

# APPLICATION OF URANIUM ISOTOPES TO GRADE OF A DEPOSIT

Y. Uvarova<sup>1</sup>, K. Kyser<sup>2</sup>, M. Lahd Geagea<sup>2</sup>, D. Chipley<sup>2</sup>

<sup>1</sup>CSIRO Mineral Resources Flagship, 26 Dick Perry Avenue, Kensington, WA, Australia 6151

<sup>2</sup>Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

## Introduction

It was predicted by Bigeleisen (1996) that uranium isotopes fractionate as a result of nuclear-field shift, which is a consequence of the difference in nuclear sizes and shapes of isotopes. Thus, <sup>235</sup>U with an odd number of neutrons has a smaller nucleus relative to nuclei with an even number of neutrons such as those of <sup>238</sup>U, and this results in different bond strengths, with <sup>238</sup>U preferentially incorporated into the more condensed, solid phase. Schauble (2007) confirmed the theoretical calculations and suggested that the nuclear-field shift results in <sup>238</sup>U/<sup>235</sup>U ratios that vary as a function of uranium oxidation state, with the highest <sup>238</sup>U/<sup>235</sup>U ratio in more reduced species. Recent investigations of natural terrestrial and extraterrestrial samples have shown variations in <sup>238</sup>U/<sup>235</sup>U ratios of ~5.5‰ and 3.5‰, respectively, commonly with more reduced hosts having higher ratios. Generally, media show <sup>238</sup>U/<sup>235</sup>U ratios increasing in the following order: CAIs (calcium-aluminium-rich inclusions) in meteorites < manganese nodules and banded iron formations (BIFs) < average chondrites < ocean water and corals < basalts and granites < suboxic margin sediments < black shales (Stirling et al. 2005; Stirling et al. 2007; Weyer et al. 2008; Brennecka et al. 2010a; Brennecka et al. 2010b; Montoya-Pino et al. 2010; Amelin et al. 2010; Bouvier et al. 2011; Tissot & Dauphas 2011; Tissot & Dauphas 2012; Telus et al. 2012; Brennecka et al. 2012; Connelly et al. 2012; Hiess et al. 2012; Goldmann et al. 2013).

Realisation that there were potential variations in the uranium isotope ratios in various media prompted studies of <sup>238</sup>U/<sup>235</sup>U ratios in uranium deposits. Bopp et al. (2009) reported that <sup>238</sup>U/<sup>235</sup>U values in sandstone-type uranium ores are higher than magmatic-related uranium ores by ~0.8‰. Similar results were reported by Brennecka et al. (2010a) for uranium ore concentrates, with sandstone-type, low-temperature deposits enriched in <sup>238</sup>U by ~0.4‰ relative to high-temperature magmatic-related deposits. Both studies relate the observed isotopic difference to the nuclear-field effect, which in turn, is temperature-dependent (Bopp et al. 2009; Brennecka et al. 2010a).

We investigated the uranium isotopic compositions of natural ores from various uranium deposit types to better understand (1) the primary mechanisms for

fractionation of  $^{234}\text{U}$  and  $^{235}\text{U}$  isotopes with respect to  $^{238}\text{U}$ , (2) the relations between the observed variations in isotope ratios and source of uranium, processes of uranium mobilisation and transport, the mechanism of uranium capture and post-depositional fluid alteration of both ore and source rocks for all of the major types of uranium deposits. Here, we propose that U isotopes can be used in exploration for uranium deposits and even estimation of their grade.

## Methodology

An aliquot of 0.02 to 0.05 g of a sample is weighed and dissolved in 1 mL of concentrated  $\text{HNO}_3$  at  $130^\circ\text{C}$  for at least 24h. The resulting solutions were evaporated to dryness and dissolved in 1.5 M  $\text{HNO}_3$ . An aliquot containing approximately 130  $\mu\text{g}$  of uranium is loaded on an ion exchange column of 0.5 mL TRU Spec, 100-200 mesh (Eichrom Technologies Inc.), and U is eluted using the procedure of Pin & Zalduegui (1997). The purified uranium solution is evaporated to dryness, redissolved in concentrated  $\text{HNO}_3$  at  $180^\circ\text{C}$  to remove residual column material, dried and dissolved in 2%  $\text{HNO}_3$  for measurement of the uranium isotope ratios by MC-ICP-MS.

