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Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the $^{238}U/^{235}U$ fractionation mechanism

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ABSTRACT

Precise measurement of the $^{238}U/^{235}U$ ratio in geologic samples is now possible with modern techniques and mass spectrometers. Natural variations in this ratio have been shown in previous studies. In this study, data obtained from uranium ore concentrates of mining facilities around the world show clear evidence that the depositional redox environment in which uranium is precipitated is the primary factor affecting $^{238}U/^{235}U$ fractionation. Low-temperature uranium deposits are, on average, isotopically ~0.4‰ heavier than uranium deposited at high temperatures or by non-redox processes. $^{238}U/^{235}U$ ratios coupled with $^{235}U/^{234}U$ ratios in the same sample provide evidence that the redox transition ($U^{VI} \rightarrow U^{IV}$) at low temperatures is the primary mechanism of $^{238}U/^{235}U$ fractionation and that aqueous alteration plays a very limited, if any, role in fractionation of the $^{238}U/^{235}U$ ratio. The isotopic variation of U is therefore a potential signature that can be used to trace the origin of uranium ore concentrate.

1. Introduction

The uranium isotope system is unusual in that it contains two long-lived natural isotopes in ^{238}U ($t_{1/2} \approx 4.5$ Ga) and ^{235}U ($t_{1/2} \approx 700$ Ma), as well as ^{234}U, a short-lived isotope ($t_{1/2} \approx 245{,}000$ a) that is part of the ^{238}U decay chain. This isotope system has been well studied not only because of the fissile properties of ^{235}U, but also because of its wide applications in the age dating of natural materials. The decay systems of $^{238}U \rightarrow {}^{206}Pb$ and $^{235}U \rightarrow {}^{207}Pb$ provide both long and short-range chronometers when utilizing intermediate decay products, such as ^{234}U.

Until very recently it was assumed that the current $^{238}U/^{235}U$ ratio was a constant value (=137.88) in our Solar System because uranium was thought to be too heavy to undergo significant isotope fractionation. Theoretical work by Fujii et al. (1989), Bigeleisen (1996), and Schauble (2006, 2007) suggested, however, that fractionation in uranium isotopes should be present and measureable with modern analytical techniques. Recent work has in fact shown variability in the terrestrial $^{238}U/^{235}U$ ratio over a range of ~1.3‰ (Stirling et al., 2007; Weyer et al., 2008). Our study utilizes modern multi-collector ICP-MS technology to analyze 40 uranium ore concentrate samples from U-ore mines across the world to search not only for differences in the $^{238}U/^{235}U$ and $^{235}U/^{234}U$ ratios, but to identify the specific mechanisms that cause the $^{238}U/^{235}U$ fractionation.

Although significant variations in the $^{238}U/^{235}U$ ratio are a recent discovery, much larger variations in the $^{234}U/^{235}U$ ratio in the terrestrial variations have long been observed. The ocean, for example, contains elevated abundances of ^{234}U. Specifically, the increased mobility of ^{234}U relative to other U isotopes reflects production from ^{238}U by α-decay and subsequent emplacement in crystal sites damaged by α-recoil. Aqueous weathering of materials containing U results in preferential leaching of ^{234}U from these α-damaged crystal sites (Kigoshi, 1971).

If preferential leaching is also the primary mechanism for $^{238}U/^{235}U$ fractionation, the magnitude of changes in $^{238}U/^{235}U$ should be positively correlated with those in $^{235}U/^{234}U$. On the other hand, $^{238}U/^{235}U$ variations have been attributed to oxidation and reduction (redox) processes (Schauble, 2006; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009). In this scenario, the ability of individual U nuclei to attract electrons varies slightly due to the different number of neutrons in the nucleus of ^{238}U and ^{235}U. This has been termed the "nuclear-volume effect."

If reduction of U^{VI} to U^{IV} is a major cause of isotope fractionation in the uranium system, then uranium ores deposited in variable oxidation conditions should show resolvable differences in uranium isotope abundances. By examining the relationship between all three

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naturally occurring uranium isotopes in samples deposited by: (1) low-temperature redox processes, (2) high-temperature redox processes and (3) non-redox processes, it should be possible to determine the relative importance of preferential leaching and redox changes at high and low temperatures in fractionation of the ^{238}U/^{235}U ratio.

2. Background

2.1. Previous ^{238}U/^{235}U-ore deposit work

Early work by Cowan and Adler (1976) on the ^{238}U/^{235}U ratio in uranium ore samples concluded that there was a bimodal distribution of uranium ores with a statistically significant, ~ +0.3‰ difference between sandstone-type and magmatic deposits. Their study also concluded that there were insufficient data to attribute the variations either to fractionation of uranium isotopes between magmatic and sandstone deposits, or ^{235}U depletion caused by Precambrian nuclear reactions. This work was performed using UF_6 gas mass spectrometers, achieving a reported precision of ~0.4‰ on the ^{238}U/^{235}U ratio. However, the UF_6 was sometimes stored in containers that previously contained depleted uranium (i.e., ^{238}U/^{235}U≫137), creating a potential source of contamination and making the results of the study somewhat ambiguous. A more recent study by Bopp et al. (2009) examined uranium ore from six uranium mines, sampling two low-temperature deposits and four high-temperature deposits. This study concluded that ^{238}U/^{235}U fractionation takes place during the low-temperature redox transition, citing higher ^{238}U/^{235}U ratios from low-temperature deposits. We have undertaken a study involving a significantly more diverse sample suite in order to determine the cause of the ^{238}U/^{235}U ratio variations in ore deposits by testing all likely modes of isotope fractionation.

