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978-1-108-73111-9 — The Uranium Isotope Paleoredox Proxy
Kimberly V. Lau , Stephen J. Romaniello , Feifei Zhang
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1 Introduction

Uranium is naturally redox sensitive: its solubility varies between its two main oxidation states, where U(VI) is soluble and U(IV) is insoluble. The intermediate U(V) is sparingly present and undergoes rapid disproportionation into U(IV) and U(VI). Because the solubility of U in natural waters is dependent on its oxidation state, U concentrations ([U]) have been used to track global marine redox conditions using chemical sediments, such as calcium carbonate precipitates (e.g., Russell et al., 1994). Such interpretations, however, are not straightforward because [U] reflect local depositional factors in addition to the size of the seawater U reservoir. Specifically, the distribution coefficient of U is sensitive to the original $CaCO_3$ polymorph as well as U speciation, which is pH dependent (Meece and Benninger, 1993; Russell et al., 2004).

Additional constraints on seawater U may be obtained through its isotopic ratios. Uranium has three naturally occurring radioactive isotopes: ^{238}U (99.28%), ^{235}U (0.72%), and ^{234}U (0.0054%), with half-lives of ~4.46×10^9, ~704×10^6, and ~245×10^3 years, respectively. Because ^{234}U has a short half-life and is readily expelled from minerals via alpha recoil during the decay of ^{238}U, U-series disequilibria and the ^{234}U/^{238}U ratio have been used to track the rate and timescale of oceanographic processes on 1–800 kyr time scales (e.g., Henderson and Anderson, 2003). Because uranium is the heaviest natural element, mass-dependent isotopic fractionation of U is relatively small, and fractionation is instead dominated by mass-independent effects related to relative differences in the size and shape of odd- and even-mass isotopes. This anomalous pattern of isotopic behavior was first observed in redox ion-exchange experiments (Fujii et al., 1989; Nomura et al., 1996). Bigeleisen (1996) subsequently provided a theoretical description for this nuclear volume effect, and these calculations were later supported by the work of Schauble (2006) and Abe et al. (2008). This isotopic fractionation was observed in natural environmental samples by Stirling et al. (2007) and Weyer et al. (2008), with results expressed in delta notation as:

$$\delta^{238}\mathrm{U} = \left(\frac{^{238}\mathrm{U}}{^{235}\mathrm{U}_{\mathrm{sample}}} \Big/ \frac{^{238}\mathrm{U}}{^{235}\mathrm{U}_{\mathrm{standard}}} - 1\right) \times 1000 \tag{1.1}$$

Although the absolute value of ^{238}U/^{235}U ratios varies with time due to radioactive decay, values expressed as δ^{238}U are time invariant because ^{238}U and ^{235}U undergo decay in samples and the reference material at the same rate. Because of this, a 1‰ fractionation of ^{238}U/^{235}U in Archean-age sediments is still preserved as a 1‰ value measured in the laboratory today.

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The first effort to use δ^{238}U to track redox conditions was in black shales deposited during oceanic anoxic event 2 (OAE2), a period of ocean deoxygenation at the Cenomanian–Turonian boundary (~94 Ma; Montoya-Pino et al., 2010). This was followed by measurements of δ^{238}U in shallow-marine carbonate rocks, with the first record from the end-Permian mass extinction (~252 Ma) suggesting that the onset of ocean anoxia was concurrent with the extinction (Brennecka et al., 2011b). This record has since been extended from the Middle Permian through the Middle Triassic, and the observed trends in δ^{238}U have been replicated in multiple locations across oceanic basins and depositional environments (Lau et al., 2016; Elrick et al., 2017; Zhang et al., 2018a, 2018b, 2018c). At the time of publication, 25 δ^{238}U papers have been published that span the last 4 Ga (Kendall et al., 2013; Wang et al., 2018), with 16 focused on the carbonate rock record. Combined, these efforts have helped to elucidate how the redox conditions of the oceans and atmosphere have evolved through time.

