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

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Abstract

Variations in the $^{238}\text{U}/^{235}\text{U}$ 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 $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ 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, $\delta^{238}\text{U}(\text{IV})$ is higher (-0.27 to -0.81) than corresponding $\delta^{238}\text{U}(\text{VI})$ (-0.64 to -1.07), with $\delta^{234}\text{U}(\text{IV})$ displaying extremely high values (~500-2000) relative to $\delta^{234}\text{U}(\text{VI})$ (-240 to -100). By comparison, the bulk $\delta^{238}\text{U}$, $\delta^{234}\text{U}$ 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 $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ values corresponding with seawater values except for a tail in $\delta^{238}\text{U}$ toward lower values. The main exception is displayed by the composition of the U(VI) fraction, which ranges towards relatively low $\delta^{238}\text{U}$ values but has a very strong positive $\delta^{234}\text{U}$ 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 $\delta^{234}\text{U}(\text{VI})$ within the samples has very high values. The evolution of $\delta^{238}\text{U}$ 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 $\delta^{238}\text{U}$ of U(IV). This is indeed the case observed here, although in addition, the evidence here shows that the $\delta^{238}\text{U}$ fractionation occurred during U oxidation and that the final differences of $\delta^{238}\text{U}$ 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)

56 over time, their relative fraction and isotopic compositions can be used to evaluate the
57 formation ages of seafloor phosphorites, which has so far not been possible using U-
58 decay series.
59

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, 1981, 1980; Steiger and Jager, 1977). This *a-priori* constant $^{238}\text{U}/^{235}\text{U}$ 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., 2010, 2008; Bigeleisen, 1996; Moynier et al., 2013; Schauble, 2007) showed that both biotic and abiotic $^{238}\text{U}/^{235}\text{U}$ 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 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 $^{238}\text{U}/^{235}\text{U}$ in natural samples and experimental data, and thereby confirmed the above theoretical predictions (e.g., Brennecka et al., 2011, 2010a, 2010b; 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 ($^{234}\text{U}/^{238}\text{U}$) 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 ($^{234}\text{U}/^{238}\text{U}$). Whereas most previous studies suggest preferential release of ^{234}U from damaged lattice sites and direct recoil

as the main mechanisms of $^{234}\text{U}/^{238}\text{U}$ 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, 1967), who analyzed a set of U- minerals, showed that in pitchblendes and in uranium black the activity ratios always correspond to:

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

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 $^{234}\text{U}/^{238}\text{U}$ activity ratios of 1.147 ± 0.001 (Henderson, 2002; Robinson et al., 2004).

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

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

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

where the “sample” subscripts mean the relevant ratio in the measured sample, the “std” subscript – the $^{238}\text{U}/^{235}\text{U}$ 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 $^{234}\text{U}/^{238}\text{U}$ isotope ratio in secular equilibrium (i.e. with a activity ratio of $^{234}\text{U}/^{238}\text{U}$ equal to 1.00).

Although $^{238}\text{U}/^{235}\text{U}$ 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 $\delta^{238}\text{U}$ 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 $\delta^{238}\text{U}$ 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(VI) from the *same* sample and analyze each for their $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$, 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-diagenetic 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 – 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 $\delta^{234}\text{U}$ in sea-floor phosphorites (Kolodny and Kaplan, 1970) showed $\delta^{234}\text{U}$ values of 0 or below, *a-priori* reflecting sample ages of 1 Ma or older (i.e., samples have reached ($^{234}\text{U}/^{238}\text{U}$) secular equilibrium). Moreover, ($^{234}\text{U}/^{238}\text{U}$) 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 5MeV 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 $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ 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 $\text{HNO}_3\text{-HCl}$, 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 $\pm 15\%$, similar to the evaluation of the co-precipitation procedure by Ervanne and Suksi (1996) who tested repeated analysis of samples of known composition. A mixed $^{236}\text{U}\text{-}^{233}\text{U}$ spike with a known ratio ($^{236}\text{U}/^{233}\text{U} = 0.981296$; IRMM3636) was added to the samples prior to column separation and to a NBL112a standard, to correct for the $^{238}\text{U}/^{235}\text{U}$ mass-bias during analysis. The $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios were determined separately:

