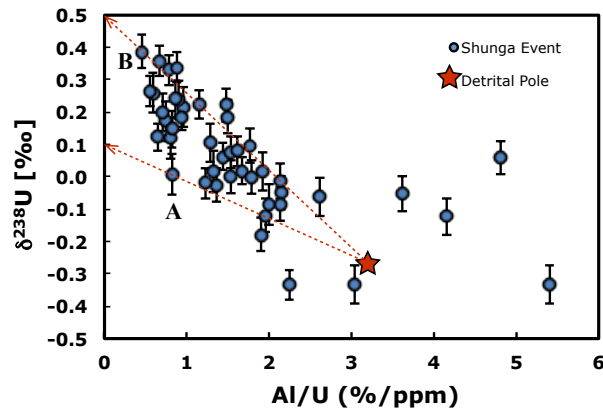
During the Great Oxidation Event (GOE – 2.4 to 2.0 Ga), atmospheric oxygen levels rose from Archean values of *ca.*  $10^{-5}$  the present atmospheric level (PAL) to  $\sim 10^{-2}$  to  $10^{-1}$  PAL by the mid-late Proterozoic. Of particular interest in this time period is the Lomagundi-Jatuli Event – the largest positive carbon isotope excursion in Earth's history (2.3–2.1 Ga) – which is associated with global burial of organic matter and release of oxygen to the atmosphere [8]. To understand the response of the global Paleoproterozoic ocean to the rise of atmospheric oxygen, we studied the Shunga Event that directly follows the Lomagundi-Jatuli Event. The formation in which the U proxy was studied (Zaonega Formation from the Onega Basin, ~2.06 Ga), is composed mainly of organic-rich shale, organo-siliceous rocks and mafic lavas and gabbro sills and also contains a petrified oil reservoir. Details of the sample preparation and U isotopic analysis can be found in [9].

XRD data show a high detrital content in all the samples. The  $\delta^{238}\text{U}$  was also found to be correlated with Al/U ratios (Fig.1). These observations indicate a mixing relationship between a low  $\delta^{238}\text{U}$  detrital endmember and a high  $\delta^{238}\text{U}$  authigenic endmember. A correction for the detrital component in the samples was thus made by extrapolating the isotopic composition at Al/U = 0 (*i.e.*, no detrital influence) using the following equation,

$$\delta^{238}\text{U}_{\text{authigenic}} = \delta^{238}\text{U} - \left(\frac{\text{Al}}{\text{U}}\right) \times \left( \frac{\delta^{238}\text{U}_{\text{det}} - \delta^{238}\text{U}}{\left(\frac{\text{Al}}{\text{U}}\right)_{\text{det}} - \left(\frac{\text{Al}}{\text{U}}\right)} \right)$$

where the *det* stands for detrital. The detrital endmember was obtained by averaging basalt and granite geo-standards measured at the Origins Lab [10] and led to  $\delta^{238}\text{U}_{\text{det}} = -0.267\text{‰}$  and  $(\text{Al}/\text{U})_{\text{det}} = 3.19$  (geometric mean of the basalts and granites Al/U ratios). Note, all values are reported in  $\delta^{238}\text{U} = [({}^{238}\text{U}/{}^{235}\text{U})_{\text{sample}}/({}^{238}\text{U}/{}^{235}\text{U})_{\text{CRM-112a}} - 1] \times 10^3$ .

The average  $\delta^{238}\text{U}$  value before and after correction is, respectively,  $0.07 \pm 0.18\text{‰}$  and  $0.35 \pm 0.22\text{‰}$ . This correction corresponds to a difference of inferred global anoxia of  $45 \pm 15\%$ . Though an additional complexity, detrital contamination can be dealt with by combining U isotope ratios with chemical data.



**Fig. 1.**  $\delta^{238}\text{U}$  vs. Al/U ratios. The data shows a mixing relationship between a detrital endmember (star symbol) and an authigenic endmember. The red arrows show the correction for sample A and B. Figure modified from [10].