Other commonly used inorganic geochemical paleoredox proxies include enrichments of other redox-sensitive elements and their isotopes. Popular proxies include iron speciation; rhenium (Re), vanadium (V), and molybdenum (Mo) concentrations; and rare earth element (REE) enrichments. The list of isotopic proxies is growing and includes iron (Fe), chromium (Cr), molybdenum (Mo), and sulfur (S) isotopes. Uranium is unique among these proxies for the following reasons. First, its redox potential is similar to iron reduction – requiring an absence of oxygen but not euxinic (i.e., sulfidic) conditions – meaning that it potentially can capture conditions that are particularly relevant for typical marine macrofauna. In contrast, iron speciation can track the prevalence of Fe^{2+} versus H_2S, and Mo is representative of H_2S concentrations. Second, its mode of reduction is unique among the elements. For example, Mo and V are generally quantitatively removed from euxinic water columns, meaning that their isotopic ratios directly reflect water column compositions. In contrast, water-column U is not quantitatively reduced in any modern setting, resulting in variable offsets between seawater and reducing settings that complicate interpretations of δ^{238}U.

Third, most or all U reduction occurs at the sediment–water interface rather than in the water column. Although U reduction is thermodynamically predicted in modern anoxic water columns, U(IV) has not been observed in the Black Sea water column, possibly because of limited mineral surfaces or because reduction is inhibited by aqueous complexation of U(VI) (Anderson et al., 1989). Thus, U is inferred to be a tracer of bottom-water anoxia – instead of water-column conditions – which is important for the habitability of benthic and epifaunal marine environments. Sedimentary U cycling can be decoupled from water-column conditions if organic carbon burial rates are high, stimulating U reduction in sediments (McManus et al., 2005; Morford et al., 2009). Fourth, U has a long residence time in the ocean (~450 kyr today; Ku et al., 1977), and thus acts as a conservative element in contrast to many other elemental and isotopic tracers. This is supported by uniform δ^{238}U values in the modern ocean (summarized in Andersen et al., 2016). In sum, if it is possible to reconstruct ancient seawater δ^{238}U, it may be possible to quantitatively estimate the global area of anoxic seafloor that is linked to U reduction.

As a global proxy, δ^{238}U provides unique information that cannot be inferred from concentrations alone, which are sensitive to factors such as sedimentation rate and mineralogy, or from explicitly local proxies such as iron speciation and REE anomalies, which reflect only the local depositional environment. As described in detail below, δ^{238}U can also be tracked using carbonate rocks, whereas many other proxies are limited to organic-rich shales. For these reasons, despite their recent arrival in the paleoredox toolkit, U isotopes have expanded in popularity and potential as a tracer of redox conditions through Earth history.

2 Systematics of the Uranium Isotope Paleoredox Proxy

The isotopic fractionation resulting from the nuclear volume effect is estimated to range from 0.7 to 1.4‰ ($\Delta = \delta^{238}\mathrm{U}_{\mathrm{U(IV)}} - \delta^{238}\mathrm{U}_{\mathrm{U(IV)}}$; e.g., Schauble, 2006; Abe et al., 2008; Stylo et al., 2015; Brown et al., 2018) with preferential removal of ^{238}U into reducing sediments. The δ^{238}U value of U in modern seawater (–0.39 ± 0.01‰; 2 S.D.) is controlled by the sources and sinks of U to the ocean (Figure 1; e.g., Weyer et al., 2008; Tissot and Dauphas, 2015; Andersen et al., 2016, 2017). The major input flux is riverine delivery of weathered U with a mean δ^{238}U of –0.26 ± 0.32‰ (1 S.D.) and a flux-normalized value of –0.34‰ (Andersen et al., 2016), which generally reflects the bulk earth δ^{238}U of –0.31 ± 0.03‰ (Andersen et al., 2015) and bulk continental crust of –0.28 to –0.30 ± 0.03‰ (Tissot and Dauphas, 2015). Minor input fluxes include dust and submarine groundwater discharge, where the δ^{238}U of dust is expected to be similar to crustal values and no constraints have been published for the latter.