1. Analysis of $^{235}\text{U}/^{238}\text{U}$:

Analyses were performed using a MC-ICP-MS, Nu Plasma II, Nu instruments, at low mass resolution ($M/\Delta M \sim 300$) and using a DSN-100 introduction system (Nu Instruments) with a PFA nebulizer of 50 $\mu\text{l}/\text{min}$. ^{238}U , ^{236}U , ^{235}U and ^{233}U were

measured on Faraday detectors with $10^{11}\Omega$ resistors. The typical sensitivity was $220\text{V}\cdot\text{ppm}^{-1}$, with average sample intensity of 30V for ^{238}U and 10V for ^{236}U and ^{233}U . Every measurement consisted of 15 cycles, each with integration time of 10s. Instrument blank was measured using ESA deflection. Sample analyses were bracketed by spiked NBL 112a standards yielding typical uncertainties of $\pm 0.07\%$ ($1\sigma, SD$). The results are reported as the conventional δ notation as a permil (‰) deviation from the NBL 112a standard (0.0072526).

U and Th blanks were tested separately for three steps in the procedure: the sodium peroxide sintering, the NdF_3 precipitation, and the ion column separation. Blank values were negligible ($< \text{few ppt}$), with measured Th yielding $< 0.01\%$ of the U signal after column separation, which assures no interference of a ^{232}Th -hydride on the 233 mass.

2. Analysis of $^{234}\text{U}/^{238}\text{U}$:

Analyses were performed using a MC-ICP-MS, Nu Plasma I, Nu instruments, equipped with 12 faraday cups and 3 ion counters (ICs). The samples were introduced to the MC-ICPMS through an Aridus II desolvating nebulizer (Cetac technologies) sample introduction system with a PFA nebulizer of $50\mu\text{l}/\text{min}$. Instrumental mass bias was corrected using the conventional $^{235}\text{U}/^{238}\text{U}$ ratio value (0.0072526). Using a different ratio for the correction has negligible effect on the reported $^{234}\text{U}/^{238}\text{U}$ ratios. Each measurement consisted of 15 cycles, each with integration time of 10s, yielding a typical analytical uncertainty of 1.2% (1σ).

3. Results

The results are given in Table 1. The total U content of the five phosphorite samples is in the range of 63-328 ppm, most of which (63-80%) is U(IV) (Fig. 2). The $\delta^{238}\text{U}$ of the bulk samples ranges between -0.42 and -0.85. The corresponding U(IV) values are only slightly higher, but those of U(VI) are consistently lower between -0.64 and -1.07 (Fig. 3). The $\delta^{234}\text{U}$ total values show little variability and are scattered around equilibrium (between -10 and 20). $\delta^{234}\text{U}(\text{IV})$ values are slightly lower (-100 to -240) and those of $\delta^{234}\text{U}(\text{VI})$ are significantly higher between 490 and 2050 (Fig. 3). Combining the different fractions, the $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ show an overall negative correlation (Fig. 4).

The value of the total $\delta^{238}\text{U}$ calculated from the $\delta^{238}\text{U}(\text{IV})$ and $\delta^{238}\text{U}(\text{VI})$ and their

percentages (Calc. $\delta^{238}\text{U}_\text{T}$) agrees, within uncertainty, with bulk $\delta^{238}\text{U}$ values obtained by independent analysis ($\delta^{238}\text{U}_\text{T}$) (Table 1). Similarly, the calculated $\delta^{234}\text{U}_\text{T}$ generally agrees with the measured value, even though the former displays slightly higher values.

