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^{238}U-^{235}U-^{234}U fractionation between tetravalent and hexavalent uranium in seafloor phosphorites

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ABSTRACT

Variations in the $^{238}U/^{235}U$ ratio are mostly observed in association with changes in the uranium oxidation state and therefore controlled by changes in the redox conditions, although evidence for this process has so far been indirect. Here, the $\delta^{238}U$ and $\delta^{234}U$ isotope composition of different redox species is studied for the first time within the same geological samples: the bulk, reduced (U(IV)) and oxidized (U(VI)) uranium species in seafloor phosphorites. In all cases, $\delta^{238}U(IV)$ is higher (-0.27 to -0.81) than corresponding $\delta^{238}U(VI)$ (-0.64 to -1.07), with $\delta^{234}U(IV)$ displaying extremely high values (~500–2000) relative to $\delta^{234}U(VI)$ (-240 to -100). By comparison, the bulk $\delta^{238}U$, $\delta^{234}U$ and U concentrations are -0.42 to -0.85, -10 to $+20$, and 63–328 ppm, respectively. These values are mostly in the range of natural variations in previously reported samples, with the bulk $\delta^{238}U$ and $\delta^{234}U$ values corresponding with seawater values except for a tail in $\delta^{238}U$ toward lower values. The main exception is displayed by the composition of the U(VI) fraction, which ranges toward relatively low $\delta^{238}U$ values but has a very strong positive $\delta^{234}U$ excursion relative to comparable samples elsewhere.

Given that the studied phosphorites formed in high productivity environments, where oxygen consumption was high and hence anoxic conditions could have been favored, it is assumed that most of the initial uranium in the samples was in reduced form. Indeed, even if some of the U oxidized over time, the studied samples still consist of approximately 60–80% U(IV). The process of ^{238}U radioactive decay resulted in the oxidation of the decay product, ^{234}U, and consequently, the $\delta^{234}U(VI)$ within the samples has very high values. The evolution of $\delta^{238}U$ is related to the effect of the 'nuclear field shift', which predicts that nuclides with higher atomic masses will be reduced preferentially over elements with lower atomic masses. Accordingly, it is easier to reduce ^{238}U than ^{235}U in the same environment, which would result in higher $\delta^{238}U$ of U(IV). This is indeed the case observed here, although in addition, the evidence here shows that the $\delta^{238}U$ fractionation occurred during U *oxidation* and that the final differences of $\delta^{238}U$ between both oxidation states reflect *the combined effect of the depositional nuclear field shift and the* in-situ *recoil-related oxidation*.

A set of quantitative models are used to evaluate the role and rate of the different processes and suggest that because of the independent evolution of U(IV) and U(VI) over time, their relative fraction and isotopic compositions can be used to evaluate the formation ages of seafloor phosphorites, which has so far not been possible using U-decay series.

1. Introduction

Uranium has conventionally been considered to be too heavy to undergo observable mass-dependent fractionation, and hence the ratio between its two longest –lived isotopes (^{238}U, ^{235}U) was assumed to be at any given time constant in our solar system (with a canonic modern value of 137.88; Chen and Wasserburg, 1980, 1981; Steiger and Jager, 1977). This a-priori constant $^{238}U/^{235}U$ ratio was used for correcting mass-dependent fractionation of U isotopes during mass spectrometric analyses, used for various applications, including U—Th and U—Pb dating, and hence potential variations in this ratio could have an impact on the accuracy and precision of many geological ages (Stirling et al., 2007). Yet, both early experimental results (e.g., Fujii et al., 1989; Nomura et al., 1996), and theoretical work (Abe et al., 2008, 2010; Bigeleisen, 1996; Moynier et al., 2013; Schauble, 2007) showed that both biotic and abiotic $^{238}U/^{235}U$ fractionation is to be expected during exchange between the two main oxidation states of uranium ((IV) and (VI)), due to what was termed the "nuclear field shift" or "nuclear-volume effect". This

