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2 **Uranium isotopic compositions of the crust and ocean:**
3 **Age corrections, U budget and global extent of modern anoxia.**
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Abstract (367 words):

The $^{238}\text{U}/^{235}\text{U}$ isotopic composition of uranium in seawater can provide important insights into the modern U budget of the oceans. Using the double spike technique and a new data reduction method we analyzed an array of seawater samples and 41 geostandards covering a broad range of geological settings relevant to low and high temperature geochemistry. Analyses of 18 seawater samples from geographically diverse sites from the Atlantic and Pacific oceans, Mediterranean Sea, Gulf of Mexico, Persian Gulf, and English Channel, together with literature data ($n=17$), yield a $\delta^{238}\text{U}$ value for modern seawater of -0.392 ± 0.005 ‰ relative to CRM-112a. Measurements of the uranium isotopic compositions of river water, lake water, evaporites, modern coral, shales, and various igneous rocks ($n=64$), together with compilations of literature data ($n=380$), allow us to estimate the uranium isotopic compositions of the various reservoirs involved in the modern oceanic uranium budget, as well as the fractionation factors associated with U incorporation into those reservoirs. Because the incorporation of U into anoxic sediments is accompanied by large isotopic fractionation ($\Delta_{\text{Anoxic/Euxinic-SW}} = +0.6$ ‰), the size of the anoxic sink strongly influences the $\delta^{238}\text{U}$ value of seawater. Keeping all other fluxes constant, the flux of uranium in the anoxic sink is constrained to be 7.0 ± 3.1 Mmol/yr (or 14 ± 3 % of the total flux out of the ocean). This translates into an areal extent of anoxia into the modern ocean of 0.21 ± 0.09 % of the total seafloor. This agrees with independent estimates and rules out a recent uranium budget estimate by Henderson and Anderson (2003). Using the mass fractions and isotopic compositions of various rock types in Earth's crust we further calculate an average $\delta^{238}\text{U}$ isotopic composition for the continental crust of -0.29 ± 0.03 ‰ corresponding to a $^{238}\text{U}/^{235}\text{U}$ isotopic ratio of 137.797 ± 0.005 . We discuss the implications of the variability of the $^{238}\text{U}/^{235}\text{U}$ ratio on Pb-Pb and U-Pb ages and provide analytical formulas to calculate age corrections as a function of the age and isotopic composition of the sample. The crustal ratio may be used in calculation of Pb-Pb and U-Pb ages of continental crust rocks and minerals when the U isotopic composition is unknown.

1. Introduction

The past several years have seen a rapid increase in the number of studies of $^{238}\text{U}/^{235}\text{U}$ uranium isotopic variations in natural samples. This was made possible by the development of an accurate ^{233}U - ^{236}U double-spike to precisely correct for isotopic fractionation introduced during chemical purification and mass spectrometry. A reason for this interest is the recognition that uranium isotope variations have some bearing on a wide variety of problems:

(i) In cosmochemistry, the search for ^{247}Cm ($t_{1/2} = 15.6\text{My}$), an extinct short-lived radionuclide that decays into ^{235}U , is important for understanding how r -process nuclides were synthesized in stars and learning about the astrophysical context of solar system formation (Chen and Wasserburg, 1981; Wasserburg et al., 1996; Nittler and Dauphas, 2006; Brennecka et al., 2010b; Tissot et al., 2015).

(ii) In both terrestrial and extraterrestrial samples, variations in the $^{238}\text{U}/^{235}\text{U}$ ratio affect Pb-Pb ages (and depending on the analytical protocols, U-Pb ages). Therefore, samples dated by these techniques need to have their U isotopic compositions measured (Stirling et al., 2005; Stirling et al., 2006; Weyer et al., 2008; Amelin et al., 2010; Brennecka et al., 2010b; Brennecka and Wadhwa, 2012; Connelly et al., 2012; Goldmann et al., 2015) or uncertainties on the U isotopic composition should be propagated into age calculations.

(iii) In low temperature aqueous geochemistry, U isotopic fractionation between U^{4+} and U^{6+} , (driven in part by nuclear field shift effects; Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008), makes U isotopes potential tracers of paleoredox conditions (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Kendall et al., 2013; Asael et al., 2013; Andersen et al., 2014; Dahl et al., 2014; Goto et al., 2014; Noordmann et al., 2015; Kendall et al., 2015).

The present paper aims at constraining some aspects of the global budget of uranium in the modern oceans using $^{238}\text{U}/^{235}\text{U}$ isotope variations, which involves characterizing the U isotopic composition of seawater and several reservoirs involved in the uranium oceanic budget. Uranium can exist in two oxidation states in terrestrial surface environments: U^{4+} is insoluble in seawater while U^{6+} is soluble (Langmuir, 1978). The contrasting behaviors of the two oxidation states of uranium explains why the disappearance of detrital uraninite after the Archean marks the rise of oxygen in Earth's atmosphere/hydrosphere (Ramdohr, 1958; Rasmussen and Buick, 1999; Frimmel, 2005). More recently, significant effort has focused on using U isotopes to constrain the past extents of anoxic vs. oxic or suboxic sediments in modern and ancient oceans (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Asael et al., 2013; Kendall et al., 2013, 2015; Andersen et al., 2014; Dahl et al., 2014; Goto et al., 2014; Noordmann et al., 2015). A virtue of this system is that it can potentially reflect the global redox state of Earth's oceans. At the same time, several difficulties have been encountered in applying U isotopes as paleo-redox indicators. For example, detrital contributions can blur the authigenic signal and have to be corrected for (Asael et al., 2013; Andersen et al., 2014; Noordmann et al., 2015), uranium isotopes can be affected by diagenesis and exchange with porewater (Romaniello et al., 2013; Andersen et al., 2014), and the exact isotopic fractionation factors relevant to various conditions of deposition are uncertain. While significant

progress has already been made to address these difficulties (Asael et al., 2013; Romaniello et al., 2013; Andersen et al., 2014; Noordmann et al., 2015), this system and others are missing some of the groundwork studies on modern environments that are needed to gain trust in their applications to ancient sediments.

In the modern ocean, water-soluble uranium behaves conservatively (*i.e.* U concentration correlates linearly to water salinity, Ku et al., 1977, Owens et al., 2011) and has a long residence time of ~400 kyr (Ku et al., 1977). The ocean is therefore a large repository of uranium, exceeding the total inventory of land-based deposits (Lu, 2014). The riverine input (40 to 46 Mmol/yr) is balanced by several sinks; including suboxic sediments, anoxic sediments, carbonates, altered oceanic crust, salt marshes and Fe-Mn nodules. Barnes and Cochran (1990), Morford and Emerson (1999), Dunk et al. (2002), and Henderson and Anderson (2003) each proposed estimates for the oceanic uranium budget that differ substantially in the fluxes that they use. Uranium isotopes are sensitive to ocean redox conditions because uranium removal in anoxic sediments imparts large uranium isotopic fractionation, so that the areal extent of this sink influences greatly the U isotopic composition of seawater relative to the riverine input. In the present paper, we report double-spike uranium isotopic measurements of 18 seawater samples, 18 continental crust lithologies, 7 individual minerals, 6 oyster samples, 3 modern evaporites samples, 2 lake water samples, 1 large river water sample and 1 coral sample. These measurements are supplemented by compilations of literature data. With this large data set ($n = 444$), we are able to constrain the flux of uranium into anoxic sediments, as well as the global extent of anoxia in the modern ocean (percent of seafloor covered by anoxic/euxinic sediments). Our findings compare well with independent estimates and rules out the most recent U budget of Henderson and Anderson (2003).

As part of our effort, we also present a data reduction method for double-spike measurements that is both comprehensive in the way the errors are propagated and simple to implement.

2. Methods

All Teflon labware used was pre-cleaned with boiling Aqua Regia (3:1 mixture of HCl:HNO₃) three times, followed by boiling Milli-Q water. Single element ICP-MS standard solutions (Spex CertiPrep) at concentrations of $1000 \pm 5 \mu\text{g.mL}^{-1}$ were used for all concentration measurements. Pre-packed, 2 mL cartridges containing U/Teva resin (diamyl amyolphosphonate, particle size 50–100 μm) were purchased from Eichrom.

2.1. Distribution coefficients of elements on U/Teva resin

To optimize the chemical separation on U/Teva resin, the partition coefficients for U and fifteen other elements (Na, Mg, Al, Ca, Sc, Ti, Fe, Ni, Y, Zr, Sn, La, Yb, Hf, Th) were measured in HNO₃, HCl and HCl + 0.1M oxalic acid (Table 1 and Fig. 1). Calibration of the elution curve was done, using the same set of elements, plus K and Gd (Table 2 and Fig. 2). As the age and repeated use of the resin are known to affect the partition coefficients (Le Fevre and Pin, 2001), all tests were done on unused resin less than a year old (maximum duration for which the partition coefficients are certified by Eichrom).

The distribution coefficient (K_d) quantifies the partition of an element between the acid solution (mobile phase) and the extractant (stationary phase) and is written as follows:

$$\text{Distribution Coefficient } (K_d) = \frac{C_{\text{solid per gram U-Teva}}}{C_{\text{solution per ml solution}}} \quad (1)$$

where C_{solid} is the concentration of element bound to the resin, in micrograms per gram of dry U/Teva resin, and C_{solution} is the concentration of ions, in micrograms per mL of solution, which remains in solution after equilibration is established between the acid and the resin. Single element standards are commercially available in combinations of dilute HF, H₂O₂, HCl, HNO₃ and C₄H₆O₆ (tartaric acid) solutions. Potential modification of the partition behavior of elements in U/Teva resin could occur if these acids were present in the mobile phase during the resin-solution equilibration. In order to avoid this problem, aliquots (5 ml for major elements Na, Mg, Al, Ca, Ti, Fe, Ni, and 0.5 ml for minor elements Y, Sc, Zr, Sn, La, Gd, Yb, Hf, Th, U) of commercially manufactured standard solutions (1000 ug.mL⁻¹) were transferred to a pre-cleaned, 35 mL Savillex Teflon-PFA beaker and the mixture was evaporated to dryness. Right before complete evaporation, the residual droplet was taken back into 2 mL of 1 M HNO₃. The process was repeated three times to ensure complete removal of other acids. In the last step, 50 mL of 1 M HNO₃ was added to the beaker and transferred to a centrifuge tube. Particles visible to the naked eye were present in the solution, which were removed by centrifugation. SEM analyses showed that the residue was made of Ti, Fe, Sn and Hf. An aliquot of the solution remaining after particle removal was analyzed by MC-ICPMS. All elements added to the standard, except Gd (not reported), were detected at levels at least one order of magnitude above blank solutions (1 M HNO₃). One third of the standard solution investigated was then sampled and saved for batch experiments in HNO₃ acid (50 ppm and 5 ppm for major and minor elements, respectively), and the remaining two thirds was dried down again, following the same process, but cycling with 1 M HCl three times for final dissolution in 33 mL of 1 M HCl investigated (50 ppm and 5 ppm for major and minor elements, respectively).

A fixed amount of the standard solution containing the 16 elements investigated was dried down into Teflon beakers, taken back into 2 mL of acid at a given molarity (from 0.1 to 15 mol.L⁻¹ for HNO₃; from 0.1 to 11 mol.L⁻¹ for HCl; and from 0.2 to 11.1 mol.L⁻¹ for HCl + 0.1M oxalic acid, hereafter HCl + 0.1 M Ox), dried again and taken back into 6 mL of the same acid. A 1 mL aliquot was taken and saved for each sample, providing a standard for normalization. The remaining 5 mL were then equilibrated with 166 ± 1.8 mg (about 0.5 mL) of dry U/Teva resin (particle size 50–100 µm). The element to resin ratio was ~300 µg per g of resin for major elements (Na, Mg, Al, Ca, Ti, Fe, Ni) and ~ 30 µg per g of resin for minor elements (Y, Sc, Zr, Sn, La, Yb, Hf, Th, U). The resin and the acid-standard solutions were stirred by placing the vials on a Thermoline Vortex shaker (~1000 rpm) for 5 to 10 min every 2 h. After 8 h of equilibration, the mixture was filtered using pre-cleaned 10 mL Bio-Rad Poly-Prep chromatography columns, to separate the resin from the mobile phase. The acid solutions were collected in centrifuge tubes and transferred back into cleaned Teflon beakers. Molarities of the equilibrated solutions (samples) and the unequilibrated aliquots (standards) were adjusted to about 1 M HNO₃. The volume was adjusted so the standards contained about 1 ppm and 0.1 ppm of the major and minor elements, respectively. A similar

dilution was done on the samples (*i.e.*, if the resin has no affinity for an element, its concentration will be the same in the equilibrated sample and in the standard). Samples (and standards) in HCl and HCl + 0.1 M Ox were dried down, taken back into 2 mL of 1M HNO₃, dried once more and finally taken back into 1 M HNO₃, while the molarity and concentration of the samples (and standards) in HNO₃ were adjusted to reach a final molarity of 1 M HNO₃ by adding directly one or several of the following: concentrated HNO₃, 1 M HNO₃ and Milli-Q water.