Uranium isotope ratios are measured with a Thermo Finnigan Neptune MC-ICP-MS at the Queen's Facility for Isotope Research, Queen's University, Canada. An APEX and Spiro (ESI) desolvating system with a 100 $\mu\text{l}/\text{min}$  PFA nebulizer (ESI) are used for sample introduction to minimize hydride interferences. All samples and standard solutions are prepared using 2%  $\text{HNO}_3$  for solution aspiration and an acid wash between measurements is 3%  $\text{HCl}$  followed by 2%  $\text{HNO}_3$ . Amplifier gain calibrations and baselines are performed before each analytical session. Additionally, because the SEM is used for measurement of  $^{234}\text{U}$ , the plateau voltage, yield and dark noise are determined daily.

Uranium isotope ratios are determined relative to NBL CRM 129-A (New Brunswick Laboratory, U.S. Department of Energy), and calculated first in delta notation using the following equations:

$$\delta^{238}\text{U}(\text{‰}) = \frac{[^{238}\text{U}/^{235}\text{U}_{\text{sample}}] - [^{238}\text{U}/^{235}\text{U}_{\text{standard}}]}{[^{238}\text{U}/^{235}\text{U}_{\text{standard}}]} \times 1000 \quad (1)$$

$$\delta^{234}\text{U}(\text{‰}) = \frac{[^{234}\text{U}/^{238}\text{U}_{\text{sample}}] - [^{234}\text{U}/^{238}\text{U}_{\text{standard}}]}{[^{234}\text{U}/^{238}\text{U}_{\text{standard}}]} \times 1000 \quad (2)$$

The values are recalculated to CRM 112-A using the  $\delta$  value of  $-0.89\text{‰}$  between the CRM 129-A and CRM 112-A. A certified ratio of 137.837 for  $^{238}\text{U}/^{235}\text{U}$  in CRM 112-A is used in all calculations (Richter et al. 2010). The  $\delta^{234}\text{U}$  values are calculated relative to secular equilibrium using the  $\delta^{234}\text{U}$  value of  $-29\text{‰}$  between CRM 129-A and the secular equilibrium and the  $^{234}\text{U}/^{238}\text{U}$  ratio of 0.000054970 (Cheng et al. 2013).

A double-spiking procedure using an IRMM-3636  $^{233}\text{U}$ - $^{236}\text{U}$  spike is applied to internally correct for instrumental mass bias. Accuracy, precision and contamination are monitored throughout preparation and measurement using various in-house ( $\text{UO}_2$  uraninite standard,  $\text{UO}_2$  solution standard, and SPEX U standard) and certified standards (CRM 129-A and CRM U0002) and procedure blanks. Each group of thirteen samples is accompanied by a procedure blank, preparation and analysis of an in-house standard  $\text{UO}_2$ -653, a uraninite from the McArthur River uranium deposit, Athabasca Basin, and an in-house stock solution  $\text{UO}_2$ -sol.-std prepared from the solid uraninite.

## Results

The  $\delta^{238}\text{U}$  and  $\delta^{234}\text{U}$  values for uranium minerals have a range of  $\sim 1.8\text{‰}$  ( $-0.30$  to  $1.52\text{‰}$ ) and of  $\sim 600\text{‰}$  (from  $-292$  to  $281\text{‰}$ ), respectively. Based on  $\delta^{238}\text{U}$  values, U deposits studied here can be divided into two distinct groups. One group has the lower  $\delta^{238}\text{U}$  values of ca.  $0.1\text{‰}$  and includes quartz-pebble conglomerate, calcrete, volcanic-associated, magmatic-related and metasomatic-related (Figure 1). A second group has higher  $\delta^{238}\text{U}$  values of ca.  $0.4\text{‰}$  and includes sandstone-hosted, vein-type, most unconformity-type and most types of mineralisation in the Beaverlodge area (Figure 1).