There are numerous processes that remove U from the ocean. Their relative proportions, calculated from the average values of published budgets (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003), and their isotope values are shown in Figure 1. Volumetrically, the most important flux is removal to sediments deposited in reducing/hypoxic settings (also referred to as the suboxic flux), which

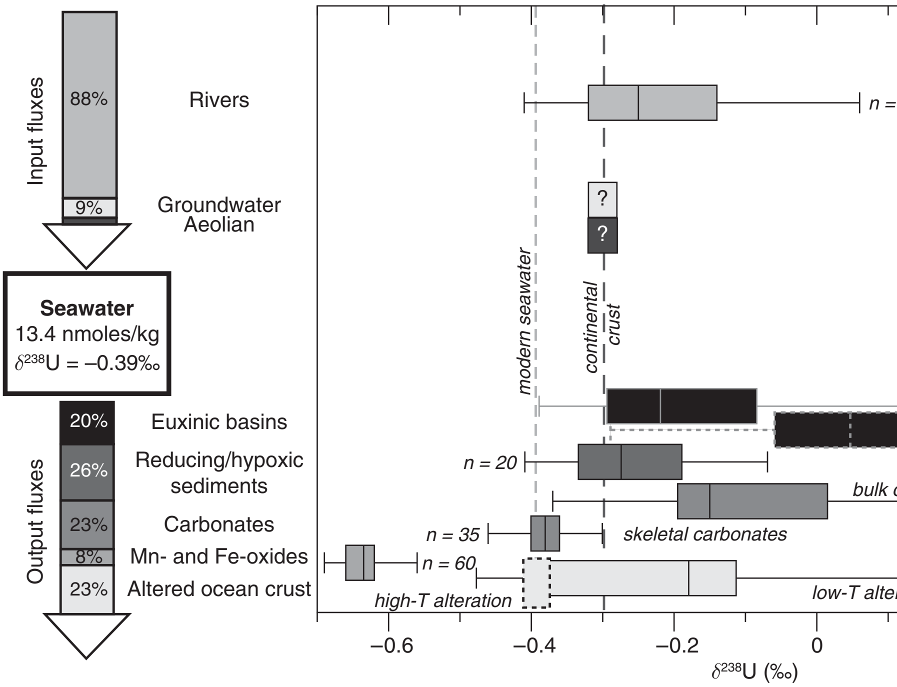

Figure 1 Overview of the modern uranium budget and the δ^{238}U of major fluxes. On the left sid major input and output fluxes of uranium to the ocean, with the height of the box sized to its relative

comprises ~26% of the total U output and has a fractionation estimated at ~0.15‰ (Weyer et al., 2008; Andersen et al., 2016). The most isotopically distinct flux is removal of U(IV) via sediments deposited in euxinic settings, which represents ~20% of U removal in total and has the most positive δ^{238}U value. The fractionation from seawater into euxinic sediments has been proposed to be 0.5 to 0.7‰ from modern observations (Andersen et al., 2014; Holmden et al., 2015; Noordmann et al., 2015; Rolison et al., 2017). Because most U reduction occurs in sediments, this observed (or effective) fractionation differs from the predicted (or intrinsic) fractionation because of diffusion limitation of U(VI) into shallow sediments (Clark and Johnson, 2008; Andersen et al., 2014).

Oxidized U can be incorporated into carbonate rocks, removing ~23% of seawater U in total with a fractionation described in detail in Section 3.1.

Caption for Figure 1 (cont.)

Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003). To the right are box-and-whisker plots of δ^{238}U data for each flux, with the range, median, and quartile values indicated. Riverine data are from Stirling et al. (2007), Noordmann et al. (2016), Tissot et al. (2015), and Andersen et al. (2016). Groundwater and aeolian δ^{238}U may represent bulk continental crust, which has a value of –0.29‰ (Tissot et al., 2015). A selection of euxinic basin δ^{238}U are plotted, from sites for which bottom-water δ^{238}U is known. These include Kyallren Fjord and Landsort Deep (Noordmann et al., 2015), Saanich Inlet (Holmden et al., 2015), and the Black Sea (Rolison et al., 2017). Bottom-water δ^{238}U data were not measured by Weyer et al. (2008), Montoya-Pino et al. (2010), and Andersen et al. (2014), and so these data are not shown. Because waters in modern euxinic basins are more negative than the open ocean due to reservoir drawdown, we also show the relative offset of sediments in this sink relative to bottom-water δ^{238}U in the dashed box. Reducing/hypoxic sediments are from high-productivity regions from the Washington Coast (Andersen et al., 2016) and the Peru Margin (Weyer et al., 2008). Bulk carbonate sediments less than 1 Ma in age are from Romaniello et al. (2013), Chen et al. (2018a), and Tissot et al. (2018). We also show δ^{238}U of modern skeletal carbonates from Stirling et al. (2007), Weyer et al. (2008), Andersen et al. (2014), and Chen et al. (2018b). The δ^{238}U of Fe and Mn oxides (ferromanganese crusts) are from Goto et al. (2014) and samples <1 Ma from Wang et al. (2016). Low-temperature alteration data are from Andersen et al. (2015); it is assumed that no fractionation occurs during exchange with basalt at high temperature (dashed box).

Additionally, U(VI) can be adsorbed onto ferromanganese crusts – a minor flux representing 8% of U removal but with a fractionation of –0.24‰ due to a change in coordination state during sorption to Mn oxides (Brennecka et al., 2011a; Goto et al., 2014; Wang et al., 2016). Incorporation into Fe oxides, such as banded iron formations or ironstones, is included with this flux. Only a few experiments have explored isotopic fractionation during sorption to Fe oxides, showing relatively little fractionation (Stylo et al., 2015). Finally, a large proportion of U is removed via basalt alteration (or altered ocean crust). Although low-temperature alteration imparts a measurable fractionation, it comprises a smaller proportion of the total flux than does high-temperature alteration, which is assumed to have no fractionation (Andersen et al., 2015; Noordmann et al., 2016). Burial of U into oxic sediments (such as hemipelagic red clays) may impact the U budget but is poorly constrained and warrants further study. Fractionation under ferruginous conditions (anoxic but not euxinic) is also not well understood.

In sum, theoretical calculations, experimental results, and observations of geologic materials indicate that the largest fractionation of $^{238}U/^{235}U$ occurs between U(VI) and U(IV), leading to the inference that isotopic fractionation occurs during reduction (Schauble, 2006; Stirling et al., 2007; Weyer et al., 2008; Stylo et al., 2015). Thus, $\delta^{238}U$ has been proposed to track U reduction, and hence, environmental redox conditions. Fractionation has been suggested to occur only during microbial reduction and exchange of U(VI) and U(IV) (Stylo et al., 2015); however, recent experiments indicate that fractionation is possible whether reduction occurs biotically or abiotically (Brown et al., 2018). Based on this framework, more extensive anoxia – globally integrated – is expected to result in more negative seawater $\delta^{238}U$, which could then be tracked in sedimentary rock archives.

3 Materials and Methods

The $\delta^{238}U$ paleoredox proxy has been measured in various chemical and siliciclastic sediments including carbonate rocks, organic-rich shales, Mn oxide crusts, and ironstones. Like any geochemical proxy, interpretations should be supported by analyzing multiple stratigraphic sections, preferably in distinct paleogeographical locations and/or across depositional environments (Lau et al., 2016; Clarkson et al., 2018; Zhang et al., 2018b). Moreover, coupling $\delta^{238}U$ records across multiple types of lithologic archives may help to characterize seawater $\delta^{238}U$ while accounting for carbonate diagenesis and local controls on U fractionation.