Measurements were performed on a ThermoFinnigan Neptune MC-ICP-MS at the Origins Lab of the University of Chicago. The 1 M HNO₃ solutions were introduced into the Neptune using a 100 µL.min⁻¹ PFA Teflon self-aspirating nebulizer. A combined quartz cyclonic and Scott-type spray chamber (Stable Introduction System from ESI) was used for measuring all distribution coefficients. Measured isotopes were selected with preference given to higher relative abundances and absence of isobaric interferences. Instrumental drift was corrected for by bracketing every batch of three samples with a multi-element standard solution (std-smp-smp-smp-std). The procedural blank and acid contributions (generally below 1 %) were subtracted from each analysis. The following equation was used to calculate the distribution coefficients for each element (*e.g.*, µg of an element per g of resin divided by µg of an element per mL of solution):

$$K_d = \frac{(C_b/C_a - 1) \times V}{w} \quad (2)$$

where C_b and C_a are the elemental concentrations in micrograms per mL of solution before and after equilibration, respectively, w is the weight of dry U/Teva resin in grams and V is the volume of acid solution in milliliters. Table 1 and Figs. 1a, 1b and 1c show the partition coefficients (logarithmic scale) on U/Teva as a function of HNO₃, HCl and HCl + 0.1 M Ox concentrations. For a given concentration, a high K_d value means that the element is preferentially retained on the resin, while a low K_d indicates the release of the element to the mobile phase (acid solution).

Previously, Horwitz et al. (1992) studied some of the properties of U/Teva extraction chromatography resin in slurry-packed gravity columns. This study graphically represented the number of free column volumes to peak maximum k' , also called resin capacity factor ($K_d = 1.7 \times k'$, see Appendix A), of five elements (Pu, U, Th, Np and Am) in HNO₃ and three (U, Th, and Np) in HCl solutions. Here, we report distribution coefficients (K_d) for 16 elements in HNO₃, HCl and HCl + 0.1M Ox solutions. This last acid type was used by Horwitz et al. (1992) to elute Np while keeping U bound to the resin, and the HCl + 0.1 M Ox experiment aimed at verifying that the change in K_d of U is indeed negligible when oxalic acid is present. The partition behaviors of U and Th on U/Teva resin are comparable between this study and that of Horwitz et al. (1992) (Fig. 3). The small differences might be due to the fact the earlier study used multi-elements stock solutions directly, while in the present study all standards were converted to HNO₃, HCl or HCl + 0.1 M Ox prior to use. The distribution coefficient from this study presented in Table 1 and Figures 1 and 3 do not show values of K_d outside of the range $15 < K_d < 10^4$ because below 15,

insufficient changes in the solution concentrations occur, while above 10^4 , the solution concentrations approach the limits of detection of the instrument.

Based on the established Kd values and earlier work by Weyer et al. (2008), an elution was performed using U/Teva pre-packed cartridge (2 mL, 1.14 cm diameter, 2.56 cm length, 50-100 μ m particle size) and a vacuum box (Table 3). The flow rate was kept between 0.5 to 2 mL per minute. The results are given in Figure 2 and Table 2. More than 99 % of the U is released during the U elution step (using 0.05 M HCl) after elution of all other elements. Less than 0.4 % of the matrix elements are released during the U elution step. This elution can be reproduced using the theory of plates (Martin and Synge, 1941) as implemented in the simulation code of Ireland et al. (2013) for a height equivalent to a theoretical plate (HETP) of ~ 0.5 mm. This value can be used in future studies to predict elution curves on U/Teva column chemistries using the same mesh size resin and elution rate as in this study.

2.2. Digestion and column chemistry

All samples were double-spiked prior to digestion using IRMM-3636 spike, which is made of 50.45 % ^{233}U and 49.51 % ^{236}U ($^{238}\text{U}/^{235}\text{U} = 5.1629 \pm 0.0118$; Verbruggen et al., 2008). Spiking after digestion, but before column chemistry, was found to have no effect on the results as shown by a test on geostandard BCR-2 and the agreement of our results with literature values, where spiking was not always done prior to digestion (Weyer et al., 2008). The amount of spike added was such that the $U_{\text{spike}}/U_{\text{sample}}$ ratio was ~ 3 % for each sample.

For rock samples, the digested mass varied from 3 mg to 1.6 g, depending on the U concentrations of the samples analyzed. The amount of U recovered thus varied between 63 to 602 ng, with most samples around 200-300 ng. All rock samples were treated with two 24 h attacks in HF/HNO₃ 2:1 followed by two 24 h attacks in HCl/HNO₃ 2:1 on hot plates at 160 °C. Between the two steps, all granites and geostandards susceptible of hosting chemically resistant phases (*e.g.*, zircons) were placed in Parr Bombs for 5 days in HF/HNO₃ 2:1 at 180 °C, to ensure complete dissolution of these phases. The final digested samples were taken back in concentrated HNO₃ and put back on hot plates for 24 h, before dilution to 3 M HNO₃.

For seawater, the samples were filtered in the field at the time of collection using 0.45 μ m polycarbonate Nuclepore (Whatman®) and Nalgene Inline filter holder (Thermo Scientific®). The filtered samples were collected in Amber Nalgene bottles to prevent further exposure to light and were acidified to a pH of ~ 2 within 3 days of sampling with concentrated HCl. The mass of water used for analysis ranged from 80 to 320 g. Seawater samples were evaporated to dryness, and taken back into 3 M HNO₃.

U separation and purification was conducted on U/Teva specific resin following the procedure described in Table 3, modified from Weyer et al. (2008). The resin was cleaned with 20 mL of 0.05 M HCl. It was then conditioned with 6 mL of 3 M HNO₃. The sample was loaded in 5 to 20 mL of 3 M HNO₃ and most elements except Th, Np and U were removed with 40 mL of 3 M HNO₃. The resin was then converted to HCl with 6 mL of 11 M HCl. Thorium and Neptunium were eluted in 20 mL of 5 M HCl + 0.1 M oxalic acid. Finally, the oxalic acid was rinsed off the resin with 10 mL of 5 M HCl before elution of U in 22-25

mL of 0.05 M HCl. This procedure was done one to three times, depending on the mass of sample digested, to ensure complete purification of uranium.

2.3. Mass spectrometry for isotopic analyses

$^{238}\text{U}/^{235}\text{U}$ ratios are reported as $\delta^{238}\text{U}$ relative to the U metal standard CRM-112a (also named SRM-960 or NBL-112-a; – CRM-145 for the solution form):

$$\delta^{238}\text{U} = [(^{238}\text{U}/^{235}\text{U})_{\text{sample}} / (^{238}\text{U}/^{235}\text{U})_{\text{CRM-112a}} - 1] \times 10^3. \quad (1)$$

The $[^{234}\text{U}/^{238}\text{U}]$ activity ratios are reported as $\delta[^{234}\text{U}/^{238}\text{U}]$ relative to secular equilibrium:

$$\delta[^{234}\text{U}/^{238}\text{U}] = [(^{234}\text{U}/^{238}\text{U})_{\text{sample}} / (^{234}\text{U}/^{238}\text{U})_{\text{eq}} - 1] \times 10^3, \quad (2)$$

where $(^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the atomic ratio at secular equilibrium and is equal to the ratio of the decay constants of ^{238}U and ^{234}U , $\lambda_{238}/\lambda_{234} = (1.5513 \times 10^{-10}) / (2.8220 \times 10^{-6}) = 5.497 \times 10^{-5}$ (Cheng et al., 2013). Unless stated otherwise, all errors are reported as 95 % confidence interval (95 % CI).

The measurements were performed at the Origins Lab of the University of Chicago on a ThermoFinnigan Neptune MC-ICP-MS upgraded with an OnToolBooster 150 jet pump (Pfeiffer) and using Jet sample cones and X-skimmer cones. An Aridus II desolvating nebulizer was used for sample introduction. Enhanced signal stability was achieved by placing a spray chamber between the Aridus II and the MC-ICPMS. Quantification and correction of mass fractionation during chemical separation and mass spectrometry was done using a $^{233}\text{U}/^{236}\text{U}$ double spike (IRMM-3636). Each sample measurement was bracketed by standards spiked to the same level as the sample. The U procedural blanks after removal of organics from the resin by drying in ~0.2 ml of $\text{HNO}_3/\text{H}_2\text{O}_2$ (1:1) (Romaniello et al., 2013; Goto et al., 2014; Murphy et al., 2014; Andersen et al., 2015; Goldmann et al., 2015) vary from 4 to 13 pg. This represents 0.02-0.05 ‰ of the signal measured. In this study, the samples were not dried in ~0.2 ml of $\text{HNO}_3/\text{H}_2\text{O}_2$ (1:1) and isobaric interferences from organics represent 50-160 pg equivalent of U based on the signal measured at mass 238.

All measurements were done using the static cup configuration shown in Table 4. Measurements were done in low resolution and consisted of 50 cycles of 4.194 s integration time. Rinsing time was adjusted to make sure that the background had decreased to a low and stable value between each sample/standard measurement, and was typically 210 s or more. For each sample solution, typically nine measurements were performed, except when the mass of sample available was the limiting factor. Measurements were done using 25 ppb solutions, corresponding to ~25 V on ^{238}U (i.e., a transfer efficient between atoms introduced into the mass spectrometer and ions analyzed of ~1 %) and signals of ~400 mV on ^{233}U and ^{236}U , ~175 mV on ^{235}U and ~1.4 mV on ^{234}U (or 90,000 cps when using the SEM). Baseline measurement and gain calibration of the amplifiers was done at least daily. Estimation of the cps to volt conversion factor was done once a week (see Table 4). The errors are calculated as $2 * \sigma_{\text{Standard}} / \sqrt{n}$, where $2 * \sigma_{\text{Standard}}$ is the daily external reproducibility of measurements of the standard CRM-112a bracketed by itself, and n is the number of sample solution measurements.

In addition to blank (on peak zero) correction, corrections were carried out on the measured intensities to account for (1) the decays of ^{233}U and ^{236}U in the spike between the date of determination of the isotopic composition of the spike and the measurement date, (2) abundance sensitivity and (3) hydride formation. Tailing of the major ^{238}U beam onto ^{236}U , ^{235}U and ^{234}U was estimated to be, respectively, 0.6×10^{-6} , 0.25×10^{-6} and 0.1×10^{-6} of the ^{238}U signal (the instrument is not equipped with an Retarding Potential Quadrupole, RPQ, filter). For a single, non-bracketed measurement, tailing corrections were found to be significant on all isotopes, but when looking at deviations from a bracketing standard (δ values), the tailing correction was only important for ^{234}U (*i.e.*, above 0.01 ‰). Formation of hydride was estimated by measuring the intensity at mass 239 ($^{238}\text{UH}^+$) in a CRM-112a U standard solution. The ratio $^{238}\text{UH}^+ / ^{238}\text{U}$ was $\sim 7.3 \times 10^{-7}$ (slightly larger than the value of 3×10^{-7} found by Weyer et al., 2008 who assessed the hydride level by measuring $^{235}\text{UH}^+$), and the hydride correction was found to have no influence on the results. However, for the purpose of consistency, on peak zero, abundance sensitivity and hydride correction were applied to all samples. Our test using amplifier rotation showed systematic bias in the measurements after transition between two amplifiers, leading to erroneous estimation of isotopic ratios, and therefore we did not consider this option further.