$\delta^{234}\text{U}$  values may or may not be at secular equilibrium. Negative  $\delta^{234}\text{U}$  values indicate only that U has been removed from the sample during the past 2.5 Ma. Positive  $\delta^{234}\text{U}$  values indicate that U has been removed from an external source or another area of the U deposit, and added to the sampled portion during the past 2.5 Ma. Further inferences from  $\delta^{234}\text{U}$  values would require knowledge of the original  $\delta^{234}\text{U}$  value of the fluid.

## Discussion

Different mechanisms are responsible for fractionation of  $^{235}\text{U}$  and  $^{234}\text{U}$  isotopes with respect to  $^{238}\text{U}$  (Uvarova et al. 2014). In contrast to  $^{234}\text{U}/^{238}\text{U}$  values that reflect recent aqueous alteration (Cheng et al. 2000),  $^{238}\text{U}/^{235}\text{U}$  values show fractionation that occurred during formation and subsequent alteration of mineralisation.

Uranium occurs naturally in two main oxidation states, generally  $\text{U}^{4+}$  as reduced insoluble species and  $\text{U}^{6+}$  as oxidised mineral or mobile species. A significant difference of  $1\text{‰}$  in  $^{238}\text{U}/^{235}\text{U}$  values between oxidised Mn crusts ( $-0.6\text{‰}$ ) and reduced black shales ( $0.4\text{‰}$ ) suggests that redox plays an important role in fractionation of  $^{238}\text{U}$  and  $^{235}\text{U}$  (Weyer et al. 2008; Montoya-Pino et al. 2010).