4. Discussion

4.1 $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ trends and correlations

The bulk phosphorite $\delta^{238}\text{U}$ corresponds with the known range of modern seawater or fossil coral compositions (except for one sample (KP65) yielding a lower value), while the hexavalent phases display $\delta^{238}\text{U}$ of 0.2-0.8‰, consistently lower than their tetravalent counterpart (Fig. 3). The observed $\delta^{238}\text{U}$ offset between the two oxidation states is independent of the relative U(VI) content (Fig. 2) and is in agreement with the range observed in other natural systems (Fig. 4), corresponding with theoretical predictions based on the nuclear field shift effect (Bigeleisen, 1996; Schauble, 2007), lab experiments (Basu et al., 2014; Stirling et al., 2015; Stylo et al., 2015) and previous mass-balance studies (e.g., Andersen et al., 2016, 2015, 2014, Bopp et al., 2010, 2009; Holmden et al., 2015; Tissot and Dauphas, 2015).

The bulk $\delta^{234}\text{U}$ values are close to equilibrium, noticeably lower than seawater values, *a-priori* reflecting a formation age of about 1Ma or older. Yet these values reflect the mass balance between extremely high $\delta^{234}\text{U}(\text{VI})$ values and negative $\delta^{234}\text{U}(\text{IV})$ values below equilibrium (Fig. 3).

Interestingly, the overall $\delta^{238}\text{U}$ - $\delta^{234}\text{U}$ correlation of the phosphorites is negative, almost perpendicular to the trend of the rest of the compiled data presented in Fig. 4. In more detail though, the dispersal of the phosphorite tetravalent and bulk U is dominated by changes in $\delta^{238}\text{U}$ with relatively little variation of $\delta^{234}\text{U}$. The latter therefore correspond to the general trend displayed by other sample groups. Thus, the somewhat unique $\delta^{238}\text{U}$ - $\delta^{234}\text{U}$ trend of the phosphorite samples is controlled by the ^{234}U -excess in the hexavalent species, which provides important hints to their history and the mechanisms of U isotope fractionation. Note that since none of the other data sets presented in Fig. 4 reported separately U(VI) and U(IV) values, it can only be assumed that their U(VI) fraction is similarly high. Indeed, one subgroup of speleothem samples presented in Fig. 4 (empty triangles; Stirling et al., 2007) displays

an overall negative trend that is in agreement with the one displayed by the phosphorites. It has been suggested (Stirling et al., 2007) that mineral surface weathering could remove both the recoil-produced ^{234}U and lattice bound ^{235}U into the aqueous phase (i.e., in the case of groundwater leaching), resulting in a negative linear correlation between $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$. This explanation could be in accord with the results of an additional compilation of river sediments whose composition was argued to reflect the average crust values in the watershed of each river together with the transport-related weathering processes (Andersen et al., 2016). Yet, since the phosphorite samples were never exposed to such weathering processes and moreover, show unequivocal evidence for the dominance of the redox state on the relative loss of ^{235}U , it is unlikely that surface weathering controls the $\delta^{238}\text{U}$ - $\delta^{234}\text{U}$ trend in this case. By contrast, seawater, plankton, sediment trap material and bottom sediments from the seasonally anoxic Saanich Inlet, show a positive correlation whereby the solid samples yield lower values of $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ relative to coeval seawater (Holmden et al., 2015). In the case of the Saanich Inlet this correlation was interpreted to reflect a mixing array between authigenic components (with seawater composition) and low- $\delta^{234}\text{U}$, detrital, U end members. Placzek et al. (2016) reported extremely large $\delta^{238}\text{U}$ differences between reduced and oxic groundwater associated with uranium ores in Texas, again, suggesting the dominance of redox processes on $\delta^{238}\text{U}$ fractionation.