The influence of the chosen set of cones and cup configuration was also tested (Fig. 4). New baseline and gain calibrations were done after aligning the cups and changing the cones. We found that using different cup configurations, (*i.e.*, using different isotopes in the axial Faraday cup), as well as different cones led to different estimates of the absolute U isotopic composition of the measured sample (Fig. 4). For instance, measurements done with Jet cones (*i.e.*, Jet Sample cones and X-skimmer cones) led to $^{238}\text{U}/^{235}\text{U}$ ratios that were offset by ~ 0.08 to 0.20 ‰ compared to measurements done with general cones and the same cup configuration. Similarly, using cup configurations that were strongly asymmetrical (*e.g.*, ^{234}U or ^{236}U on the center cup) offset the $^{238}\text{U}/^{235}\text{U}$ ratio measured by ~ 0.05 to 0.23 ‰ relative to a more symmetrical configuration (*i.e.*, ^{235}U on the center cup). When measuring ^{235}U in the axial cup, which corresponds to the most symmetric cup configuration of those tested, and with general cones, we found good agreement with literature data for both $^{238}\text{U}/^{235}\text{U} = 137.842 \pm 0.003$ (95 CI) (against literature value, 137.837 ± 0.015 , Richter et al., 2010) and $\delta[^{234}\text{U}/^{238}\text{U}] = -40.8 \pm 2.3$ (95 CI) (against literature value, -38.5 ± 0.3 , Cheng et al., 2013). This is not the case for the other configurations that put other isotopes in the central cup. Because of this bias, and even though we use double spike, it is important to bracket sample measurements by standard measurements to obtain reliable absolute isotopic ratios.

2.4. Data reduction

For any element that has four isotopes or more, double spike is a well-adapted technique to achieve high precision measurements. Double spiking allows for correction of instrumental mass bias as well as fractionation occurring during chemical separation (provided spiking of the sample is done before chemistry). Initially described by Dodson (1963), it has since then been applied to a large number of elements (*e.g.*, Ca, Ti, Fe, Sr, Mo, Ba, Pb, U, first developed by, respectively, Hirt and Epstein, 1964;

Niederer et al., 1985; Johnson and Beard, 1999; Patchett, 1980; Wetherill, 1964; Eugster et al., 1969; Compston and Oversby, 1969; Dietz et al., 1962). By decomposing the measured signal into a proportion coming from the spike and sample (Eq. 5), it is possible to extract the isotopic composition of the sample from measurement of the spike-sample mixture. A data reduction method (applicable to any double spike) is presented below that is both comprehensive in the way the errors are propagated and simple to implement. The reduction scheme uses Newton methods for system resolution (thus avoiding risky trial-and-error two nested iterations, Siebert et al., 2001) and Monte-Carlo simulations to propagate analytical errors (see Supplementary Material; Lehn et al., 2013; Pourmand et al., 2014; Millet and Dauphas, 2014).

When using the double spike technique, various sources of errors have to be taken into account, namely: (i) the error on the measurement itself (counting statistics), (ii) the error introduced by conversion from counts per second (cps) to volts of the signal when measuring an isotope on the secondary electron multiplier (SEM), (iii) the error on the mass of spike added to the sample and on the mass of sample digested (for concentration calculations). In addition, correlations between isotope ratio errors must be taken into account when a common normalizing isotope is involved. To propagate all errors mentioned above, the raw data are reduced as follows:

1) The measured ratios are corrected for on peak zero contribution, abundance sensitivity of the dominant ^{238}U isotope onto the minor ^{236}U , ^{235}U and ^{234}U isotopes (the contribution on ^{233}U is completely negligible), hydride contribution (even though the effect on the measurement was found to be insignificant) and decay of the spiked isotopes since the certificate was issued.

2) For each measured ratio of two isotopes $i1$ and $i2$ (noted $R_{\text{Measured}}^{i1/i2}$), the following equation can be written,

$$R_{\text{Measured}}^{i1/i2} = \left[p \cdot R_{\text{Spike}}^{i1/i2} + (1 - p) \cdot R_{\text{Sample}}^{i1/i2} \right] \cdot \left(\frac{M_{i1}}{M_{i2}} \right)^{\beta}, \quad (3)$$

where p is the ratio of abundance of isotope $i2$ in the spike over $i2$ in the mix spike-sample, $R_{\text{Spike}}^{i1/i2}$ and $R_{\text{Sample}}^{i1/i2}$ are the isotopic ratios $i1$ over $i2$ in the spike and the sample, respectively, M_i is the molar mass of isotope i , and β is the instrumental mass fractionation factor assuming that isotopic fractionations in the instrument and during column chromatography follow the exponential law. Note that other fractionation laws, such as the generalized power law (Marechal et al., 1999) can be used just as well but do not affect the results significantly because samples are bracketed by double-spiked standards, which eliminates the influence of instrumental mass-fractionation. By convention, we write that the isotopic ratios in the sample are related to those in the standard following the exponential mass-fractionation law,

$$R_{\text{Sample}}^{i1/i2} = R_{\text{Standard}}^{i1/i2} \cdot \left(\frac{M_{i1}}{M_{i2}} \right)^{\alpha}, \quad (4)$$

where α is the fractionation factor between the standard and the sample (natural fractionation). Though uranium isotopic fractionation is known to be driven by nuclear field shift effects (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008), which are not mass-dependent, the convention of using Eq. 4 for

reporting uranium isotopic composition has no consequence for the double-spike inversion because uranium has only two-naturally occurring isotopes. Combining equations (3) and (4), we have,

$$R_{\text{Measured}}^{i1/i2} = \left[p \cdot R_{\text{Spike}}^{i1/i2} + (1 - p) \cdot R_{\text{Standard}}^{i1/i2} \cdot \left(\frac{M_{i1}}{M_{i2}} \right)^\alpha \right] \cdot \left(\frac{M_{i1}}{M_{i2}} \right)^\beta. \quad (5)$$

The equation has three unknowns: proportion of spike (p), natural fractionation (α) and instrumental fractionation (β). To solve the system we need at least four isotopes (i.e., three isotopic ratios). In the data reduction scheme that we adopted, the system of three equations given by $R_{\text{Measured}}^{233\text{U}/238\text{U}}$, $R_{\text{Measured}}^{235\text{U}/238\text{U}}$ and $R_{\text{Measured}}^{236\text{U}/238\text{U}}$ is solved exactly using the Newton method. The reason why $R_{\text{Measured}}^{234\text{U}/238\text{U}}$ is not used to solve the system is that ^{234}U is a decay product of ^{238}U , and as such the variations in this ratio are not expected to follow mass-fractionation. The ratio $R_{\text{Sample}}^{234\text{U}/238\text{U}}$ is calculated after the system of equation has been solved by rearranging Eq. 3 into

$$R_{\text{Sample}}^{234\text{U}/238\text{U}} = \frac{R_{\text{Measured}}^{234\text{U}/238\text{U}} / \left(\frac{M_{234\text{U}}}{M_{238\text{U}}} \right)^\beta - p \cdot R_{\text{Spike}}^{234\text{U}/238\text{U}}}{(1-p)} \quad (6)$$

Note that for isotopic systems where four (or more) ratios are available and are affected by the same mass fractionation law, the system would be over-constrained (4 equations, or more, in 3 unknowns) and an exact solution would not exist. In such a case, a solution can be obtained using a least square approach.

3) The last step in the data reduction is the propagation of errors via a Monte-Carlo simulation (Lehn et al., 2013; Pourmand et al., 2014; Millet and Dauphas, 2014). For each variable, a large number (1000) n of random values is generated. This provides us with n sets of randomly generated simulated data (in our case the set comprises the $^{233}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios). The mean, standard deviations, and underlying structure of the real data are used to generate the synthetic data. In particular, the covariant character of the four isotopic ratios is taken into account by using the covariance matrix of the mean ratios, noted S_m , which is the covariance matrix of the ratios divided by the number of cycles in the measurement. Let us denote U , V , X and W the isotopic ratios, $^{233}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$, respectively. S_m is thus written:

$$S_m = \begin{pmatrix} \text{Var}[U] & \text{Cov}[U, V] & \text{Cov}[U, W] & \text{Cov}[U, X] \\ \text{Cov}[U, V] & \text{Var}[V] & \text{Cov}[V, W] & \text{Cov}[V, X] \\ \text{Cov}[U, W] & \text{Cov}[V, W] & \text{Var}[W] & \text{Cov}[W, X] \\ \text{Cov}[U, X] & \text{Cov}[V, X] & \text{Cov}[W, X] & \text{Var}[X] \end{pmatrix} / \text{Number of cycles}. \quad (7)$$

For each synthetic data, a solution to the double spike system of equation is calculated (in our case p , α and β). Other sources of error (SEM to Faraday conversion, mass of spike added, mass of sample digested, concentration of the spike) are propagated in the double-spike data reduction using the same Monte-Carlo approach. The Monte-Carlo treatment allows one to easily propagate errors that would otherwise be difficult to propagate (such as errors on U-Th ages, Pourmand et al., 2014). Another benefit of the Monte-Carlo simulation is that it allows one to examine the distribution of errors resulting from the propagation rather than assuming an a priori Gaussian distribution. The final errors are estimated by looking at the

statistical dispersion of the solutions of a large enough number of simulated data ($n \geq 1000$, Anderson, 1976). Because all samples had nearly Gaussian distribution, the uncertainties on the double-spike inversion are reported as the 95 % confidence interval; i.e., (97.5 percentile – 2.5 percentile)/2. As emphasized in Rudge et al. (2009), the normalizing isotope should not be one that is of minor abundance to “avoid the numerical problems of dividing by small quantities”. In the U system, the choice of ^{238}U is obvious as any other isotope is minor compared to ^{238}U .

In addition to double spike corrections, the sample measurements were bracketed by standard measurements, spiked to the same level as the sample (3 %).

3. Results

The uranium isotopic compositions and concentrations of geostandards and seawater samples are reported in Tables 5 and 6. A total of 41 geostandards were measured, 32 of which have not been analyzed before. Some samples were measured several times, starting from powder or seawater storage container. These replicate measurements are entered as separate entries in Tables 5 and 6.

3.1. Data quality control

A quality control for double spike measurements is presented in Figure 5a. It is a plot of the $\delta^{238}\text{U}_{\text{DS+SSB}}$ values obtained from the double spike data reduction (Sect. 2.4) as a function of the $\delta^{238}\text{U}_{\text{SSB}}$ values obtained from the raw $^{238}\text{U}/^{235}\text{U}$ ratios (corrected only for on peak zero, hydride formation and tailing of ^{238}U onto lighter isotopes) bracketed by standard measurements but without double spike correction (SSB). Each point in the figure represents a different sample. As the spike isotopes (^{233}U and ^{236}U) are different from the naturally occurring isotopes (^{235}U and ^{238}U), the data reduction using the double spike is sensitive to artifacts such as isobaric interferences on any of the four isotopes, while the ratio obtained by SSB is sensitive to fractionation during sample digestion and purification, and artifacts affecting only ^{235}U and ^{238}U . As can be seen on Fig. 5a, the data for double-spike and SSB agree, which is a strong internal validation of the quality of the measurements. This test can be applied to all double spikes where at least two naturally occurring isotopes have small contributions from the spike. As can be readily seen on Fig. 5a, the double spike approach offers much better precision than the SSB approach. Agreement is also found between DS+SSB and SSB for $\delta[^{234}\text{U}/^{238}\text{U}]$ values (Fig. 5b).

A few samples yielded different $\delta^{238}\text{U}$ values by double spike or standard bracketing (Fig. 5a and 5c). There are two main reasons for the observed discrepancies:

(1) The $U_{\text{Spike}}/U_{\text{Sample}}$ ratio in the sample is far above the optimal 3% value (red points in Fig. 5), and therefore the level of spike in the sample is different from the one in the bracketing standard. As the amount of spike in the sample increases, the $^{238}\text{U}/^{235}\text{U}$ ratio of the *sample + spike* mixture evolves along a mixing line between the natural $^{238}\text{U}/^{235}\text{U}$ ratio of ~ 137.837 and the spike $^{238}\text{U}/^{235}\text{U}$ ratio of ~ 5.163 (Fig. 5c). A similar mixing relationship is found for $\delta[^{234}\text{U}/^{238}\text{U}]$ values (Fig. 5d).