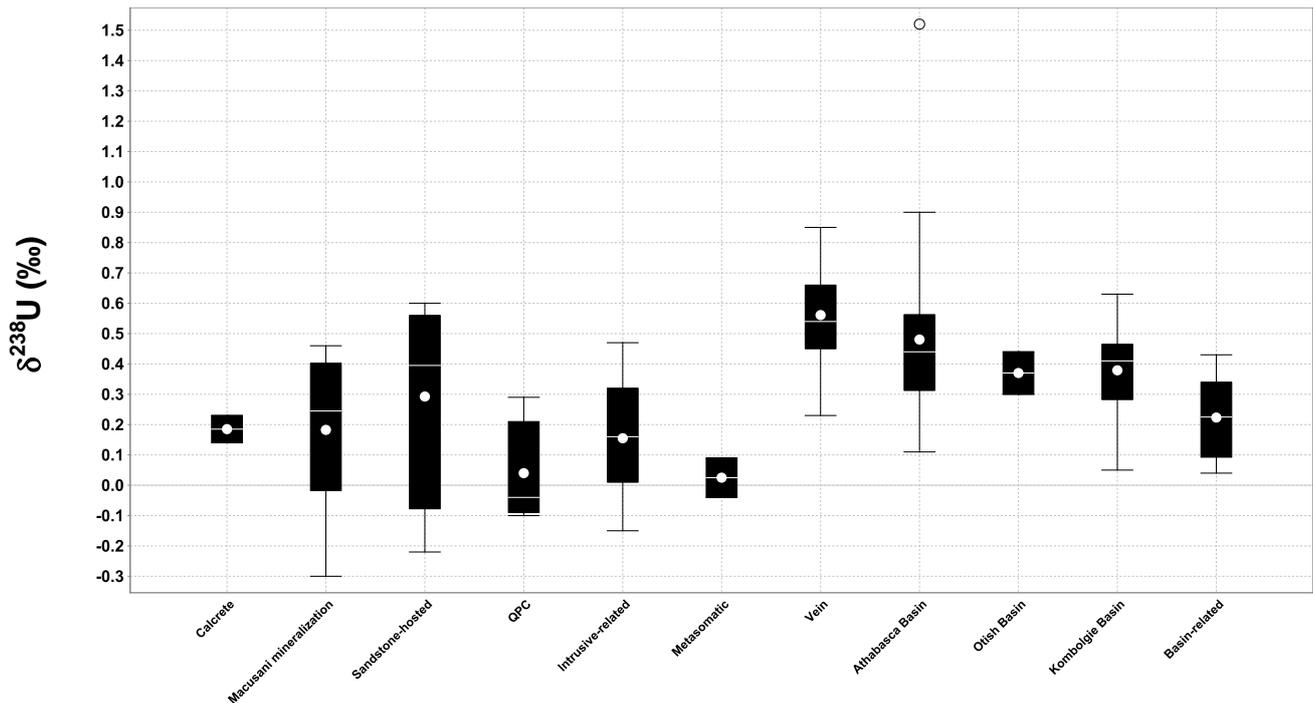


Figure 1. Tukey box-and-whisker plots of  $\delta^{238}\text{U}$  values for uranium ore minerals from various deposits and prospects. Each box is defined by the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the data and represents the inter-quartile range (IQR). The median is represented by a white horizontal line and the mean by a white dot. Whiskers are extended from the box to the last value at  $<1.5$  IQR, towards the maximum and the minimum. Samples beyond the whiskers are considered outliers or anomalies (circles)

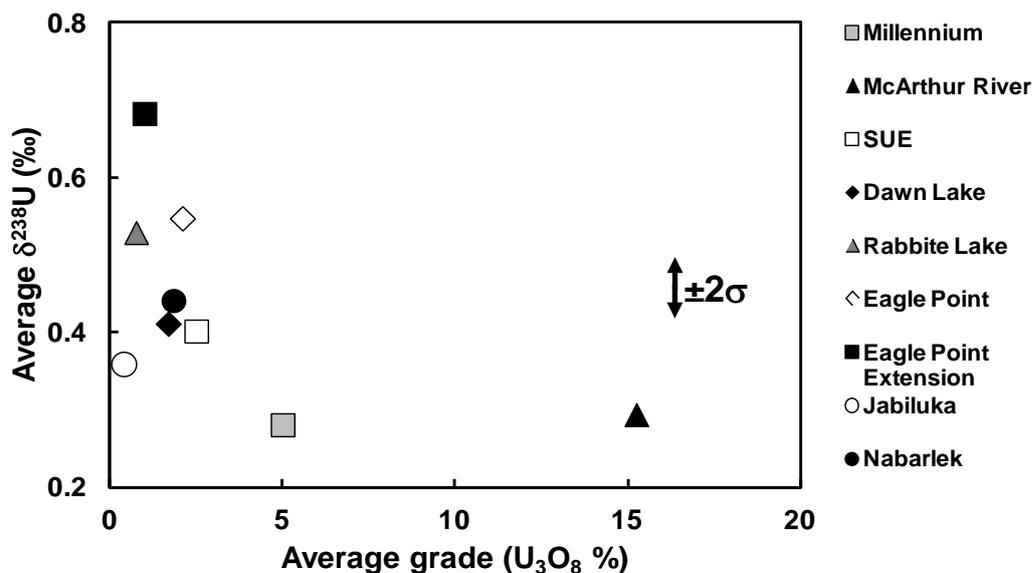


Figure 2. Relation between  $\delta^{238}\text{U}$  values for unconformity-related mineralisation in Athabasca and Kombolgie basins and the corresponding deposit grade.