4.2 $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ fractionation mechanisms

Evidently, the $\delta^{238}\text{U}$ - $\delta^{234}\text{U}$ correlations are complex and follow two different trends: a negative “general” trend displayed by the phosphorites (and possibly by the speleothems), and a secondary positive (but negligible) trend. The fractionation of ^{235}U and ^{238}U between the two oxidation states could be the result of 1) a partial *oxidation* of what originally was reduced uranium in apatite, 2) partial *reduction* of originally hexavalent sea-water uranium (Stylo et al., 2015; Wang et al., 2015), similar to the process envisioned by Andersen et al. (2014), or 3) equilibrium removal of U in its two oxidation states from sea-water into the phosphorite. The third possibility can be readily rejected because it is very unlikely that the redox of the phosphorite forming sediments varies so significantly between locations as to accommodate such variable U(IV) percentages.

In this context it is noted that phosphorites form and accumulate in high

productivity marine environments, where an abundance of organic matter enhances oxygen consumption and results in the development of anoxic conditions. Accordingly, most if not all initial U incorporated into the phosphorite would have been in reduced (IV) form. This is supported by the high content of U(IV) in our samples (which are all very young) ranging between ~60-80% (Fig. 2). As mentioned, the studied samples are initially assumed to be older than at least ~1Ma because their bulk $\delta^{234}\text{U}=0$, i.e., is in secular equilibrium (although we challenge this assumption in the following discussion). Hence, over time, the decay of $^{238}\text{U}(\text{IV})$ could have resulted in the oxidation of the decay product, ^{234}U , and yielded high $\delta^{234}\text{U}(\text{VI})$. It should be further mentioned that typically, the decay process in fine clastic solid particles results in the loss of ^{234}U from the sample (the “recoil effect”). Yet, in the case of large samples, where there is no loss of ^{234}U , but only internal redistribution, the ^{234}U accumulates in the U(VI) fraction within the sample, yielding extremely high $\delta^{234}\text{U}$ values (Figs. 3,4,5). There is no reason to assume that a similar process would not be observed in other large bulk samples from other settings, although if they do not contain considerable U(IV) to begin with, it would be hard to isolate the “recoiled” ^{234}U .

The different $\delta^{238}\text{U}$ for U(IV) and U(VI) (Fig. 3) suggests that these are related to the effect of the nuclear field shift, which predicts that elements 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 $\delta^{238}\text{U}$ of U(IV). This is indeed the case observed here (Fig. 4), where the evidence shows that the $\delta^{238}\text{U}$ fractionation occurred (also) during U *oxidation* and that the final differences of $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ between both oxidation states reflect *the combined effect of the depositional nuclear field shift, the recoil-related oxidation, and overall oxidation of uranium*. It is unlikely that direct reduction of U(VI) from seawater *after* the formation of the phosphorite induced additional $\delta^{238}\text{U}$ fractionation.

4.3 Model of ^{238}U - ^{235}U - ^{234}U distribution and fractionation in seafloor phosphorites

In the following section we present a series of calculations describing the evolution of U in seafloor phosphorites. For the purpose of developing a quantitative model we assume that the formation of the phosphorite samples was instantaneous relative to the

geological timescale and that at the time of formation the phosphorite $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ were homogenous in the samples and identical to seawater compositions (-0.4 and 147, respectively). We also assume that the relative ratio between U(IV) and U(VI) was similar to present, i.e., any oxidation and related isotopic fractionation had only a negligible quantitative impact on the U(IV) and U(VI) distributions, but is sufficient for significant changes in the corresponding $\delta^{238}\text{U}$ values.

The conceptual model of the evolution of uranium isotopes in these samples is summarized in Fig. 5, where the primary processes to be considered are the radioactive decay of ^{238}U , ^{235}U and ^{234}U , the preferential oxidation of ^{235}U over ^{238}U , and the additional transition of ^{234}U between the (IV) and (VI) oxidation state as a result of the recoil effect. In addition, we tentatively assume that a fraction of the decay products of $^{238}\text{U(VI)}$ are lost into surrounding seawater due to the recoil effect.