(2) A large mass of sample was digested and passed through column chemistry (yellow points in Fig. 5). Even though the resin has a much stronger affinity for U than for matrix elements (K_d of U higher by at least 1 order of magnitude), matrix elements can stick to the column in a sufficient amount so as to be partially released at the same time as U and affect the measurement, and/or matrix elements can saturate the binding sites of the resin and prevent U from being fully retained on the resin, leading to isotopic fractionation on the column, which would not affect the DS+SSB result but would affect the SSB result.

To test the second hypothesis, ~120 g of a seawater sample (Moulleau, Bassin d'Arcachon, Atlantic coast, France) was spiked and run through column chemistry three times. An aliquot was sampled after each column step. The three cuts show little difference in their values of $\delta^{238}\text{U}$ obtained from double spike (Table 5), but the values obtained from raw intensities start far off the expected value (at -0.88 ‰ instead of -0.35 ‰) and get closer with the number of column passes (-0.42 ‰ after two). Isotopic fractionation on the column thus seems unlikely, as there would be no reason for the situation to improve with more passes through the column, and we take matrix effect during isotopic measurement as the most likely cause of the isotopic fractionation observed after the first chemistry for this sample. In a second test, ~400 g of a seawater sample (San Francisco) was spiked and split into 5 different beakers (~80 g of seawater each). The first split was passed through chemistry only once, the second split twice, and so on until the fifth split. At this matrix level, we did not observe the same deviation of the raw $^{238}\text{U}/^{235}\text{U}$ ratio, possibly because there is insufficient matrix to saturate the column (80 g seawater for the San Francisco samples vs. 120 g for Moulleau). We recommend that no more than ~1 g of matrix be loaded on 2 mL U/Teva cartridges to avoid elution of matrix elements in the U cut.

3.2. Uranium isotopic compositions of geostandards

Table 5 reports the isotopic compositions of 41 geostandards (from USGS, GIT-IWG, ANRT and GSJ) covering commonly encountered rock types. In agreement with previously published values (Stirling et al., 2007; Weyer et al., 2008; Telus et al., 2012; Goldmann et al., 2015), basalts show an average $\delta^{238}\text{U}$ of -0.29 ± 0.04 ‰, and the four granites measured in this study are at -0.23 ± 0.10 ‰. When combined with the larger granite data set previously measured (Telus et al., 2012), the average $\delta^{238}\text{U}$ of granites is -0.32 ± 0.05 ‰. Consistent with limited U isotopic fractionation in rocks affected by terrestrial weathering (Wang et al., 2015), one soil sample (SoNE-1) and one bauxite sample (BX-N, a product of high weathering and good drainage), show $\delta^{238}\text{U}$ values close to basalts and granites. Most magmatic rocks have $\delta^{238}\text{U}$ values close to granites and basalts with the notable exception of two igneous rocks of intermediate compositions (andesite AGV-1 and AGV-2; and granodiorites GSP-1 and GSP-2) that display heavier isotopic compositions (-0.16 ± 0.04 ‰, -0.18 ± 0.06 ‰, -0.04 ± 0.04 ‰ and $+0.17 \pm 0.05$ ‰, respectively). These are outliers as a larger granodiorite data set previously obtained (Telus et al., 2012), gave an average $\delta^{238}\text{U}$ value for granodiorites of -0.22 ± 0.09 ‰, which is well within error of all other crustal rocks.

The shales measured in this study generally display heavier isotopic compositions than other crustal rocks (-0.26 to -0.17 ‰). SDO-1, a Devonian Black Shale deposited under euxinic conditions, shows a $\delta^{238}\text{U}$ of -0.08 ± 0.03 ‰, a value +0.31 ‰ higher than seawater.

Individual minerals show a small spread of isotopic compositions, with albite, biotite, kyanite and quartz having $^{238}\text{U}/^{235}\text{U}$ ratio identical to basalts and granites (~ -0.25 ‰), while glauconite, phlogopite and zinwaldite show lighter isotopic compositions from -0.38 to -0.50 ‰ (see Section 4.1 of the Discussion for implications on Pb-Pb and U-Pb dating of individual minerals).

3.3. Uranium isotopic compositions of river, lake, evaporites and seawater samples

Table 6 reports the isotopic compositions of several seawater samples along with selected river water, lake water, oysters, evaporites and coral samples (Fig. 6a). The Atlantic ocean, the Pacific ocean, the Mediterranean sea, the Gulf of Mexico and the English Channel have identical isotopic compositions within error bars that agree with previously published values (Stirling et al., 2007; Weyer et al., 2008; Andersen et al., 2014; Andersen et al., 2015). The samples measured in this study define an average seawater $\delta^{238}\text{U}$ value of -0.38 ± 0.01 ‰ (n=13). When combined with literature data (n=9), the average seawater $\delta^{238}\text{U}$ value is calculated as -0.392 ± 0.005 ‰. This is the current best estimate of the modern ocean seawater U isotopic composition. The Persian Gulf and the Bassin d'Arcachon (Atlantic coast, France) show slightly heavier isotopic composition at -0.33 ± 0.03 ‰ and -0.32 ± 0.04 ‰ respectively. The Bassin d'Arcachon is a partially confined gulf in which spatial gradients driven by tidal hydrodynamics have been observed for water temperature, salinity and both N and C isotopes (Bouchet, 1968; Dang et al., 2009). Similar gradients might exist for U isotopes and could explain the slightly higher $\delta^{238}\text{U}$ value measured. This hypothesis could also explain the value measured on the south coast of the Persian Gulf: another partially confined gulf where strong temperature and salinity gradients have been observed (Reynolds, 1993). Alternatively, and even though U behaves mostly conservatively in estuaries (Carroll and Moore, 1994; Saari et al., 2008), various uptake and release processes can take place in those areas such as flocculation of colloidal U or adsorption and/or reduction of U associated with organic matter, which might also influence the isotopic composition of the U remaining in solution (for more details see references in Dunk et al. 2002).

Two samples from the Garonne river (France), taken a year apart, gave identical $\delta^{238}\text{U}$ of -0.22 ± 0.03 ‰, in excellent agreement with other major rivers (Stirling et al., 2007; Noordmann et al., 2011). Two samples from Lake Michigan, taken on the same day 30 miles apart, yielded identical results at -0.37 ± 0.04 ‰. Oysters were more difficult to measure due to their low U concentrations (~ 20 ng/g). Their isotopic compositions are typically within error of seawater. A modern coral measured twice shows a $\delta^{238}\text{U}$ indistinguishable from seawater within 0.02 ‰, in agreement with earlier yet less precise measurements (± 0.10 ‰, Stirling et al., 2007, Weyer et al., 2008). Finally, three modern evaporite samples were measured: their U concentrations range from 6 to 13 ng/g, and their isotopic compositions average -0.57 ± 0.03 ‰.

3.4. Natural variability of stable uranium isotopes: data compilation

To evaluate the current state of knowledge about the variability of the $^{238}\text{U}/^{235}\text{U}$ ratio in natural samples, we compiled 1297 isotopic measurements on 1140 samples from 32 studies (including this work, which comprises 101 measurements on 64 samples). All $^{238}\text{U}/^{235}\text{U}$ ratios were converted back to $\delta^{238}\text{U}$ values and renormalized to CRM-112a. This compilation (Table S2 in the Supplementary Material) is graphically summarized in Figure 6 (see figure caption for references).

The top panel of Fig. 6 presents the modern U isotope taxonomy. The horizontal blue line represents the seawater average of -0.392 ± 0.005 ‰. Most crustal rocks and detrital sediments show isotopic compositions between -0.40 and -0.20 ‰ (*i.e.*, andesites, basalts, basalts alkali, rhyolites, trachytes, diorites, granites, granodiorites, syenite, mica-schist, soils, coals, arc lavas, ocean island basalts –OIBs, and mid ocean ridge basalts –MORBs), while altered oceanic crusts and 1 dunite show heavier compositions (up to $+0.20$ ‰). Large rivers have a $\delta^{238}\text{U}$ of -0.24 ‰, while the one lake measured in this study has a composition indistinguishable from seawater. Also very close to seawater are the 2 pelagic clays, 5 seafloor volcanoclastic sediments and modern corals. Fossil corals, oysters and speleothems show a large spread of $\delta^{238}\text{U}$ values, centered on the seawater value. Samples in which U is mostly adsorbed (a Ca-dolomite chimney from a hypersaline lagoon, evaporites and Fe-Mn crusts) have a distinctly light isotopic composition (-0.52 to -0.83 ‰), while samples incorporating U under euxinic or anoxic conditions have isotopic compositions on average heavier than seawater ($\delta^{238}\text{U}$ up to $+0.40$ ‰).

The bottom panel of Fig. 6 presents the U systematics in individual minerals, ore deposits, past sediments and meteoritic bodies/inclusions (note the change of scale relative to the top panel, see figure caption for details). Of particular interest for paleoredox applications, is the fact that ancient anoxic sediments have compositions close to modern black shales (median $\delta^{238}\text{U}$ value of $+0.29$ ‰), with the exceptions of Archean black shales, which are much closer to modern crustal rocks (median $\delta^{238}\text{U}$ value of -0.26 ‰). The shift from crustal-like values to modern black shales-like values tracks the onset of oxidative weathering during the Great Oxidation Event, between 2.50 and 2.05 Ga ago (Montoya-Pino et al., 2010; Kendall et al., 2013; Asael et al., 2013; Kendall et al., 2015). On the contrary, smaller scale variations in the $\delta^{238}\text{U}$ values of End Permian carbonates (decrease from $+0.15$ to -0.79 ‰) and Late Cambrian carbonates (excursion from -0.20 down to -0.76 ‰) are thought to reflect increases of anoxia in the ocean at the time of sample deposition (Brennecka et al., 2011a; Dahl et al., 2014).

4. Discussion

4.1. $^{238}\text{U}/^{235}\text{U}$ variability and implications for Pb-Pb and U-Pb ages

The U-Pb (Boltwood, 1907) and Pb-Pb (Patterson et al., 1955; Patterson, 1956) dating methods are based on the decay scheme of the long lived isotopes of U: ^{238}U decays into ^{206}Pb with a half-life of 4468 My ($\lambda_{238} = 1.551 \times 10^{-10}$) and ^{235}U decays into ^{207}Pb with a half-life of 704 My ($\lambda_{235} = 9.846 \times 10^{-10}$). In the case of a sample where no loss/gain of either Pb or U occurred, the radiogenic component of

lead is directly proportional to (1) the time since closure of the system and (2) the U isotopic composition of the sample.

Recent work has shown that the isotopic composition of uranium varied from one sample to another, and that it could affect Pb-Pb and U-Pb ages at a level that matters for geochronologic inferences (Weyer et al., 2008; Hiess et al., 2012). Below we evaluate the extent to which the range of U isotopic variations documented in this study would affect Pb-Pb and U-Pb ages, and derive simple formulas to calculate the age correction to apply to a sample of any age and any isotopic composition.

Let us first consider Pb-Pb ages. The Pb-Pb dating equation is written as follows:

$$\frac{{}^{207}\text{Pb}^*}{{}^{206}\text{Pb}^*} = \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right) \cdot \frac{(e^{\lambda_{235} \cdot t} - 1)}{(e^{\lambda_{238} \cdot t} - 1)} \quad (8)$$

where the star denotes the radiogenic component, and t the time since closure of the system. If the actual ${}^{238}\text{U}/{}^{235}\text{U}$ ratio is different from the assumed ratio, an age correction will apply. The magnitude and direction of the age correction is a function of the age of the sample and its U isotopic composition. Because the variations on the ${}^{238}\text{U}/{}^{235}\text{U}$ ratio (noted R_U) are small, the age correction will be small compared to the age of the sample, and we can write:

$$\Delta t = \frac{\Delta R_U}{\partial R_U(t)/\partial t} \quad (9)$$

From Eq. 8, we get the expression of $R_U(t)$, which we derive to obtain the following:

$$\Delta t = \frac{\Delta U \cdot (e^{\lambda_{238} \cdot t} - 1) \cdot (e^{\lambda_{235} \cdot t} - 1)}{1000 \cdot (\lambda_{238} \cdot e^{\lambda_{238} \cdot t} - \lambda_{235} \cdot e^{\lambda_{235} \cdot t} + (\lambda_{235} - \lambda_{238}) \cdot e^{(\lambda_{235} + \lambda_{238}) \cdot t})} \quad (10)$$

where ΔU is the difference between the actual and assumed U isotopic composition of the sample (in delta notation, ‰), t is the Pb-Pb age of the sample obtained using an “assumed” U isotopic composition, and Δt is the age correction to apply to the sample age. Figure 7a shows the age correction required for various ΔU values as a function of the age of the sample. The various curves are obtained using Eq. 10.