Theoretically,  $^{235}\text{U}$  is preferentially retained in oxidised species such as dissolved  $\text{U}^{6+}$ , whereas  $^{238}\text{U}$  is preferentially partitioned into reduced species such as uraninite (Bigeleisen 1996; Schauble 2007). A simplified model for formation of many uranium deposits involves oxidation and mobilisation of uranium from an initial source followed by reduction and deposition of  $\text{U}^{4+}$  minerals or chemical precipitation of  $\text{U}^{6+}$  minerals. Uranium isotopic fractionation can occur at any of these steps. Based on the results of this study, we propose that observed  $^{238}\text{U}/^{235}\text{U}$  values in uranium ore minerals primarily reflect the source of the uranium, the efficiency of uranium capture in the environment in which the uranium is fixed, the degree to which uranium was previously removed from the fluid and the presence or absence of later fluid alteration of the ore, and perhaps some effect of temperature. Influence of these factors on the isotopic signatures of uranium ore minerals were previously discussed (Uvarova et al. 2014). Here, we would like to articulate how the efficiency of uranium capture results in a gradient of  $^{238}\text{U}/^{235}\text{U}$  ratios that can be used in exploration for uranium deposits and even for estimation of their grade.

If a mineralising fluid carrying  $\text{U}^{6+}$  interacts with a very effective reductant barrier and all of the uranium is deposited as ore, the isotopic signature of this ore should be identical to that of the uranium in the fluid. If, however, a portion of uranium was not reduced and deposited, the isotopic composition of the precipitated ore will be enriched in  $^{238}\text{U}$ , as  $^{235}\text{U}$  will preferentially fractionate into the fluid. Unconformity-type uranium deposits in the Athabasca Basin show that the highest grade deposits (McArthur River and Millennium) have the lowest  $\delta^{238}\text{U}$  values, which we interpret as resulting from the effective reduction of uranium from the mineralising fluid and absence of later alteration (Figure 2). Disseminated mineralisation located below the main ore body at Millennium has a  $\delta^{238}\text{U}$  value of 0.51‰ and  $\delta^{234}\text{U}$  value of -51‰. Other Athabasca unconformity-type deposits have higher  $\delta^{238}\text{U}$  values and these deposits are of lower grade, as do low-grade Jabiluka and Nabarlek Australian unconformity-type deposits with average  $\delta^{238}\text{U}$  values of 0.3 to 0.4‰ (Figure 2). Thus, using a Rayleigh fractionation model, the lower  $\delta^{238}\text{U}$  values in high-grade deposits may reflect more efficient reduction processes (Figure 3).

Thus, unconformity-type deposits in Canada and Australia, which display large variations in their  $\delta^{238}\text{U}$  values from 0.05 to 1.52‰, reflect primarily the role that an effective trapping mechanism plays. The difference between uraninites from high-grade deposits having lower  $^{238}\text{U}/^{235}\text{U}$  values and uraninites from low-grade deposits and disseminated mineralisation having higher  $^{238}\text{U}/^{235}\text{U}$  values can be attributed to two processes in the formation of uranium mineralisation in unconformity-type deposits. One process involves continuous precipitation of uranium from the U-bearing fluids, wherein  $^{238}\text{U}$  is relatively enriched in the first precipitates so that there is a zonation in uranium isotopes as a function of the ability of the system to effectively reduce the uranium (Fig. 3). The more effective this mechanism, the more constant and lower the  $\delta^{238}\text{U}$  values are, because this is a closed system. The second process involves alteration of primary ore wherein  $^{235}\text{U}$  is preferentially