The rate of change in the abundance of the different nuclides is described in equations 1-4:

$$(1) \frac{d^{238,5}\text{U}_{(IV)}}{dt} = -\lambda_{238,5}N_{238,5(IV)} - k_{238,5}N_{238,5(IV)}$$

$$(2) \frac{d^{234}\text{U}_{(IV)}}{dt} = (1 - F_\alpha)\lambda_{238}N_{238(IV)} - \lambda_{234}N_{234(IV)} - k_{234}N_{234(IV)}$$

$$(3) \frac{d^{238,5}\text{U}_{(VI)}}{dt} = -\lambda_{238,5}N_{238,5(VI)} + k_{238,5}N_{238,5(IV)}$$

$$(4) \frac{d^{234}\text{U}_{(VI)}}{dt} = F_\alpha\lambda_{238}N_{238(IV)} + (1 - f_\alpha)\lambda_{238}N_{238(VI)} - \lambda_{234}N_{234(VI)} + k_{234}N_{234(IV)}$$

where N_i marks the number of atoms of nuclide i , λ_{238} , λ_{235} and λ_{234} are the corresponding decay constants (1.55125E-10, 9.8458e-10, and 2.8263E-06 y^{-1} , respectively; Cheng et al., 2000; Jaffey et al., 1971), and k_i is the oxidation rate of nuclide i . F_α and f_α are the recoil fraction factors for $^{238}\text{U(IV)}$ and $^{238}\text{U(VI)}$, respectively, representing the fraction of ^{238}U -decays that result in one of the daughter isotopes (either ^{234}Th or ^{234}U) being lost. The measured fraction of U(IV) in the

samples is in the range of 63-80% (Table 1) and we arbitrarily pick the high range (80%) to start off the calculations.

We first consider a scenario where no oxidation takes place, i.e., $k_i=0$, and where we use a value of 0.17 for both F_a and f_a , corresponding to the average offset of $\delta^{234}\text{U(IV)}$ from equilibrium (Table 1). The assumption here is that all the nuclides in the (IV) state affected by recoil were oxidized and transferred to the (VI) state, and we assume that the same process resulted in the loss of $^{234}\text{U(VI)}$, though this is harder to observe. This scenario was simulated for a time period of 1Ma and the results are presented in Fig. 6a,b (scenario parameters detailed in Table 2). Accordingly, $\delta^{234}\text{U(IV)}$ decays from initial seawater values (red curve in Fig. 6a) while $\delta^{234}\text{U(VI)}$ is gradually enriched in ^{234}U (blue curve). Both the latter, as well as the evolution curve of the bulk fraction (black curve) reach steady state values after about 1Ma (Fig. 6a). By contrast, because $k_i=0$, all three evolution curves of $\delta^{238}\text{U}$ are identical, corresponding to the lack of mobility between the redox states, reflected by the black curve in Fig. 6b. When imposing shifts from U(IV) to U(VI) due to oxidation, the $\delta^{238}\text{U}$ of both redox states displays unique and contrasting evolution, whereby $\delta^{238}\text{U(IV)}$ evolves toward more positive values while $\delta^{238}\text{U(VI)}$ evolves towards more negative values (dashed red and blue curves, respectively, in Fig. 6b). In this scenario (#2; Table 2), the composition of the bulk remains similar to before and corresponds with the black curve. Although a wide range of k_i values could be applied, we find that using $k_{238}=6.5\text{E-}10$, $k_{235}=9.5\text{E-}10\text{ y}^{-1}$ and $k_{234}=k_{238}$, yields the results that best fit the measured results. Iterations around these values yield similar results with little effect on the conceptual understanding of these processes, and in fact, it appears that these results are much more sensitive to the initial fraction of U(VI) than to the exact choice of oxidation rate (k_i). For example, when using an initial U(IV)=63% (corresponding to the lowest value measured in this study; Table 1), but keeping the rest of the parameters unchanged (scenario 3; Table 2) the $\delta^{234}\text{U(VI)}$ approaches an unrealistically low value of 280 (Fig. 6c), and the $\delta^{238}\text{U(IV)}$ displays a very small increase over time, rather than an expected decrease (Fig. 6d), and does not correspond with the values measured in the phosphorites. Further iterations with the discussed parameters do not yield reasonable fit between model and observations; primarily, the values measured for $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ in each oxidation state do not converge to a similar age range. Hence, it is reasonable to suggest that because of the