Turning to U-Pb ages, it is possible, in theory, to measure the abundance of ${}^{235}\text{U}$, ${}^{238}\text{U}$, ${}^{206}\text{Pb}$ and ${}^{207}\text{Pb}$ without making any assumption on the ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of the sample, which would mean that no age correction should be applied on U-Pb ages. In practice, however, the ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of the sample is rarely estimated and the consensus value (137.88) is often assumed to represent the sample value (Schmitz and Schoene, 2007; McLean et al., 2011), thus calling for an age correction of both ${}^{207}\text{Pb}$ - ${}^{235}\text{U}$ and ${}^{206}\text{Pb}$ - ${}^{238}\text{U}$ ages. Figure 7b and c show the typical age corrections required for various ΔU values as a function of the age of the sample, assuming (1) that the measurements were done using the EARTHTIME distributed ‘ET535 tracer’, (2) a sample/tracer ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of 1 and (3) typical analytical parameters (see Supplementary Material; Schmitz and Schoene, 2007; McLean et al., 2011). The use of a ${}^{233}\text{U}$ - ${}^{236}\text{U}$ double spike in U-Pb dating would be advantageous in that it would allow the simultaneous determination of (1) the instrumental mass fractionation and (2) the ${}^{238}\text{U}/{}^{235}\text{U}$ ratio of the sample, leading to ${}^{207}\text{Pb}$ - ${}^{235}\text{U}$ and ${}^{206}\text{Pb}$ - ${}^{238}\text{U}$ ages free of any “consensus value” assumption.

The importance of these age corrections are better understood when comparing them to the current precisions of Pb-Pb and U-Pb ages. With current instrumentation, uncertainties on Pb-Pb ages of early solar system materials can be as low as 0.2 My (*e.g.*, Amelin et al., 2009), which is equivalent to a difference of 0.15 ‰ between the actual and assumed U isotopic composition of the sample. The typical spread of $\delta^{238}\text{U}$ values in coarse-grained CAIs (Calcium-Aluminum rich inclusions) is ~ 1 ‰, which could mean an age difference of up to 1.5 My between two CAIs thought to be of equal age under the “consensus value” assumption. Because CAIs are thought to have formed within the first 1-2 My of the Solar System, determination of their U isotopic composition is required for proper dating using the Pb-Pb technique.

In geochronology, U-Pb is one of the most important isotopic dating method (due to its high precision over a large age spectrum) and is being applied to bulk rocks as well as individual minerals: predominantly zircons, and in recent years, more and more to monazite, apatite, xenotime, titanite, rutile, baddeleyite, allanite, or perovskite (see Schoene, 2014 and references therein). With the exception of a few minerals (titanites, zircons) with $\delta^{238}\text{U}$ values up to ~ 5 ‰, both rocks and minerals show a roughly similar range variations in their U isotopic compositions of ± 0.30 ‰ (Fig. 6a and 6b; Hiess et al., 2012; this study). Though the age corrections on ^{206}Pb - ^{238}U ages for such isotopic variability are small compared to the uncertainties on the ages (on the order of 1 %), the effect on ^{207}Pb - ^{235}U ages can be significant. For instance, for a 1 Gyr sample (and using typical analytical parameters from Schmitz and Schoene, 2007), a 0.6 ‰ deviation from consensus value in the $^{238}\text{U}/^{235}\text{U}$ ratio of the sample will translate into an age correction of 1.2 Myr (80 % of the error on the age). Considering an arbitrary maximum variability of 5 ‰ between individual zircons, the age corrections needed will range from 7 to 12 My (for Pb-Pb ages) and 0 to 5 Myr (for ^{207}Pb - ^{235}U ages) depending on the age of the sample. Clearly the characterization of the U isotopic composition of individual minerals is a necessary step in order to obtain ages both accurate and precise with the Pb-Pb and U-Pb dating methods.

4.2. The U isotopic composition of the continental crust

U is a highly lithophile element, mostly present in the crust and the mantle of the Earth, as it is not expected to partition into the core (McDonough, 2014). Though a recent study (Wohlert and Wood, 2015), invoking sulfide-silicate equilibration under extremely reduced conditions, argued that the core could contain up to 8 ppb of U, such a statement remains speculative. Even under this hypothesis, the core would contain only a minor fraction of the U of the Earth ($< 17\%$), and we therefore consider in the following discussion that the crust and the mantle are the only two U reservoirs of the Earth. Constraining the isotopic composition of the continental crust is thus an important first step in trying to constrain the U isotopic composition of the Earth. Knowledge of the isotopic composition of both the continental crust and the mantle will in turn give us insight into (i) whether or not the bulk Earth is chondritic, (ii) whether or not any isotopic fractionation is accompanying crustal extraction, or (iii) what the effect of crustal recycling is on uranium stable isotopes (this last point has been extensively discussed by Andersen et al., 2015).

The fractions of various rock types in both continental and oceanic crusts are used to calculate the concentrations and isotopic compositions of uranium in both types of crusts. Two studies (Poldervaart, 1955; Ronov and Yaroshevsky, 1969) based on isostatic equilibrium suggest a two layer model of the continental crust in which a granodioritic upper crust is overlaying a basaltic lower crust. Both models provide a breakdown of the whole (continental + oceanic) crust in percent volumes and percent masses of the main rock types. Though more recent estimates of the composition of the crust are available, they are either mostly based on these two studies (Wedepohl, 1995) or only report chemical compositions and not the details of the rock types present (Rudnick and Gao, 2014; and references therein).

Table 7 shows the abundances, masses, U concentrations and isotopic compositions of the main types of rocks in the continental crust, the oceanic crust and the whole crust. The U concentrations are taken from Rogers and Adams (1969), while the isotopic compositions are from this study (see Table S3 in Supplementary Material). Andersen et al. (2015) showed that, because of incorporation of fractionated U in the oceanic crust during low T hydrothermal circulation, the upper layer (500 m) of the altered oceanic crust (AOC) has a distinctly higher $\delta^{238}\text{U}$ compared to MORBs and OIBs (-0.17 ± 0.03 vs. -0.29 ± 0.01 ‰). In our assessment of the composition of the oceanic crust, we used the value of -0.17 ± 0.03 ‰ for the top 500 m of the AOC ([U] = 400 ppb), and a basalt-like value of -0.29 ± 0.01 ‰ (Table S3 in Supplementary Material) for the remaining 5500 m of oceanic crust ([U] = 50 ppb).

The two crustal models (Poldervaart, 1955; Ronov and Yaroshevsky, 1969) lead to similar average U concentrations and yield identical U isotopic compositions for the both the continental and the oceanic crust. The total average $\delta^{238}\text{U}$ of the crust is calculated as -0.29 ± 0.03 ‰ (Table 7). This value takes into account the errors on the isotopic compositions of each lithology as well as a conservative 25 % uncertainty on their masses and uranium concentrations.

Our crustal value is in agreement with the value proposed by Kaltenbach (2012) at -0.30 ± 0.06 ‰ and Goldmann et al. (2015) at -0.30 ± 0.05 ‰. Those earlier estimates are, however, not well constrained. The estimate of Kaltenbach (2012) is based on repeat measurements of only 6 volcanic and 6 plutonic rocks and the one of Goldmann et al. (2015) is solely based on basalt analyses (n=14). Our approach, based on estimates of the major rock types in the crust (n=101) taking into account the uncertainty on the isotopic compositions of the various rock types, is more robust. Using the CRM-112a $^{238}\text{U}/^{235}\text{U}$ ratio of 137.837 from Richter et al. (2010) the absolute $^{238}\text{U}/^{235}\text{U}$ ratio of the crust is 137.797 ± 0.005 , which can be used in U-Pb or Pb-Pb dating of crustal rocks when the $^{238}\text{U}/^{235}\text{U}$ ratio is not available otherwise.

Now that we have defined the isotopic composition of the crust, we turn to the question of the $\delta^{238}\text{U}$ of the bulk Earth. If the Earth is chondritic, then the following mass balance equation must be satisfied,

$$\delta^{238}\text{U}_{\text{Bulk Earth}} \times U_{\text{Bulk Earth}} = \delta^{238}\text{U}_{\text{Crust}} \times U_{\text{Crust}} + \delta^{238}\text{U}_{\text{Mantle}} \times U_{\text{Mantle}} \quad (11)$$

where U is the quantity of uranium (ng) and $\delta^{238}\text{U}$ the isotopic composition of each reservoir. The bulk uranium concentrations of the Earth is estimated to be 15 ppb (McDonough and Sun, 1995; Allegre et al., 1995; McDonough, 2014), which, combined with the mass of the Earth of 5.97×10^{27} g, gives $U_{\text{Bulk Earth}} =$

8.96e19 g of U. The mass of the crust if taken as 24e24 g (Poldervaart, 1955) which using a concentration of U of 2 ppm (Table 7, in agreement with Hofmann, 1988; Rudnick and Gao, 2014), gives $U_{\text{Crust}} = 4.8\text{e}19$ g of U, leaving $4.2\text{e}19$ g of U in the mantle (U_{Mantle}). We use our estimate of the isotopic composition of the continental crust ($\delta^{238}\text{U}_{\text{Crust}} = -0.29 \pm 0.03 \text{ ‰}$), and previously reported U isotopic compositions of MORBs and OIBs as proxies for the mantle composition ($\delta^{238}\text{U}_{\text{Mantle}} = -0.29 \pm 0.02 \text{ ‰}$; Stirling et al., 2005; Weyer et al., 2008; Kaltenbach, 2012; Goldmann et al., 2015; Andersen et al., 2015). The similarity between the crust and the mantle composition suggest that no isotopic fractionation occurs during crustal extraction. With this data, we calculate a bulk Earth $\delta^{238}\text{U}_{\text{Bulk Earth}}$ value of $-0.29 \pm 0.02 \text{ ‰}$ (the error takes into account the uncertainty on the crust and mantle composition).

The range of composition observed in meteorites is very large (-1.14 to $+0.39 \text{ ‰}$, Fig. 6), and uncertainties remain concerning the actual average solar system value. Nevertheless, the $\delta^{238}\text{U}_{\text{Bulk Earth}}$ we calculate agrees with the two estimates of the average U isotopic composition of the solar system by Goldmann et al (2015) and Andersen et al. (2015) at, respectively, $-0.31 \pm 0.04 \text{ ‰}$ ($n=30$) and $-0.306 \pm 0.026 \text{ ‰}$ ($n=2$). Part of the spread observed in meteoritic data could be the result of two artifacts: nugget effect and recent open-system behavior. Because meteorites are in limited supply, relatively small masses are used for U isotope analyses (typically 500 mg or less). Uranium is concentrated in minor phases such as apatite or oldhamite, and as a result, its measurement can be affected by a nugget effect (Dauphas and Pourmand, 2015). Large sample masses would thus need to be processed to get a representative average composition for each sample. On the other hand, secondary processes, such as aqueous alteration on Earth, can mobilize U and fractionate its isotopic composition (especially in meteorite Finds). One way to identify recent mobilization of U is to measure the $^{234}\text{U}/^{238}\text{U}$ ratio. Indeed, any recent disturbance of the system (in the last 2.5 My), will result in addition/loss of ^{234}U (which, unlike ^{235}U and ^{238}U , is not lattice bound), thus shifting the $^{234}\text{U}/^{238}\text{U}$ ratio away from secular equilibrium. Because secondary processes may also affect the $^{235}\text{U}/^{238}\text{U}$ ratio, a conservative approach would be to only consider samples whose $^{234}\text{U}/^{238}\text{U}$ ratio is at secular equilibrium. At present only 7 large mass samples (>10 g) have been characterized for both $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ isotopic ratios (Andersen et al., 2015), and out of these, only two samples are at secular equilibrium (ordinary chondrite Zag and eucrite Juvinas). We strongly encourage future works to use large sample masses and to report both the $^{238}\text{U}/^{235}\text{U}$ ratio and the $^{234}\text{U}/^{238}\text{U}$ ratio, in order to consolidate our current estimate of the average solar system U isotopic composition.