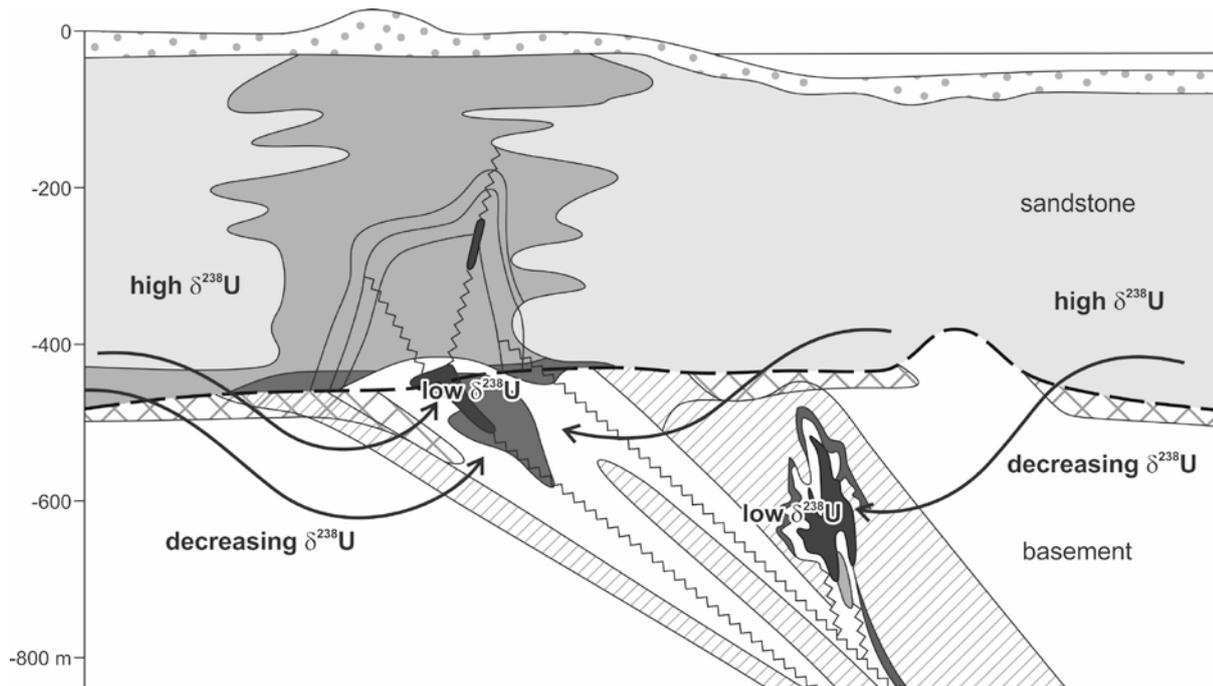
mobilised into the fluid phase and the recrystallised uraninite preferentially uptakes  $^{238}\text{U}$ . The first process initially precipitates uraninites with high  $^{238}\text{U}/^{235}\text{U}$  values, as the  $^{238}\text{U}$  is preferentially removed from the fluid following precipitation of uraninite during Rayleigh processes, and this results in lower  $^{238}\text{U}/^{235}\text{U}$  values in the remaining fluid. The second process affects the uranium isotope ratios because  $^{235}\text{U}$  is preferentially partitioned into the fluid phase and the primary ore becomes more enriched in  $^{238}\text{U}$ , whereas uranium leached from ore during alteration/recrystallisation and then reprecipitation is enriched in  $^{235}\text{U}$ .

## Conclusions

The  $^{234}\text{U}/^{238}\text{U}$  disequilibria ratios indicate recent fluid alteration (in the past 2.5 Ma) caused by preferential leaching of  $^{234}\text{U}$  or addition of previously leached  $^{234}\text{U}$  to the system. The  $^{238}\text{U}/^{235}\text{U}$  isotope fractionation occurs as a function of nuclear-field shift, however, variations in  $^{238}\text{U}/^{235}\text{U}$  ratios are small in high-temperature magmatic- and metasomatic-related deposits and in cases where mobilised uranium from an igneous protolith is effectively precipitated in a closed system. Significant variations in  $^{238}\text{U}/^{235}\text{U}$  values also occur during Rayleigh fractionation as a result of reduction of  $\text{U}^{6+}$  to uraninite or during fluid alteration/recrystallisation of uraninite wherein  $^{235}\text{U}$  is preferentially mobilised into the fluid. This potentially can be used in exploration for uranium deposits because the isotopic composition of uranium minerals changes gradually with proximity to mineralisation and is related to the grade of the deposit. As there is a gradient of  $^{238}\text{U}/^{235}\text{U}$  values with the highest ratios distal from the redox centre, uranium isotopes may be used as exploration vectors and even for estimation of the deposit size.