2.2. Sample types

Uranium ore concentrate (UOC; née, yellowcake) is a fungible commodity traded worldwide and is the final product of uranium mining and milling operations. Uranium deposits occur worldwide in a variety of geologic settings and can be divided into 3 major depositional settings based on the temperature and the redox environment of deposition. The major settings, coupled with examples of typical uranium deposit types, are described briefly below.

1) *Low-temperature, redox sensitive* — consist primarily of sandstone or "roll front" deposits, but also included in this category are black shale uranium deposits. Uranium mineralization occurs below the water table where low-temperature, oxidized fluids (carrying soluble U^{VI}) interact with a reducing agent, usually carbonaceous material, sulfides, or hydrocarbons, and precipitate uranium as insoluble U^{IV} (IAEA-TEC-DOC-328, 1985). Major examples include the sandstone deposits of the Syr-Darya basin in Kazakhstan, the Arlit district of Niger, and the gulf coast deposits of Texas, USA.
2) *High-temperature, redox sensitive* — includes some of the largest and richest uranium deposits in the world. Like sandstone and black shale deposits, this category includes uranium deposited because of the reduction of U^{VI} to U^{IV}, but at higher temperatures associated with igneous and metamorphic processes. Uranium deposits in this category include unconformity deposits, vein-type deposits, intrusive deposits, metamorphic core complex deposits and collapse breccia-pipe deposits. Major examples include the massive Olympic Dam breccia complex and unconformity-style Ranger deposits of Australia, as well as Namibia's intrusive-style Rössing deposit.
3) *Non-redox sensitive* — this setting exclusively contains quartz–pebble conglomerate deposits. These are ancient deposits formed from fluvial oligomictic detritus (including pyrite and uraninite) prior to the emergence of an oxygenated atmosphere on Earth, and therefore not deposited by a redox-related mechanism (IAEA-TEC-DOC-427, 1987). The Stanleigh, Stanrock and Denison deposits of Canada are all examples of quartz–pebble conglomerate deposits.

By examining the uranium isotope composition of samples from these deposits, we hope to constrain the potential roles preferential leaching, oxidation, and temperature play in fractionating the isotopes of uranium in the terrestrial environment. If fractionation patterns reflect preferential leaching of isotopes, variations in ^{238}U/^{235}U and ^{235}U/^{234}U will be positively correlated and not dependent on the oxidation environment. If, in contrast, the pattern of U-isotope shifts reflects oxidation/reduction, as suggested by Weyer et al. (2008), U-isotope fractionation will be pronounced in the redox-related deposits and absent from the non-redox deposits. The role that temperature may play in U isotopic fractionation is evaluated by analyzing U ores that formed at both low and high temperatures.

3. Methods

3.1. Sample preparation

Samples were obtained as UOC; an aliquot of ~100 mg was removed and placed into a 50 ml centrifuge tube. The sample was dissolved using 20 ml of 4 M HNO_3. From the solution, an aliquot of 250 µl was removed and brought to 4 ml in a 3 M HNO_3 + 0.05 M HF acid mixture. This solution was passed through a column containing Eichrom® UTEVA resin, following a revised procedure outlined in Weyer et al. (2008) to separate uranium from the matrix. Due to the extremely high uranium concentrations associated with these samples, a ^{236}U/^{233}U double spike was added to sample aliquots only after uranium concentrations were determined using a Thermo XSII quadrupole Inductively Coupled Plasma Mass Spectrometer and samples were appropriately diluted for isotope ratio measurements. It has been shown that no measureable U-isotope fractionation occurs during the column elution for the procedure used, so timing of spike addition does not affect measured ratios (Weyer et al., 2008).

3.2. Isotope ratio measurements

High precision uranium isotope ratio measurements were collected on a ThermoFinnigan Neptune MC-ICP-MS instrument at Arizona State University (ASU). Samples dissolved in 2% HNO_3 were introduced by an Apex-Q sample introduction system. ^{238}U/^{235}U measurements were performed at concentrations of ~120 ppb U to obtain ~35 volt signal (3.5×10^{-10} amperes) on ^{238}U. A second, more concentrated aliquot was used for the ^{235}U/^{234}U measurement to obtain ~25 volt signal on ^{235}U. A ^{236}U/^{233}U double spike was used to correct for instrumental mass bias during the measurements. In order to minimize analytical error associated with the addition of ^{234}U, ^{235}U, and ^{238}U from the spike, samples were spiked to achieve ^{236}U and ^{233}U signals of ~2.5 times the lowest natural isotope for each run. This spiking technique maximizes the counting statistics on the spike masses while minimizing the tailing contributions at mass 235. The spike was calibrated at ASU and has an isotopic composition of ^{236}U/^{233}U=1.00525, ^{238}U/^{233}U = 0.000958, and ^{235}U/^{233}U = 0.000108.

Uranium isotopic data are reported as an average of multiple runs (2 or more), differing by an average value (^{238}U/^{235}U) of less than 0.007, or 0.05‰. Each measurement session included multiple (10 or more) runs of CRM 129-A, a certified uranium standard (New Brunswick Laboratory, 2003) obtained as a uranium oxide and was put through the same chemistry as all samples. Uncertainties are based on the errors calculated on the replicate runs for the CRM129-A standard (^{238}U/^{235}U ± 0.018; ^{235}U/^{234}U ± 0.42), and are reported at the bottom of Table 1 for both ratios measured. The standard error of each individual run (30 cycles, 8.4 second integration per cycle) was, in all cases, less than 0.009 for the ^{238}U/^{235}U