high productivity and high content of organic matter occurring in the waters from which the phosphorites formed, it could be possible that some fraction of the initial $\delta^{238}\text{U(IV)}$ originated in marine organics, which are characterized by lower $\delta^{238}\text{U(IV)}$ relative to seawater (Stirling et al., 2015). Assuming an initial $\delta^{238}\text{U(IV)}$ ca. -0.9 yields much better compatibility between model and observations (Fig. 6f). It is important to note that incorporation of a fraction of biologically fractionated $\delta^{238}\text{U(IV)}$ into the initial phosphorite, would not be likely to influence the initial $\delta^{234}\text{U(IV)}$ composition, nor would it have an effect on the U(VI) phases.

In addition, the large $^{234}\text{U(VI)}$ -excess indicates that once accumulated in the (VI) state, very little $^{234}\text{U(VI)}$ was lost to the surrounding aqueous phase. This scenario can be described by $f_a=0$, and F_a between 0.24, corresponding to the lowest measured $\delta^{234}\text{U(IV)}$ value (scenario 4, full curves in Fig. 6e), and 0.4 (which yields better agreement with the high range of measured $\delta^{234}\text{U(IV)}$ values; scenario 5, dashed curves in Fig. 6e). The measured bulk $\delta^{234}\text{U}$ values are approximately at secular equilibrium suggesting an age of *at least* 1Ma. Yet as discussed above, the $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ values of the measured and calculated model values converge reasonably well over a much shorter time frame between ~0.2-1Ma (Fig. 6e,f). Thus, the separated $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ oxidation states allow deriving the approximate formation age of these seafloor phosphorites. Moreover, it is noted that one of the samples (KP65) displays the most extreme values within this data set ($\delta^{238}\text{U(IV)}=-0.81$, $\delta^{238}\text{U(VI)}=-1.07$, $\delta^{234}\text{U(VI)}=2050$, $\delta^{234}\text{U(IV)}=-240$), and rejecting it yields better convergence of the extrapolated ages for the other sample.

Clearly, variations in the different constant k values, U(IV) contents, and F_a and f_a values for different samples from completely different environments around the world, along side analytical uncertainties, could explain the large deviations from a unique result (i.e., the data of each sample converging toward a singular age), and we thus refrain from investigating the exact fit of parameters for each sample. Importantly, it is shown that isotopic fractionation between U(IV) and U(VI) in seafloor phosphorites with a substantial initial U(IV) content is controlled by both ongoing bulk sediment oxidation as well as recoil-related oxidation, and that these differences can be used to evaluate the age of marine phosphorites.

5. Conclusions

The content of bulk, reduced and oxic species of uranium, and their corresponding $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ compositions were studied in five seafloor phosphorite samples. Tetravalent U comprises 63-80% of the samples, with $\delta^{238}\text{U}(\text{IV})$ being consistently higher than $\delta^{238}\text{U}(\text{VI})$ in each sample (-0.5 to -0.81, and -0.64 to -1.07, respectively), confirming by direct measurement, that the fractionation between ^{235}U and ^{238}U is redox related, in accord with the Bigeleisen - Schauble hypothesis.