#### Sequential leaching of carbonates:

In the modern ocean U is present dominantly as the uranyl carbonate ion  $\text{U}^{\text{VI}}\text{O}_2(\text{CO}_3)_3^{4-}$ , which is readily incorporated into both calcite and aragonite. As such, and unlike black shales, carbonates should and seem to record directly the U isotopic composition of the seawater they formed from, albeit with a possible shift [5]. However, given the usually low concentration of U in carbonates ( $\sim 2$  ppm for aragonite,  $\sim 0.3$  ppm for calcite), a large mass of sample (0.05 to 2g) will be needed to make a precise enough isotopic measurement. Obtaining such masses of pristine carbonates (*i.e.*, non altered, non metamorphosed) can become a challenge. For instance, [11] showed that, in the case of radiogenic Sr analyses, bulk rock values differ significantly from *in-situ* analyses. Using a step leaching approach they showed specifically that a strong contamination was introduced by 1) non-authigenic Sr adsorbed on the surface of the carbonates and 2) Sr enclosed in non carbonate residuum. We followed a similar approach for U.

In a centrifuge tube, we digested a total of 2 g of a modern coral from Florida ([U]  $\sim 1.96$  ppm), using dilute acetic acid and increment steps of 200 mg digestion (*i.e.*, 10% of the total mass). To speed up the digestion, the tube was placed on a vortex shaker. Digestion was considered complete when bubble formation stopped, in usually less than 24 hours. After each 10 % digestion step, the tube was centrifuged for 5 min and

the supernate was collected. Attention was paid to not collect any particles during the supernate extraction. After the nominal full carbonate digestion, a residue of less than 3 % of the total starting mass was left undigested by this protocol, containing less than 0.5 % of the total U of the sample. Each supernate cut was dried down and taken back into 3 M  $\text{HNO}_3$  before being processed through the typical U purification protocol in place at the Origins Lab on U/Teva resin [10, 12]. Isotopic analyses were performed on a Thermo Neptune MC-ICP-MS, with an OnTool Booster 150 Jet pump (Pfeiffer), using a combination of Aridus-II desolvating nebulizer and a spray chamber for improved stability of the signal. The signal intensity was  $\sim 1$  V/ppb with a flow rate of  $\sim 100$  ml/min. Mass fractionation during sample preparation and spectrometry was corrected for using the IRMM-3636  $^{233}\text{U}/^{236}\text{U}$  double spike. Routine additional corrections were made: sample-standard bracketing, tailing of  $^{238}\text{U}$  onto  $^{236}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$  and on peak zero. The procedural blank was estimated to be 0.15 ng U.

The experiment was conducted twice. In the second iteration the coral powder was precleaned in Milli-Q water and in ammonium acetate 1 M, 24 h each time.

The amount of U recovered in each step differs from what was expected given the bulk U concentration of the coral. The first and last phases to be attacked by the acid are indeed depleted in U while the intermediate leachates show higher than bulk concentrations. Similarly, the isotopic composition of the U collected in each step is not constant and can differ from the  $\delta^{238}\text{U}$  of modern seawater by up to 0.2 ‰. Precleaning was found to have no effect on the results.

For future work applying the U paleoredox proxy on carbonate rocks, we thus recommend a step digestion protocol in order to access the isotopic composition of the seawater in which the samples formed.

**References:** [1] Stirling, C.H. et al (2007) *EPSL* 264, 208-225. [2] Weyer, S. et al (2008) *GCA*, 72, 345-359. [3] Abe, M. et al (2008) *J. or Chem. Physics*, 129, 164309. [4] Dunk, R.M. et al (2002) *Chem. Geol.*, 190, 45-67 [5] Romaniello, S.J. et al (2013) *Chem. Geol.*, 362, 305-316. [6] Montoya-Pino, C. et al (2010) *Geology*, 38, 315-318. [7] Brennecka, G.A. et al (2011) *PNAS*, 108, 17631-17634. [8] Melezhik, V.A. et al (1999) *Earth Sci. Rev.*, 48, 71-120 [9] Asael, D. et al (2013) *Chem. Geol.*, 362, 193-210. [10] Tissot, F.L.H et al (2012) *LPCS XLIII*, 1981. [11] Bailey, T.R. et al (2000) *Chem. Geol.*, 167, 313-319. [12] Telus, M. et al (2012) *GCA* 97, 247-265.