4.3. The U isotopic composition of the ocean and the modern oceanic U budget

The isotopic composition of authigenic uranium in ancient sediments was used to reconstruct paleoredox conditions in the oceans (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Kendall et al., 2013; Asael et al., 2013; Andersen et al., 2014; Dahl et al., 2014; Kendall et al., 2015). The rationale is that, at steady state, the uranium isotopic composition of seawater should be influenced by the proportions of sediments formed under different conditions because the extent of uranium isotopic fractionation differs in anoxic, euxinic, suboxic, and oxic sediments. Important work has been done over the past several years to

assess uranium isotopic fractionation factors between seawater and sediments formed under various conditions (Rademacher et al., 2006; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2010; Brenneka et al., 2011b; Romaniello et al., 2013; Shiel et al., 2013; Andersen et al., 2014; Goto et al., 2014; Basu et al., 2014; Murphy et al., 2014; Noordmann et al., 2015; Wang et al., 2015; Stirling et al., 2015; this study). In all cases, these fractionation factors are derived from local case studies, and it is unknown to what extent these are representative of the diverse conditions encountered in the oceans, where accumulation rate, organic matter burial, and mineral mode can vary. One approach to test the assumptions in U isotope systematics is to calculate the $\delta^{238}\text{U}_{\text{SW}}$ ($\delta^{238}\text{U}$ of seawater) predicted by several modern oceanic uranium budgets using the present best estimates isotopic fractionation factors. Are the sedimentary sinks balancing the riverine input and is the ocean in steady-state?

Figure 8 and Table 8 show details of the four most recent oceanic U budgets (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003), along with the isotopic compositions of the sources of U to the ocean and the fractionation factors relative to seawater of the U sinks. In all modern uranium budgets, the main source of U in the ocean is the riverine input, which displays an average $\delta^{238}\text{U}_{\text{River}} = -0.24 \text{ ‰}$ (Stirling et al., 2007; Noordmann et al., 2011; this study). The uncertainty on this value is not known precisely, but from published data it seems to be no larger than 0.05 ‰. In particular, Noordmann et al. (2011) measured the isotopic composition of a large number of rivers and found all major rivers to average at -0.24 ‰ with only small rivers showing departure from this value, most likely due to variations in the lithologies of their watersheds. The small difference between the isotopic composition of the upper crust ($-0.29 \pm 0.04 \text{ ‰}$) and that of the riverine flux suggests that little to no isotopic fractionation occurs during oxidative weathering. This hypothesis is supported by (1) our measurements of bauxite and soil samples which have $\delta^{238}\text{U}$ values identical to basalts and granites, and (2) a recent experiment of uranium oxidation of solid tetravalent U (Wang et al., 2015), where only weak fractionation was observed, probably due to a “rind effect”, where the surface layer of U(IV) must be completely oxidized before the next layer can be exposed to the oxidant.

Other U sources to the ocean are negligible and/or very poorly characterized. The aeolian input represents only a minor source of U (~4 % of the riverine input), and likely has the same isotopic composition as the upper continental crust; $\delta^{238}\text{U}_{\text{aeolian}} = -0.29 \text{ ‰}$. U released from shelf sediments could represent up to 15 % of the riverine input, as a study of the Amazon shelf sediments suggested (Mckee et al., 1987), and submarine groundwater discharge could represent from 1 to 34 % of the riverine input (Dunk et al., 2002). The actual U fluxes from these sources are difficult to assess and their isotopic compositions are unknown. In the following discussion, we therefore consider the $\delta^{238}\text{U}$ of the rivers to represent the isotopic composition of the entire U input to the ocean (*i.e.*, including release from shelf sediments and submarine groundwater discharge).

The isotopic mass-balance for uranium requires knowledge of the isotopic fractionation between sedimentary sinks and seawater, which is noted,

$$\Delta_{\text{sedimentary sink-SW}} = \delta^{238}\text{U}_{\text{sedimentary sink}} - \delta^{238}\text{U}_{\text{SW}}. \quad (12)$$

In the following paragraphs we justify the different $\Delta_{\text{sedimentary sink-SW}}$ values used in our model, discussing in more details the environments for which such values are not well constrained.

To first order, anoxic/euxinic sediments (anoxic: $[\text{O}_2]$ and $[\text{H}_2\text{S}] \sim 0 \mu\text{mol/L}$; euxinic: $[\text{O}_2] \sim 0 \mu\text{mol/L}$ and $[\text{H}_2\text{S}] \geq 11 \mu\text{mol/L}$; Berner, 1981; Murray et al., 2007) display a much heavier isotopic composition than seawater. In details, the data shows a large spread of isotopic compositions (Weyer et al., 2008; Montoya-Pino et al., 2010; Andersen et al., 2014) equivalent to $0 \leq \Delta_{\text{Anoxic/Euxinic-SW}} \leq +0.83 \text{ ‰}$. This is because in-situ reductive authigenic U accumulation in anoxic/euxinic sediments occurs via coupled U diffusion and reduction in the porewater. Therefore, the fractionation expressed in the sediment will depend on depositional setting of the sediment (*e.g.*, restricted basin or open setting; full or incomplete U extraction from pore water; oxic or anoxic overlaying water; Andersen et al., 2014). For the present purpose, the average fractionation in anoxic/euxinic sediments of $\Delta_{\text{Anoxic/Euxinic-SW}} = +0.6 \text{ ‰}$ is used. This value is only half the fractionation obtained from first principle calculations in the case of pure U reduction (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008), and is in good agreement with values derived from several case studies (+0.4 ‰, Murphy et al., 2014; +0.7 ‰, Noordmann et al., 2015) and biologically-mediated U reduction experiments (+0.46 ‰, Bopp et al., 2010; +0.68-0.99 ‰, Basu et al., 2014; +0.85 ‰, Stylo et al., 2015; +0.77 ‰, Stirling et al., 2015). One experiment of U reduction by anaerobic bacteria observed a negative fractionation (-0.3 ‰, Rademacher et al., 2006), and the same group later suggested that their original finding may have been the result of adsorption of the UO_2Cl_2 onto microbial cells. Interestingly, abiotic reduction experiments have, to date, only produced U isotopic fractionation in direction opposite to the one imparted by biotic processes (Stylo et al., 2015), or no measurable isotopic fractionation at all (with Zn^0 : Stirling et al., 2007; with Fe^0 : Rademacher et al., 2006; with S^{2-} or organics, Stylo et al., 2015). The systematic shift to heavier isotopic composition of reduced sediments thus suggests that, in the modern ocean, U reduction is principally the product of biologically-mediated reduction (Stylo et al., 2015), in agreement with earlier works which found that inorganic U reduction did not occur at *in-situ* concentrations of U and H_2S , or only extremely slowly (Anderson et al., 1989; Lovley et al., 1991; Barnes and Cochran, 1993; Tribovillard et al., 2006).

Similarly to anoxic sediments, the average fractionation expressed in suboxic sediments ($[\text{O}_2] \leq 10 \mu\text{mol/L}$ and $[\text{H}_2\text{S}] \leq 10 \mu\text{mol/L}$; Berner, 1981; Murray et al., 2007) depends on the conditions of deposition, but unlike anoxic/euxinic sediments, the authigenic enrichment in suboxic sediments is small (for more details see Andersen et al., 2014). Little literature data is available for such samples and we use the average fractionation of $\Delta_{\text{Suboxic-SW}} = +0.1 \text{ ‰}$ (Weyer et al., 2008).

Biogenic carbonates, a sink representing between 10 and 30 % of the U output from the modern ocean, seem to record the isotopic composition of the seawater from which they formed with a small, and well constrained, fractionation: $\Delta_{\text{Biogenic_Carbonates-SW}} = +0.2 \text{ ‰}$ (Stirling et al., 2007; Weyer et al., 2008; Romaniello et al., 2013; Andersen et al., 2014; this study). This value includes the effect of early diagenesis under euxinic conditions, in the first 40 cm of below water/sediment interface (Romaniello et al., 2013).

Mn nodules and metalliferous sediments have a fractionation factor of $\Delta_{\text{Metalliferous-SW}} = -0.24 \text{ ‰}$, well constrained by both natural samples (Stirling et al., 2007; Weyer et al., 2008; Goto et al., 2014; this study) and adsorption experiments (Brennecke et al., 2011b).

Another important sink of U is described as the “coastal retention zone” in Dunk et al. (2002) and encompasses salt marshes, swamps and mangroves. In these estuarine settings, the salinity is low ($< 12 \text{ psu}$) and, when the colloid fraction dominates, U behaves non-conservatively (*e.g.*, Carroll and Moore, 1994; Church et al., 1996; Porcelli et al., 1997; Swarzenski and McKee, 1998; Andersson et al., 2001; Pogge von Strandmann et al., 2008). U removal occurs initially through sorption of U onto Fe-oxyhydroxides/organic colloids (in surface salt marshes $\sim 65 \%$ of the U exists in adsorbed or complexed form, Church et al., 1996). The colloids are then scavenged and buried into sediments on a short timescale before U reduction occurs at depth within the sediment (Swarzenski et al., 2004). For lack of measurement of salt marshes or mangrove sediments, we make the observation that phases with adsorbed/complexed U have similar isotopic composition (evaporites, Fe-Mn nodules, Stirling et al., 2007; Weyer et al., 2008; Goto et al., 2014; this study) and hypothesize that the same adsorption-complexation mechanism is at play in these samples and in coastal retention zones, leading to a similar isotopic fractionation. We thus use $\Delta_{\text{Coastal_Retention_Zone-SW}} = -0.24 \text{ ‰}$, but further work is needed to ascertain this value.

The last important sink of U in the modern ocean is linked to hydrothermal circulation and seafloor alteration at high ($> 100^\circ\text{C}$) and low ($< 100^\circ\text{C}$) temperatures. High temperature hydrothermal circulation occurs at depth in the oceanic crust ($> 1000 \text{ m}$), close to the spreading ridge axis, and U removal in this environment is thought to be nearly quantitative (Michard and Albarede, 1985; Chen et al., 1986b). We therefore assume that no fractionation occurs and use $\Delta_{\text{High_T_Alteration-SW}} = 0 \text{ ‰}$. Since the HT hydrothermal flux is 2 to 10 times smaller than the LT hydrothermal flux, this assumption has no bearing on our exercise. Low temperature alteration occurs at ridge flanks through percolation of relatively low-temperature seawater (all the way down to $60\text{--}70^\circ\text{C}$, Mottl et al., 1998; and even at temperatures as low as $20\text{--}30^\circ\text{C}$, Fouillac and Javoy, 1978; Storzer and Selo, 1979) and only affects the top 500 m to 1000 m of the oceanic crust. Basalts affected by low temperature hydrothermal circulation have high U concentrations (up to 500-1000 ppb, Dunk et al., 2002) and display $\delta^{238}\text{U}$ values significantly higher than fresh MORBs (up to $+0.16 \text{ ‰}$, Andersen et al., 2015). To quantify the fractionation associated with low temperature alteration, $\Delta_{\text{LT_Alteration-SW}} = \delta^{238}\text{U}_{\text{LT_Alteration}} - \delta^{238}\text{U}_{\text{Seawater}}$, we consider the following mass balance:

$$\delta^{238}\text{U}_{\text{Altered}} = f \cdot \delta^{238}\text{U}_{\text{Fresh}} + (1 - f) \cdot \delta^{238}\text{U}_{\text{LT_Alteration}}, \quad (13)$$

where $\delta^{238}\text{U}_{\text{Altered}}$, and $\delta^{238}\text{U}_{\text{Fresh}}$ are the isotopic composition of the altered and fresh basalts, respectively, and f is the fraction of U of the altered basalt that was present before alteration. The average U concentrations in non-altered and altered basalts are, respectively, 78 ppb and 390 ppb (Hart and Staudigel, 1982; Dunk et al., 2002; Kelley et al., 2005; Staudigel, 2014), yielding $f = 78 / (390 - 78) = 25 \%$. The $\delta^{238}\text{U}_{\text{Fresh}}$ value of fresh basalt is -0.29 ‰ (this study), and the $\delta^{238}\text{U}_{\text{Altered}}$ value of basalts altered by low-T hydrothermal circulation was recently estimated to be $-0.17 \pm 0.03 \text{ ‰}$ (Andersen et al., 2015) using the “Super” composite sample from OPD Site 801 whose composition represents a weighted average of the top

420 m of altered oceanic crust (Kelley et al., 2003; Alt and Teagle, 2003; Kelley et al., 2005). With these input values, the isotopic composition of U incorporated during low-T hydrothermal circulation, $\delta^{238}\text{U}_{\text{LT Alteration}}$, is calculated to be -0.14 ‰, equivalent to $\Delta_{\text{LT Alteration-SW}} = +0.25$ ‰.