Upon formation the phosphorites are dominated by U(IV), which undergoes continuous direct oxidation of U(IV), as well as additional oxidation of the recoil product of the $^{238}\text{U}(\text{IV})$ decay, i.e., $^{234}\text{U}(\text{IV}) \rightarrow ^{234}\text{U}(\text{VI})$. These processes result in a net transfer of U to the (VI) state, with preference to ^{235}U (over ^{238}U) and ^{234}U (recoil product), although a different process controls each of them. While $\delta^{234}\text{U}(\text{IV})$ displays values lower than equilibrium (-100 to -240), the very high $\delta^{234}\text{U}(\text{VI})$ values between 490-2050 suggest that despite significant redistribution of uranium within the phosphorites, very little of it is lost to the surrounding seawater, resulting in the accumulation of excess $^{234}\text{U}(\text{VI})$. Moreover, although both U(IV) and U(VI) phases originated from coeval seawater and should therefore be expected to have the same initial isotopic composition, the observations and model results suggest that in fact, the initial $\delta^{238}\text{U}(\text{IV})$ was lower than that of seawater (and $\delta^{238}\text{U}(\text{VI})$; ca. -0.5%), displaying a value of approximately -1%, due to the partial incorporation of marine organic material consisting of biologically fractionated U(IV).

The persistent relationship of $\delta^{238}\text{U}_{(\text{IV})} > \delta^{238}\text{U}_{(\text{VI})}$, opens the possibility for reconstructing past anoxic conditions even when they are masked by subsequent weathering and oxidation. Moreover, this relationship enables estimating the formation age of the samples, which cannot otherwise be determined because their bulk $\delta^{234}\text{U}$ composition is at secular equilibrium.

Acknowledgments

We benefited greatly from the efforts by A. Starinsky, A. Katz and M. Stein as well as two extremely useful critical reviews by E. Schauble and an anonymous reviewer. Their help is gratefully acknowledged. Funding was provided by the USA-Israel Bi-National Science Foundation (grant #2010441 to Y.K. and A.T.) and EU Marie Curie CIG (grant #618350 to A.T.).

Tables

Sample #	KP26	KP51	KP57	KP63	KP65
Locality	Off California	Off California	Aghuls Bank	Chatham Rise	Chatham Rise
U_T (ppm)	83	63	286	328	144
$\pm$	2	1	6	7	3
$U_{(IV)}$ (ppm)	52	43	222	264	114
$\pm$	1	1	4	5	2
$U_{(IV)}$ (%)	63	68	77	80	79
$\delta^{238}U_T$	-0.501	-0.49	-0.42	-0.65	-0.85
$\delta^{238}U_{(IV)}$	-0.504	-0.43	-0.26	-0.51	-0.81
$\delta^{238}U_{(VI)}$	-0.74	-0.64	-1.03	-1.06	-1.07
Calc. $\delta^{238}U_T$	-0.59	-0.5	-0.44	-0.62	-0.86
$\delta^{234}U_T$	10	10	-10	0	20
$\delta^{234}U_{(VI)}$	490	490	1250	1550	2050
$\delta^{234}U_{(IV)}$	-100	-150	-160	-200	-240
Calc. $\delta^{234}U_T$	30	10	50	30	40

Table 1- Data summary. Five phosphorite samples were measured. Sample numbers and locality follow Kolodny and Kaplan (1970). Typical isotope ratio uncertainties (1σ) are $\pm 0.07\%$ for $\delta^{238}U$, and $\pm 1.2\%$ (activity ratio) for $\delta^{234}U$.

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
$\delta^{238}U_{(IV)initial}$	-0.4	-0.4	-0.4	-0.4	-1
$K_{238}(y^{-1})$	0	$6.5E-10$	$6.5E-10$	$6.5E-10$	$6.5E-10$
$K_{235}(y^{-1})$	0	$9.5E-10$	$9.5E-10$	$9.5E-10$	$9.5E-10$
$K_{234}(y^{-1})$	0	$6.5E-10$	$6.5E-10$	$6.5E-10$	$6.5E-10$
$U_{(IV)}$ (%)	80	80	63	80	80
F_a	0.17	0.17	0.17	0.24	0.4
f_a	0.17	0.17	0.17	0	0

Table 2- Model parameters. The parameters defining the five different scenarios presented in Fig. 6 are detailed. In all scenarios, the initial $\delta^{234}U$ and $\delta^{238}U$ of both oxidation states was assumed to be that of seawater (147, and -0.4, respectively) except for scenario 5, where the initial $\delta^{238}U_{(IV)}$ was assumed to be -1 (see text for details).