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effect is the ability of individual U nuclei to slightly differ in their attraction of electrons due to the different number of neutrons in the nucleus of ^{238}U and ^{235}U. Nuclear field shifts usually become larger with increasing atomic number and they are important in the heavy-element isotopes (e.g., Schauble, 2007). Early efforts to explore these directions were limited by analytical capabilities (e.g., Cowan and Adler, 1976), but advances in recent years (e.g., the use of ICP-MS with stable mass bias and the use of double spikes) have allowed distinguishing between minute changes in the ^{238}U/^{235}U in natural samples and experimental data, and thereby confirmed the above theoretical predictions (e.g., Brennecka et al., 2010a, 2010b, 2011; Fujii et al., 2006; Hiess et al., 2012; Stirling et al., 2007; Weyer et al., 2008).

The shorter lived uranium isotope ^{234}U, is sensitive to an additional process termed the "recoil effect", whereby the (^{234}U/^{238}U) ratio (rounded brackets note activity values) can deviate from secular equilibrium in a solid mineral due to direct recoil, displacement and electron stripping of ^{234}U (Cherdyntsev et al., 1955), or as a result of preferential release of ^{234}Th across grain boundaries via the recoil associated with the energetic α–decay of ^{238}U (e.g., Fleischer, 1980; Kigoshi, 1971). A substantial fraction of ^{234}Th, and its decay product ^{234}U, can be lost from the solid mineral lattice resulting in ^{234}U depletion and disequilibrium of (^{234}U/^{238}U). Whereas most previous studies suggest preferential release of ^{234}U from damaged lattice sites and direct recoil as the main mechanisms of ^{234}U/^{238}U fractionation, Kolodny and Kaplan (1970) stressed the possibility of greater ^{234}U mobility due to decay-induced oxidation and electron stripping or as a result of the β – decay. Similarly, Chalov and Merkulova (1966, 1968), who analyzed a set of U- minerals, showed that in pitchblendes and in uranium black the activity ratios always correspond to:

$$\left(^{234}U/^{238}U\right)_{(IV)}<\left(^{234}U/^{238}U\right)_{(bulk)}<\left(^{234}U/^{238}U\right)_{(VI)}$$

Whatever the explanation, terrestrial waters mirror this ^{234}U loss from the solid and typically display excess in ^{234}U, yielding for example modern seawater ^{234}U/^{238}U activity ratios of 1.147 ± 0.001 (Henderson, 2002; Robinson et al., 2004).

The notation usually used for expressing the ^{238}U/^{235}U and the ^{234}U/^{238}U isotope ratios is respectively:

$$\delta^{238}U(‰) = \left(\frac{\left(^{238}U/^{235}U\right)_{sample}}{\left(^{238}U/^{235}U\right)_{std}} - 1\right) \times 10^3$$

$$\delta^{234}U(‰) = \left(\frac{\left(^{234}U/^{238}U\right)_{sample}}{\left(^{234}U/^{238}U\right)_{sec.eq.}} - 1\right) \times 10^3$$

where the "sample" subscripts mean the relevant ratio in the measured sample, the "std" subscript – the ^{238}U/^{235}U ratio in a known standard, in this case NBL-112a (137.8493; New Brunswick Laboratory, U.S. Department of Energy), and the "*sec. eq.*" subscript the ^{234}U/^{238}U isotope ratio in secular equilibrium (i.e. with a activity ratio of ^{234}U/^{238}U equal to 1.00).

Although ^{238}U/^{235}U fractionation during redox transformation is inferred from both observational data and theoretical calculations, *direct* proof of that phenomenon has so far been very limited. Stirling et al. (2015) found large isotopic fractionation during the biologically-mediated reduction of U(VI) to U(IV). In other cases, the differences in δ^{238}U between the two oxidation states of uranium was examined *indirectly* on bulk samples from environments with contrasting redox conditions such as manganese nodules vs. black shales (Weyer et al., 2008), oxic vs. anoxic interstitial water (Andersen et al., 2014), oxic vs. anoxic water in a fjord (Holmden et al., 2015), the Baltic Sea (Noordmann et al., 2015), and groundwater (Placzek et al., 2016).