The sink noted as “Deep Sea” in Fig. 8 and Table 8 encompasses pelagic red clays, siliceous and calcareous deep-sea sediments. Only two pelagic clays have been measured thus far (Andersen et al., 2015), and these samples have virtually the same $\delta^{238}\text{U}$ value as seawater: $\Delta_{\text{Pelagic Clays}} = +0.04$ ‰. With the exceptions of pelagic clays, there are no other constraints on the U isotopic fractionation associated with the “Deep Sea” sink, which represents at most 10 % of the U budget and can therefore be neglected. No data exists for biogenic silica (opaline silica) but this U sink represents only about 1% of the total flux out, so it has no influence on the mass-balance.

The isotopic fractionation factors and fluxes relevant to the modern oceanic uranium budget are summarized in Fig. 8 and Table 8. Several studies (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003) have given estimates of uranium fluxes in the oceanic budget that differ in both the relative size of the U sinks and even in the sinks themselves. For each oceanic budget, we calculate the modern seawater isotopic composition that is predicted using a simple mass balance model. Steady state is assumed (*i.e.*, the flux of U in the ocean is equal to the flux out into the various sinks) and the riverine input is the only source of U in the ocean. In these conditions, the following mass-balance equation can be written,

$$\delta^{238}\text{U}_{\text{Seawater predicted}} = \delta^{238}\text{U}_{\text{River}} - \sum_j \Delta^{238}\text{U}_j^{\text{sink}} \times f_j^{\text{sink}} \quad (14)$$

where $\Delta^{238}\text{U}_j^{\text{sink}}$ and f_j^{sink} are, respectively, the isotopic fractionation factor relative to seawater for U sink *j* and the fraction of total U incorporated in sink *j*.

The most recent budget by Henderson and Anderson (2003) fails to reproduce the actual seawater composition and predicts a lighter isotopic composition (-0.502 ‰). The other three budgets (Barnes and Cochran, 1990; Morford and Emerson, 1999 and Dunk et al., 2002) show very good agreement with the measured oceanic U isotopic composition of $\delta^{238}\text{U}_{\text{SW}} = -0.392 \pm 0.005$ ‰ (Figs. 8 and 9). The budget of Dunk et al. (2002) is the only one to include uncertainties on the fluxes and when propagated predicts a seawater composition of -0.403 ± 0.062 ‰, undistinguishable from the actual open ocean value that we measured. $^{238}\text{U}/^{235}\text{U}$ systematics therefore points to a modern oceanic U budget in steady state, as was suggested by the estimation of the U fluxes in and out of the ocean.

In addition to testing the steady state assumption and isotopic fractionation factors, the budget comparison in Fig. 8 and Table 8 allows us to constrain the magnitude of the flux of U into anoxic sediments (F_{Anoxic}) in the modern ocean. Indeed, because the uptake of U into anoxic reservoirs is accompanied by a large isotopic fractionation compared to other sinks ($\Delta_{\text{Anoxic/Euxinic-SW}} = +0.6$ ‰ while other Δ values are between -0.24 and +0.25 ‰), the size of the anoxic sink has a major influence on the predicted $\delta^{238}\text{U}_{\text{SW}}$ value. While keeping all other fluxes constants, we adjust the value of F_{Anoxic} in each one of the four budgets considered (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003), so that the $\delta^{238}\text{U}_{\text{SW}}$ predicted by the model matches the value measured in

the open ocean (at -0.392 ± 0.005 ‰). The results are presented in Table 9 and give a value for F_{Anoxic} of 7.0 ± 3.1 Mmol/yr. Using an accumulation rate of U into anoxic sediments of $9.2 \mu\text{mol}/\text{m}^2/\text{yr}$ (Dunk et al., 2002) and a total surface of ocean floor of $3600 \times 10^{11} \text{ m}^2$ (Turekian, 1969), this value translates into a percent of ocean floor covered by anoxic sediments of 0.21 ± 0.09 %. This value is in good agreement with values derived from mass balance considerations of U and Mo (two redox sensitive elements), as respectively, 0.35 ± 0.05 % (Veeh, 1967) and 0.23 % (Bertine and Turekian, 1973).

From this test we can also see that if the model of Henderson and Anderson (2003) fails at predicting the correct seawater isotopic composition, it is because it overestimates the flux of U into anoxic sediments relative to the total U flux out of the ocean, using a value of 35 %, when the maximum flux consistent with the isotopic composition of the modern seawater is 14 ± 3 %.

Based on the above work, the modern U budget of the ocean is presented in Fig. 10. The isotopic composition of each U reservoir can be read on the x-axis, and is derived from the compilation of data from 19 studies (including this work, see Table S3 in Supplementary Material). For the sinks, the area of the boxes is proportional to the U flux out of the ocean (fluxes from Dunk et al., 2002). Fig. 10 represents the current best estimate of the modern U oceanic budget.

Conclusion

A detailed methodology for high-precision routine analysis of the $^{238}\text{U}/^{235}\text{U}$ ratio (± 0.05 ‰) in low-resolution mode is provided, from column chemistry (Table 3) to MC-ICPMS measurements with a static cup configuration (Table 4). The partition coefficients (K_d ; Fig. 1 and Table 1) and elution behaviors (Fig. 3 and Table 2) of 16 elements on the uranium specific resin U/Teva are reported and the height equivalent to a theoretical plate (HETP) of the U/Teva resin is quantified ($\text{HETP} = 0.5 \text{ mm}$). A data reduction procedure is presented (Supplementary material) to properly propagate uncertainties on $^{238}\text{U}/^{235}\text{U}$ ratios corrected for laboratory and mass spectrometry-induced mass fractionation using the IRMM-3636 double spike. A quality control test is introduced that takes advantage of the fact that at least two naturally occurring isotopes have small contributions from the spike (Fig. 5).

The uranium isotopic compositions of 41 geostandards were measured (Table 5), along with an array of seawater samples and selected river, lake, oysters, evaporites and coral samples (Table 6). These measurements are augmented with a thorough compilation of published data from 32 studies (Fig. 6. and Supplementary Material Table S2 and S3).

The implications of the natural variability of the $^{238}\text{U}/^{235}\text{U}$ ratio on Pb-Pb and U-Pb ages is discussed and analytical formulas are provided to calculate the age correction necessary as a function of the age of the sample and its U isotopic composition (Fig. 7).

Using abundances of different rock types in the crust and estimates of their U isotopic compositions (Table 7), the composition of the continental crust is estimated to be $\delta^{238}\text{U}_{\text{Crust}} = -0.29 \pm 0.03$ (95 CI) ‰. Combining this with U isotopic analyses of oceanic basalts, taken as proxies for the

composition of the mantle, a bulk Earth U isotopic composition is calculated ($\delta^{238}\text{U} = -0.29 \pm 0.02$), which is identical to recent estimates of the average meteoritic $\delta^{238}\text{U}$ of -0.30 ± 0.03 (Goldmann et al., 2015; Andersen et al., 2015).

Measurements of a large number of seawater samples show that the open ocean has a homogenous isotopic composition at $\delta^{238}\text{U}_{\text{SW}} = -0.392 \pm 0.005 \text{‰}$ (Table 6 and Fig 9). Three of the four most recent U oceanic budgets (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002) predict a seawater isotopic composition in very good agreement with the observed $\delta^{238}\text{U}_{\text{SW}}$ (Figs. 8 and 9), which strengthens our confidence in the isotopic fractionation factors associated with each deposition environment and the fact that U is at steady-state in the modern ocean. The U oceanic budget of Henderson and Anderson (2003) does not reproduce the observed seawater composition because they assumed that the U flux to anoxic sediments relative to the total U flux out of the ocean was high, which our analysis shows cannot be correct. The U isotopic composition of seawater is used to constrain the extent of anoxia in the modern ocean (percent of seafloor covered by anoxic sediments), which is $0.21 \pm 0.09 \%$ (Table 9). This work demonstrates that stable isotopes of U can trace the extent of anoxia in the modern global ocean (Fig. 10), thereby validating the application of U isotope measurements to paleoredox reconstructions. However, more work is needed to identify which lithologies most faithfully record the global U isotopic composition of seawater through time.

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Appendix A: Relation between resin capacity factor (k') and weight distribution ratio (Kd)

The resin capacity factor k' (also called free column volume to peak maximum) is defined as the time spent by the analyte in the stationary phase over the time spent in the mobile phase, and under isocratic conditions is equal to ratio of the number of atoms of the analyte in the stationary phase to the number of atoms in the mobile phase, at any time (Neue, 1997):

$$k' = \frac{N_S}{N_M} = \frac{C_S \text{ in g per ml of solid}}{C_M \text{ in g per ml of liquid}} \times \frac{V_S}{V_M} \quad (\text{A.1})$$

where C is the concentration and V the volume, and the indexes S and M refer to, respectively, the stationary phase (solid) and the mobile phase (liquid).

The weight distribution ratio (or partition coefficient Kd , also sometimes noted Dw) is defined as follow:

$$K_d = \frac{C_S \text{ per gram of resin}}{C_M \text{ per ml solution}} \quad (\text{A.2})$$

The relation between the capacity factor (k') and the weight distribution coefficient (Kd) is thus given by the following equation:

$$k' = K_d \times \frac{d_{ext} \times V_S}{V_M} \quad (\text{A.3})$$

where d_{ext} is the density of the extractant-loaded beads in g/ml. Note that some studies report V_S as the volume of the extractant contained in the extractant loaded beads (e.g. Horwitz et al., 1992; Horwitz et al., 2006) in which case the right hand side of equation (A.3) must be divided by the extractant loading (L_{ext} , in percent) and the equation becomes:

$$k' = K_d \times \frac{d_{ext} \times V_S}{L_{ext} \times V_M} \quad (\text{A.4})$$

On U/Teva resin $Kd = 1.7 \times k'$ (Horwitz et al., 1992).

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Figure captions

Fig. 1. Distribution coefficients (K_d) of selected elements on U/Teva resin as a function of acid molarity in (a) HNO_3 , (b) HCl and (c) $\text{HCl} + \text{Oxalic acid } 0.1 \text{ M}$ (Table 1). The solid curves are polynomial fits to the data.

Fig. 2. Elution curves for 18 elements on a 2 mL cartridge (1.14 cm diameter, 2.56 cm length) of U/Teva resin (50-100 μm particle size). Except for Th and Np, all matrix elements are removed during the load, followed by rinsing in 3 M HNO_3 . Th and Np are removed in 5 M $\text{HCl} + \text{oxalic acid}$, see Horwitz et al. (1992) for the K_d values of Np.

Fig. 3. Comparison with Horwitz et al. (1992) of the distribution coefficients (K_d) on U/Teva resin of U and Th in (a) HNO_3 and (b) HCl . The curves are polynomial fits to the data. Filled symbol and solid curves are data from this study (see Fig. 1) while open symbols and dashed curves are from Horwitz et al. (1992).