## Acknowledgments

The authors would like to thank research colleagues and the laboratory staff at Queen's Facility for Isotope Research for valuable discussion and laboratory assistance. We would also like to thank the personnel at the Royal Ontario Museum (Toronto, Canada) for providing some of the samples for the study. This project was funded by NSERC Postdoctoral Fellowship to YAU and NSERC research and operating grants to TKK.



**Figure 3. Schematic diagram showing general alteration and geologic features of basement- and basin-hosted unconformity uranium deposits with distributions in  $\delta^{238}\text{U}$  values as a result of Rayleigh fractionation of  $\text{U}^{6+}$  in a fluid being reduced to uraninite. The vertical axis is the depth in meters from the modern surface. The unconformity between the basin sandstones (light grey) and the basement (white and striped) is shown as a black dashed line. The unconformity-type uranium mineralisation is shown in black: the basin-hosted ore body is located directly at the unconformity, and the basement-hosted ore body is located below the unconformity. Darker grey area in the basin sandstone represents typical clay alteration zone above the basin-hosted U mineralisation, while striped areas in the basement represent inner and outer chlorite-illite alteration zones around basement-hosted mineralisation.**

## References

- AMELIN, Y., KALTENBACH, A., IIZUKA, T., STIRLING, C.H., IRELAN, T.R., PETAEV, M. & JACOBSEN, S.B. 2010. U-Pb chronology of the Solar System's oldest solids with variable  $^{238}\text{U}/^{235}\text{U}$ . *Earth and Planetary Science Letters*, **300**, 343-350.
- BIGELEISEN, J. 1996. Nuclear size and shape effects in chemical reactions. Isotope chemistry of the heavy elements. *Journal of American Chemical Society*, 1996, 3676-3680.

BOPP IV, C.J., LUNDSTROM, C.C., JOHNSON, T.M. & GLESSNER, J.G. (2009) Variations in  $^{238}\text{U}/^{235}\text{U}$  in uranium ore deposits: Isotopic signatures of the U reduction process? *Geology*, **37**, 611-614.

BOUVIER, A., SPIVAK-BIRNDORF, L.J., BRENNECKA, G.A. & WADHWA, M. 2011. New constraints on early Solar System chronology from Al-Mg and U-Pb isotope systematics in the unique basaltic achondrite Northwest Africa 2976. *Geochimica et Cosmochimica Acta*, **75**, 5310-5323.

BRENNECKA, G.A., BORG, L.E., HUTCHEON, I.D., SHARP, M.A. & ANBAR, A.D. 2010a. Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the  $^{238}\text{U}/^{235}\text{U}$  fractionation mechanism. *Earth and Planetary Science Letters*, **291**, 228-233.

BRENNECKA, G.A., WYER, S., WADHWA, M., JANNEY, P.E., ZIPFEL, J. & ANBAR, A.D. 2010b.  $^{238}\text{U}/^{235}\text{U}$  variations in meteorites: Extant  $^{247}\text{Cm}$  and implications for Pb-Pb dating. *Science*, **327**, 449-451.

BRENNECKA, G.A. & WADHWA, M. 2012. Uranium isotope compositions of the basaltic angrite meteorites and the chronological implications for the early Solar System. *Proceedings of the National Academy of Sciences*, **109**, 9299-930.

CHENG, H., EDWARDS, R.L., HOFF, J., GALLUP, C.D., RICHARDS, D.A. & ASMEROM, Y. 2000. The half-lives of uranium-234 and thorium-230. *Chemical Geology*, **169**, 17-33.

CHENG, H., EDWARDS, R.L., SHEN, C.-C., POLYAK, V.J., ASMEROM, Y., WOODHEAD, J., HELLSTROM, J., WANG, Y., KONG, X., SPÖTL, C., WANG, X. & CALVIN ALEXANDER Jr., E. 2013. Improvements in  $^{230}\text{Th}$  dating,  $^{230}\text{Th}$  and  $^{234}\text{U}$  half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth and Planetary Science Letters*, **371-372**, 82-91.