3.1 Carbonate Rocks

Shallow marine carbonate rocks are ideal archives because they have been deposited continuously since ca. 3.8 Ga and are often preserved in multiple oceanic basins. Primarily comprised of calcite/aragonite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), their precipitation and preservation are linked with ocean conditions, making them suitable recorders of marine chemistry. If precipitated under geochemical conditions that result in comparable aqueous U speciation, aragonite and calcite should exhibit similar fractionation (Chen et al., 2018b). As discussed in detail in Section 4.2, the reliability of the shallow marine carbonate δ^{238}U record is supported by the reproducibility of multiple congruent δ^{238}U records showing the same pattern and absolute values in carbonate sediments deposited during the Late Permian to Early Triassic from multiple locations in the Tethys Sea and the Panthalassic Ocean (Brennecka et al., 2011b; Lau et al., 2016; Elrick et al., 2017; Zhang et al., 2018a, 2018b, 2018c).

The geochemistry of carbonate rocks is susceptible to syn- and postdepositional geochemical alteration. Early diagenesis imparts a positive offset of 0.2 to 0.3‰ relative to seawater, with a mean of 0.24 to 0.27‰ observed in late Neogene shallow-marine carbonate sediments (Romaniello et al., 2013; Chen et al., 2018a; Tissot et al., 2018). The speciation of U, which is strongly related to pH, Ca concentration, ionic strength, and alkalinity, can impart variable isotopic fractionation (Chen et al., 2017). Primary carbonate precipitates such as skeletal grains and ooids record seawater δ^{238}U with a minor fractionation (0.0 to 0.09‰; Romaniello et al., 2013; Chen et al., 2018b), with subsequent recrystallization, changes in U speciation, and incorporation of U(IV) into carbonate cements all having a role in producing the positive offset in δ^{238}U (Chen et al., 2017; Chen et al., 2018a; Tissot et al., 2018). Moreover, the microfacies in a carbonate rock may represent different phases of precipitation and recrystallization, potentially resulting in distinct initial and subsequent δ^{238}U values (Hood et al., 2016, 2018). Nonetheless, existing studies demonstrate that if diagenetic offsets are considered, the δ^{238}U of marine carbonates can faithfully track seawater patterns.

3.2 Organic-Rich Shales

Organic-rich shales (or black shales) can also be used to track seawater δ^{238}U. Because of their relatively low permeability, shales are generally thought to be less prone to diagenesis. This application relies on the assumption that the isotopic offset between U in seawater and organic-rich sediments is known. The δ^{238}U of the Middle Devonian Marcellus shale and its interbedded limestone units was used to determine the isotopic fractionation during this time interval and found that it matches estimates for this fractionation in modern settings of 0.6‰ (Phan et al., 2018). In addition to reconstructing anoxic events (such as OAE2; Montoya-Pino et al., 2010), δ^{238}U data in organic-rich shales

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have also been used to infer the rise of atmospheric pO_2 (Asael et al., 2013; Kendall et al., 2013; Yang et al., 2017; Wang et al., 2018). This is based on the premise that without atmospheric O_2, the U(IV)O_2 mineral uraninite would be weathered from continental rocks, transported as a detrital grain, and buried in sediments with the δ^{238}U value of bulk Earth. Once atmospheric pO_2 reached the threshold to oxidize uraninite, the seawater U(VI) reservoir increased, permitting U redox-cycling and isotopic fractionation.

Although δ^{238}U records in organic-rich shales show promise, these sedimentary rocks represent a complex combination of local and global signatures because U does not undergo quantitative water-column reduction. This is further complicated by the fact that organic-rich shales are often deposited in isolated, semirestricted basins. Partial drawdown of U in such environments leads to isotopic Rayleigh distillation effects, resulting in water-column δ^{238}U that is lower than global average seawater – as is observed in the Black Sea (Rolison et al., 2017). In turn, this results in authigenic δ^{238}U in Black Sea sediments that is lower than would be expected for highly reducing sediments in direct contact with global average seawater (Andersen et al., 2014). This is discussed in further detail in Section 4.3.