Figure captions

Figure 1. Work flow sheet.

Figure 2. Relative content of bulk and (IV) uranium.

Figure 3. $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$ the samples.

Figure 4. $\delta^{238}\text{U}$ vs. $\delta^{234}\text{U}$. Sources: (a) Stirling et al., 2007, (b) Holmden et al., 2015, (c) certified reference value, (d) Placzek et al., 2016. Black Sea and Cariaco basin data from Andersen et al. (2016). Additional $\delta^{238}\text{U}$ - $\delta^{234}\text{U}$ values of modern and paleo (sediments) seawater, corresponding to the presented seawater array, are reported by Goto et al. (2014) and Romaniello et al. (2013) but not shown here for clarity. In addition, not shown is a compilation of river particle samples yielding a range of -0.72 to 0.06 and 6 to 1632 for $\delta^{238}\text{U}$ and $\delta^{234}\text{U}$, respectively (Andersen et al., 2016), which is thought to represent the average crust composition in the watershed of each river, with little fractionation during transport. The thick black-dashed curve marks the spread of data from phosphorite samples reported in this paper.

Figure 5. Conceptual description of fractionation mechanisms between U(IV) and U(VI). The basic working assumption, and the reason the seafloor phosphorites are advantageous in this case, is that the initial samples formed under anoxic conditions with all, or almost all, U as U(IV). The abscissa on the diagram is the direction of radioactive decay (such as ^{238}U to ^{234}U); the ordinate is the direction of oxidation (such as U(IV) oxidizing to U(VI)). The decay of ^{238}U to ^{234}U involves a partial oxidation of the decay product. The oxidation of U involves also a change in $\delta^{238}\text{U}$. See more details in the text.

Figure 6. Model simulations of the $\delta^{238}\text{U}$ vs. $\delta^{234}\text{U}$ fractionation between U(IV) and U(VI). Black, red and blue lines, represent bulk U(IV) and U(VI), respectively. For reference, the measured sample values are presented along the y-axis as black, red, and blue circles, respectively. Panels (a) and (b) follow the parameters of scenarios 1 and 2 detailed in the text and in Table 2. Scenario 1 assumes no direct oxidation and

490 hence no fractionation of $\delta^{238}\text{U}$ (i.e., both oxidation states evolve with the same values,
491 described by the black line in (b)). The only fractionation occurs due to the recoil
492 effect and the ongoing depletion of $^{234}\text{U}(\text{IV})$ and corresponding enrichment of
493 $^{234}\text{U}(\text{VI})$. In scenario 2, imposed oxidation of $^{238}\text{U}(\text{IV})$ results in the divergence of
494 $\delta^{238}\text{U}$ between both oxidation states (dashed curves), with the bulk composition
495 remaining the same as scenario 1. Scenario 3 is different to scenario 2 in the initial
496 fraction of $\text{U}(\text{IV})$, reflecting the dominance of this parameter over the fractionation
497 values. In scenarios 4 and 5 (full and dashed lines, respectively), the model is tuned to
498 present the optimal fit to the data, by applying changes to the recoil factors in both
499 oxidation states. The extrapolation of the measured data onto the model calculations
500 for scenarios 4 and 5 in (e) and (f), suggests that the age of the phosphorite samples is
501 less than 1 Ma, which is surprising given the secular equilibrium displayed by the
502 bulk $\delta^{234}\text{U}$.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6