CONNELLY, J.N., BIZZARRO, M., KROT, A.N., NORDLUND, Å., WIETLANDT, D. & IVANOVA, M.A. 2012. The absolute chronology and thermal processing of solids in the solar protoplanetary disk. *Science*, **338**, 651-655.

GOLDMANN, A., BRENNECKA, G., NOORDMANN, J., WEYER, S. & WADHWA, M. 2013. The  $^{238}\text{U}/^{235}\text{U}$  of the earth and the Solar System. *Mineralogical Magazine*, **77H** Goldshmidt 2013. p.1188 (abstr.).

HIESS, J., CONDON, D.J., MCLEAN, N. & NOBLE, S.R. (2012)  $^{238}\text{U}/^{235}\text{U}$  systematic in terrestrial uranium-bearing minerals. *Science*, **335**, 1610-1614.

MONTOYA-PINO, C., WEYER, S., ANBAR, A.D., PROSS, J., OSCHMANN, W., SCHOOTBRUGGE, B. & ARZ, H.W. 2010. Global enhancement of ocean anoxia

during Oceanic Anoxic Event 2: A quantitative approach using U isotopes. *Geology*, **38**, 315-318.

PIN, C. & ZALDUEGUI, J.F.S. 1997. Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Analytica Chimica Acta*, **339**, 79-89.

RICHTER, S., EYKENS, R., KÜHN, H., AREGBE, Y., VERBRUGGEN, A. & WEYER, S. 2010. New average values for the  $n(^{238}\text{U})/n(^{235}\text{U})$  isotope ratios of natural uranium standards. *International Journal of Mass Spectrometry*, **295**, 94-97.

SCHAUBLE, E.A. 2007. Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochimica et Cosmochimica Acta*, **71**, 2170-2189.

STIRLING, C.H., HALLIDAY, A.N. & PORCELLI, D. 2005. In search of live  $^{247}\text{Cm}$  in the early solar system. *Geochimica et Cosmochimica Acta*, **69**, 1059-1071.

STIRLING, C.H., ANDERSEN, M.B., POTTER, E.-K. & HALLIDAY, A.N. 2007. Low-temperature isotopic fractionation of uranium. *Earth and Planetary Science Letters*, **264**, 208-225.

TELUS, M., DAUPHAS, N., MOYNIER, F., TISSOT, F.L.H., TENG, F.-Z., NABELEK, P.I., CRADDOCK, P.R. & GROAT, L.A. 2012. Iron, zinc, magnesium and uranium isotopic fractionation during continental crust differentiation: The tale from migmatites, granitoids, and pegmatites. *Geochimica et Cosmochimica Acta*, **97**, 247-265.

TISSOT, F. & DAUPHAS, N. 2011. Development of high precision  $^{238}\text{U}/^{235}\text{U}$  ratio measurements for cosmochemical applications. Proceedings of the 42<sup>nd</sup> Lunar and Planetary Science Conference, Lunar Planet. Inst., Houston. #1082 (abstr.).

TISSOT, F. & DAUPHAS, N. 2012.  $^{238}\text{U}/^{235}\text{U}$  ratios of anagrams: angrites and granites. Proceedings of the 43<sup>rd</sup> Lunar and Planetary Science Conference, Lunar Planet. Inst., Houston. #1981 (abstr.).

UVAROVA, Y.A., KYSER, T.K., LAHD GEAGEA, M. & CHIPLEY, D. 2014. Variations in the uranium isotopic compositions of uranium ores from different types of uranium deposits. *Geochimica et Cosmochimica Acta*, **146**, 1-17.

WEYER, S., ANBAR, A.D., GERDES, A., GORDON, G.W., ALGEO, T.J. & BOYLE, E.A. 2008. Natural fractionation of  $^{238}\text{U}/^{235}\text{U}$ . *Geochimica et Cosmochimica Acta*, **72**, 345-359.