3.3 Other Sedimentary Archives

Alternative δ^{238}U archives include Mn oxides and iron chemical sediments (ironstones or banded iron formations). Mn oxides can be attractive because they have a well-constrained isotopic fractionation (Brennecka et al., 2011a; Goto et al., 2014) and can provide a long record of seawater δ^{238}U. Surprisingly, the ferromanganese crust record reveals that the long-term seawater δ^{238}U, integrated over ~1 Myr of time for each sample, may have been nearly invariant over the past 80 Ma (Wang et al., 2016) and suggests that redox events lasting over 1 Myr were absent. Interpretations of δ^{238}U in ironstones – deposited in the Archean and Proterozoic – offer an important glimpse of U cycling on early Earth, although the mechanisms and isotopic fractionation of U incorporation into ironstones are not as well understood as for modern ferromanganese precipitates. Last, the δ^{238}U of paleosols may fingerprint the presence of mobile U(VI) (Wang et al., 2018). A compilation of δ^{238}U in ironstones, black shales, and paleosols suggests that a shift in the Mesoarchean may be linked to the onset of uraninite oxidative weathering (Wang et al., 2018).

3.4 Analytical Methods

The ^{238}U/^{235}U proxy is commonly measured using multicollector ICP-MS with a double-spike method to correct for instrument mass bias. Ratios are typically reported relative to the CRM-145 or CRM-112a standard (CRM-145 is the solution derived from the CRM-112a metal) with an absolute $^{238}U/^{235}U$ ratio of 137.844 (Condon et al., 2010). Samples are typically spiked using the IRMM-3636 ^{233}U-^{236}U double spike, and U is separated and purified via column chromatography using a U-specific resin (e.g., Eichrom UTEVA^{TM}) following procedures introduced by Stirling et al. (2007) and Weyer et al. (2008). Because U is present as a trace element in sedimentary rocks, sample sizes are relatively large and typically range from 100 to 400 mg for shales (e.g., Kendall et al., 2013; Wang et al., 2018) and from 1 to 9 g for carbonates (e.g., Dahl et al., 2014; Azmy et al., 2015). However, analytical techniques can be improved to allow for small sample sizes (e.g., Wang et al., 2016), and some research groups utilize repeated or additional purification steps to improve the analytical precision for challenging samples (e.g., Chen et al., 2018b).

A challenge specific to carbonates is that the dissolution procedure to extract the geochemical constituents may selectively target detrital, organic, or diagenetic phases that are not representative of the primary or initial $\delta^{238}U$. Carbonates are usually leached to obtain the carbonate fraction and to avoid detrital and organic components by using a weaker acid (e.g., 0.25 to 1 M HCl, 1 M HNO_3, 1 M CH_3COOH), which varies between labs (reviewed in Tissot et al., 2018). Currently, most methods aim to completely dissolve the carbonate fraction. Although the published data do not indicate that either the acid strength or type have a measurable impact on the analyzed $\delta^{238}U$ values, there is the potential to produce data that are not directly comparable. Digestion of siliciclastic sedimentary rocks is more routine, utilizing an ashing step followed by a multistep acid dissolution procedure (see Asael et al., 2013).

4 Case Studies

4.1 Compilations across Geologic Time

A current compilation of all published $\delta^{238}U$ data from all sedimentary archives is provided in Figure 2. Despite the temporal gaps, the compiled records demonstrate several key points. First, the overall trend shows an increase in $\delta^{238}U$ values over time, with mean values in shale and carbonate rock archives increasing from –0.13‰ ($n = 292$) and –0.56‰ ($n = 205$) prior to 500 Ma to –0.06‰ ($n = 59$) and –0.37‰ ($n = 613$) after 500 Ma, respectively. These averages do not include sediments deposited within the last 3 Ma, and as a result this compilation highlights the lack of Cenozoic $\delta^{238}U$ data. Note that the oldest carbonate data are in the Cryogenian, approximately 2.8 Ga younger than the oldest shale data. Nonetheless, the observed increases in shale and carbonate $\delta^{238}U$ after 500 Ma are significant (Wilcoxon rank sum test p-value = 0.0006