Combined, the abovementioned studies confirm that the *reduced* U is typically enriched in ^{238}U. By contrast, Rademacher et al. (2006) observed a δ^{238}U shift in the opposite direction, with 0.34‰ enrichment in ^{238}U in the *oxidized* phase during reduction of U(VI) to U(IV) by zero-valent iron and *Geobacter sulfurreducens* and *Anaeromyxobacter dehalogenans*, the remaining oxidized phase being enriched in ^{238}U.

A direct proof of fractionation in a natural environment as a function of redox requires, however, the occurrence of both reduced and oxidized uranium in an otherwise identical setting.

Here, we target uranium in marine phosphorites, and specifically, the major phosphorite mineral – carbonate-fluor- apatite (francolite), which contains both U(IV) and U(VI). We chemically *separate* U(IV) and U(IV) from the *same* sample and analyze each for their δ^{238}U and δ^{234}U, which provides the opportunity to directly quantify the isotopic fractionation between the two oxidation states in the same rock powder.

The association of uranium with carbonate-fluor-apatite, the major vertebrate fossil mineral (though pre-diagentic bones have very low U concentrations), has been recognized since the early days of radioactivity studies at the beginning of the 20th century (Strutt, 1908). In their classic study, Altschuler et al. (1958), investigated this relationship in detail, showing that marine phosphorites typically contain between 50 and 200 ppm uranium, which is ~20–75 times greater than the crustal abundance of U. Phosphorites contain two oxidation states of U, most of it as U(IV) which substitutes for Ca^{+2} in the apatite lattice, though some uranyl (VI) can also enter the rather loose apatite structure (Altschuler et al., 1958). A previous study of U concentrations and δ^{234}U in sea-floor phosphorites (Kolodny and Kaplan, 1970) showed δ^{234}U values of 0 or below, a-priori reflecting sample ages of 1 Ma or older (i.e., samples have reached (^{234}U/^{238}U) secular equilibrium). Moreover, (^{234}U/^{238}U) of tetravalent uranium was always lower than that of its hexavalent analog. These observations were explained by assuming that about 30% of the ^{238}U is oxidized (or moved into oxidizable sites) during its decay to ^{234}U, which results in its mobilization. It was further argued that the recoil products were displaced from their original location in the lattice, stripped of some electrons, and thus became more susceptible to oxidation into the soluble and more leachable U(VI) form. By contrast, the same observations could be explained solely by the recoil effect causing loss of ^{234}Th and ^{234}U from the solid into the surrounding solution (e.g., following Kigoshi (1971) and others). Whatever the case, expulsion of an α particle from a mass-238 uranium nucleus, with an energy of about 5 Mev must be accompanied by a recoil of the heavy nucleus with an energy of the order of several tens of kev, sufficient to break chemical bonds and displace the recoiled nucleus in the lattice.

In addition to studying the δ^{238}U and δ^{234}U differences between U(IV) and U(VI) in the same sample, we aim to quantify the relative roles of the fractionation processes and present a model that explains the isotopic evolution of each of the valence states over time.

2. Methods

This study focuses on five dredged seafloor phosphorite samples, which are a subset of the samples reported by Kolodny and Kaplan (1970). All samples come from areas of present and Neogene time upwelling and have never been exposed to surface weathering. Splits of the original solid samples were crushed and homogenized.

Uranium isotope analysis was performed in two steps: first, the isotope ratio was measured in the whole sample (bulk isotope ratio); and in the second step U(IV) and U(VI) were chemically separated from the same powder (Fig. 1). Approximately 500 mg of the homogenized powder was weighted and digested using a concentrated mix of HNO_3—HCl, and U(IV) and U(VI) were separated from the digested solution by co-precipitation with NdF_3 (Anderson, 1984). U(VI) remained in solution while the precipitate NdF_3 contained U(IV). Reproducibility of the U(IV)/U(VI) separation was estimated as ± 15%, similar to the evaluation of the co-precipitation procedure by Ervanne and Suksi (1996) who tested repeated analysis of samples of known composition. A

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