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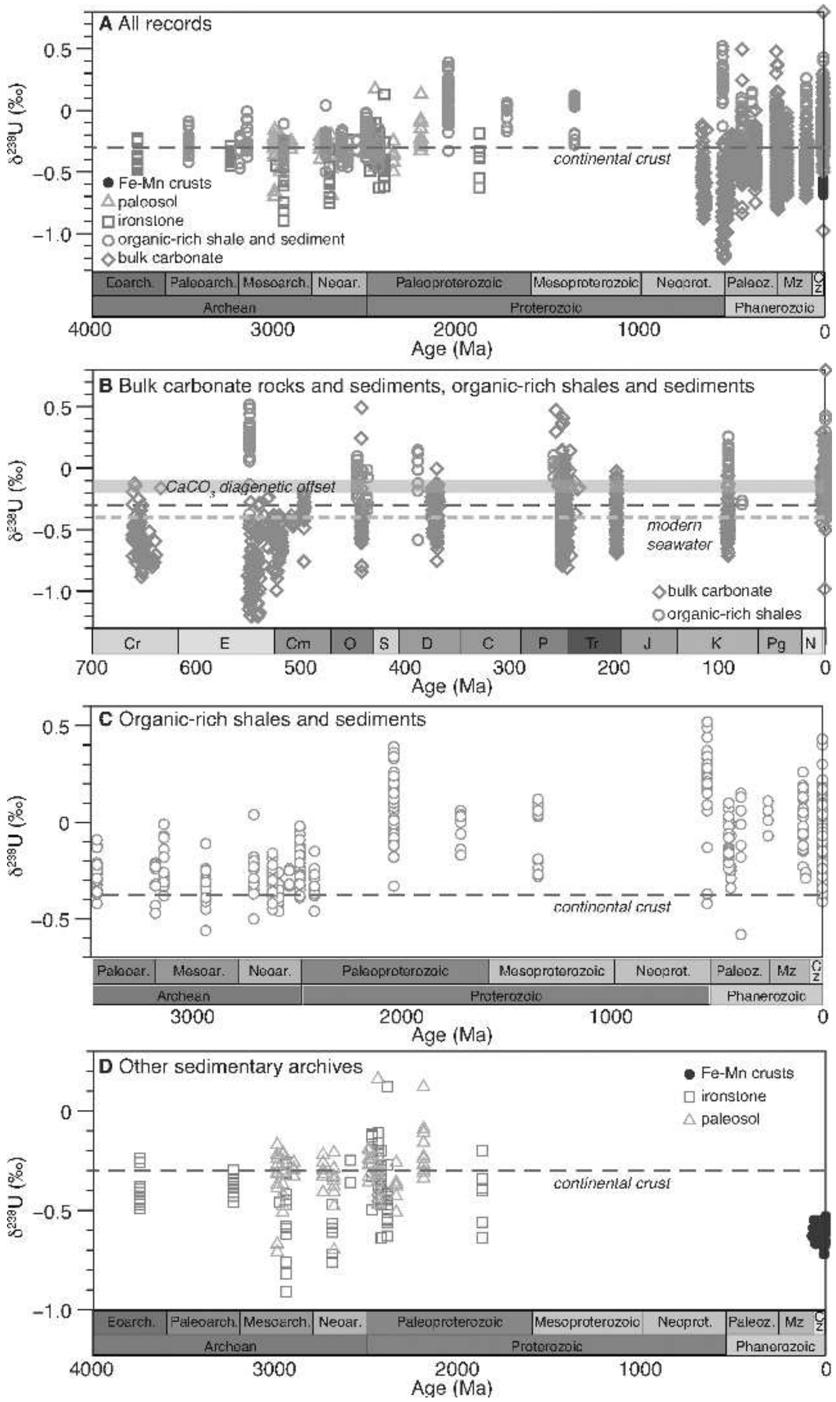

Figure 2 Compilation of δ^{238}U data. The gray dashed line marks the continental crust δ^{238}U value. **(A)** δ^{238}U in bulk carbonate rocks (diamonds), organic-rich