Fig. 4. (a) Schematic representations of test measurements done to assess the effect of the cup configuration on U isotopic composition measurement, with $\delta^{238}\text{U}$ reported relative to the CRM-112a certificate value. The incident angles of the ion beams are exaggerated for clarity purposes. The uranium isotopic compositions using either general cones or jet cones (*i.e.*, Jet sample cones and X-skimmer cones) are given. (b) $\delta^{238}\text{U}/^{235}\text{U}$ (left) and $\delta[^{234}\text{U}/^{238}\text{U}]$ (right) of CRM-112a plotted as a function of the isotope measured in the axial collector: ^{234}U , ^{235}U or ^{236}U . $\delta^{238}\text{U}$ is reported relative to the CRM-112a certificate value (dotted line), while $\delta[^{234}\text{U}]$ is relative to secular equilibrium, using the half-lives from Cheng et al. (2013) (dotted line shows the CRM-112a value measured by Cheng et al. 2013). It can be seen that the choice of the center isotope has a large impact on the determined absolute U isotopic composition of the measured solution. U isotopic analyses using the most symmetrical cup configuration (^{235}U in the axial cup) and regular cones gives isotopic ratios that are not biased relative to values reported previously using other techniques (TIMS). This effect should be investigated for other systems, and kept in mind when assessing absolute ratios.

$\delta^{238}\text{U}$ (relative to CRM-112a certificate values)

Fig. 5. (a) $\delta^{238}\text{U}$ obtained from double spike data reduction plotted against the raw $\delta^{238}\text{U}$ measured, all values are standard bracketed (SSB). (b) Same plot as (a) but $\delta[^{234}\text{U}/^{238}\text{U}]$. Ratios obtained from double spike data reduction are sensitive to interferences on all four isotopes (^{233}U , ^{235}U , ^{236}U and ^{238}U), while ratios obtained by SSB are sensitive to interferences on the two isotopes of interest only and to isotopic fractionation during column chromatography. Despite being subject to different artifacts most samples plot on a line of slope one, which is an internal validation of the quality of the results. Deviation from the 1:1

line (dotted line) can be explained if the $\delta^{238}\text{U}$ obtained by SSB was affected by one of the following: (1) the ratio U from the spike to U from the sample was far above the optimal 3% (red symbols), or (2) the mass of sample digested was high (>1 g) and matrix elements competed with U for the resin during column chemistry (yellow symbols). Samples showing both overspiking and high sample mass are shown in red and yellow symbols. (c) Difference between the $\delta^{238}\text{U}$ values obtained by double spike and by SSB as a function of the $U_{\text{Spike}}/U_{\text{Sample}}$ ratio. (d) Same plot as (c) but for $\delta[^{234}\text{U}/^{238}\text{U}]$. The solid black curves represent mixing lines between the sample composition and the spike composition. The overspiked samples plot exactly on the mixing line, showing clearly that the excess of spike in the sample relative to the bracketing standard is responsible for the apparent discrepancy in $\delta^{238}\text{U}$ values obtained from DS+SSB and SSB only. This is also true for $\delta[^{234}\text{U}/^{238}\text{U}]$ values.

Fig. 6. Compilation of the $\delta^{238}\text{U}$ values obtained from this study and literature data (Stirling et al., 2005; Stirling et al., 2006; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Amelin et al., 2010; Brennecke et al., 2010a; Brennecke et al., 2010b; Montoya-Pino et al., 2010; Bouvier et al., 2011; Brennecke et al., 2011a; Larsen et al., 2011; Brennecke and Wadhwa, 2012; Connelly et al., 2012; Hiess et al., 2012; Telus et al., 2012; Kaltenbach, 2012; Asael et al., 2013; Cheng et al., 2013; Kendall et al., 2013; Romaniello et al., 2013; Andersen et al., 2014; Dahl et al., 2014; Goto et al., 2014; Iizuka et al., 2014; Murphy et al., 2014; Uvarova et al., 2014; Andersen et al., 2015; Goldmann et al., 2015; Kendall et al., 2015; Noordmann et al., 2015) (see Supplementary Material Table S2 for actual values). The top panel shows the modern U taxonomy, while the bottom panel shows the data of individual minerals, ore deposits, past sediments and meteoritic bodies and inclusions. Note the different scale on the two panels. In the modern ocean, strong positive isotopic fractionation relative to seawater (horizontal blue line) is recorded into sediments forming in euxinic/anoxic environments (*e.g.*, black shales), while Fe-Mn crusts and evaporites show negative fractionation. Subsurface modern carbonates include carbonates down to 40 cm below water/sediment interface. The modern U oceanic budget is explained in more details in Figure 10. Minerals show a much larger range of isotopic composition than crustal rocks (from -0.68 to +0.52 ‰ with a few minerals up to +4.8 ‰), which has implications for Pb-Pb and U-Pb ages. AOC stand for altered oceanic crust, OAE for oceanic anoxic event, ORM for organic-rich mudrocks, BIF for banded iron formations, OC for ordinary chondrites, CC for carbonaceous chondrites, and EC for enstatite chondrites. Minerals encompass albite, apatite, baddeleyite, glauconite, biotite, phlogopite, monazite, quartz, titanite, xenotime, zircon. Effusive rocks* encompass andesites, basalts, basalts alkali, rhyolites and trachytes. Intrusive rocks* encompass diorites, granites, granodiorites, syenite, and mica-schist. HEDs* encompass howardites, eucrites, aubrite, and acapulcoite.

Fig. 7. Age correction for various ΔU values as a function of the age of the sample, for (a) ^{207}Pb - ^{206}Pb ages, (b) ^{207}Pb - ^{235}U ages and (c) ^{206}Pb - ^{238}U ages. If the age of a sample was calculated with an “assumed” $^{238}\text{U}/^{235}\text{U}$ ratio (such as the consensus value, 137.88), which is different from the actual $^{238}\text{U}/^{235}\text{U}$ ratio in

the sample ($\Delta U = [^{238}\text{U}/^{235}\text{U}_{\text{Sample}} / ^{238}\text{U}/^{235}\text{U}_{\text{Assumed}} - 1] * 1000$), then an age correction is likely needed. Lines of equal ΔU values are 0.25 ‰ apart and were calculated using Eq. 10 (main text), and Eq (S.9) and Eq. (S.14) (Supplementary Material).

Fig. 8. Schematic representation of the sources, sinks and fluxes of U in the modern ocean along with their isotopic compositions (sources) or associated isotopic fractionations (sinks). Fluxes are in Mmol/yr, and isotopic compositions and fractionation factors are in permil (‰). Except for the ocean, the surface area of the boxes is proportional to the U flux. The four most recent oceanic budgets are compared (from left to right: Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003). For each budget the predicted isotopic composition of the seawater is compared to the modern seawater value of $\delta^{238}\text{U}_{\text{SW}} = -0.392 \pm 0.005$ ‰ (this study). The most recent budget of Henderson et Anderson (2003) fails at reproducing the actual seawater composition (-0.502 ‰ predicted vs. -0.392 ‰ measured). The other three budgets show very good agreement with the measured oceanic U isotopic composition.

Fig. 9. Uranium isotopic compositions predicted by the four most recent oceanic budgets (Barnes and Cochran, 1990; Morford and Emerson, 1999; Dunk et al., 2002; Henderson and Anderson, 2003) and measurements of open ocean water samples (Atlantic ocean, Pacific ocean, Mediterranean sea, English Channel, Gulf of California and Gulf of Mexico) from this study (Table 6) and the literature (Stirling et al., 2007; Weyer et al., 2008; Andersen et al., 2014; Andersen et al., 2015). The blue bar shows the weighted average of the modern open seawater value at $\delta^{238}\text{U}_{\text{SW}} = -0.392 \pm 0.002$ ‰ (this study).

Fig. 10. Schematic representation of the modern U oceanic budget. The isotopic composition of each U reservoir can be read on the x-axis. For the sinks, the area of the boxes is proportional to the U flux out of the ocean (fluxes from Dunk et al. 2002). The isotopic compositions of each reservoir are given in Table S3 in the Supplementary Material. $\delta^{238}\text{U}$ values from this study (Table 5 and 6) and the literature (Stirling et al., 2005; Stirling et al., 2007; Weyer et al., 2008; Amelin et al., 2010; Montoya-Pino et al., 2010; Larsen et al., 2011; Brennecke and Wadhwa, 2012; Telus et al., 2012; Kaltenbach, 2012; Cheng et al., 2013; Romaniello et al., 2013; Andersen et al., 2014; Dahl et al., 2014; Goto et al., 2014; Iizuka et al., 2014; Andersen et al., 2015; Goldmann et al., 2015; Noordmann et al., 2015).

Table 1Distribution coefficients (Kd) on U/Teva resin as a function of acid molarity for HNO₃, HCl and HCl + Oxalic acid 0.1 mol/L

Element	Molarity HNO ₃ (M)																			
	0.10	0.20	0.40	0.66	1.03	1.53	2.00	3.09	4.11	5.23	6.18	7.31	8.23	9.5	12.23	15.45				
Sc	<15	<15	<15	<15	<15	<15	<15	15.7	17.3	18.8	19.2	<15	<15	<15	<15	22.5	103	589	611	
Ti	<15	17.7	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	26.6	110	117	
Y	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	41.1	42.6	
Zr	23.4	37.6	<15	<15	<15	<15	16.4	20	21.6	58	58	121	358	851	2210	4872	3394	575	574	
Yb	<15	<15	<15	<15	<15	<15	<15	<15	<15	15.1	15.5	<15	<15	<15	<15	<15	<15	26.1	75	78
Hf	40.1	71	<15	<15	<15	<15	<15	<15	<15	24.8	24.1	23.5	72	210	605	1710	792	113	120	
Th	<15	<15	<15	15.6	36.8	66	136	229	243	388	383	385	562	555	521	544	392	192	213	
U	<15	15.9	85	119	191	243	402	559	606	829	827	710	749	607	385	332	263	200	223	
Fe	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	31.9	2039	470
Sn	94	72.2	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	23.2	78	32.6

Elements with Kd<15 for most molarities: Na, Mg, Al, Ca, Ni and La.

Element	Molarity HCl (M)														
	0.10	0.20	0.40	0.64	1.02	1.50	2.01	3.02	4.13	5.03	6.05	7.08	8.13	9.13	11.38
Sc	<15	<15	<15	<15	<15	<15	<15	<15	<15	17.3	86	1090	7137	>10 ⁴	>10 ⁴
Ti	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	51	130	602
Zr	68	83	34.2	59	55	30.5	64	45.3	27.4	49.1	235	2692	>10 ⁴	>10 ⁴	>10 ⁴
Hf	82	220	64	109	64	33.2	70	47.8	29.3	50	160	1168	>10 ⁴	>10 ⁴	>10 ⁴
Th	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	33.2	134	470	602
U	<15	<15	<15	<15	<15	<15	19.5	69	162	304	415	409	307	195	65
Fe	<15	<15	<15	<15	<15	<15	65	894	7291	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴	>10 ⁴
Sn	<15	<15	61	148	312	830	1810	>10 ⁴	8179	>10 ⁴	>10 ⁴	8641	752	522	61

Elements with Kd<15 for most molarities: Na, Mg, Al, Ca, Ni, Y, La and Yb.

Element	Molarity HCl M + Oxalic Acid 0.1 M																
	0.11	0.13	0.16	0.19	0.30	0.49	0.75	1.11	1.59	2.10	3.10	4.20	5.19	6.10	7.10	7.95	8.80
Sc	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	57	817	3772	6686
Ti	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	23.0	55
Zr	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	194	4701
Hf	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	15.9	>10 ⁴
Th	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	134	1971
U	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15	54	153
Fe	<15	<15	<15	<15	<15	<15	<15	<15	<15	19.4	45.9	107	223	316	342	331	417
Sn	<15	<15	<15	<15	<15	26.4	65	133	267	435	1308	2524	4442	6515	2725	1859	584

Elements with Kd<15 for most molarities: Na, Mg, Al, Ca, Ni, Y, La and Yb.^a NB: Only values between 15 and 10⁴ are reported because of limitations with the experimental set up.

Table 2 Elution yields

Table 2
Elution behaviors of 16 elements on U/Teva. Values are percent eluted in each step.

Elution step	Loading		Rinse			Conversion	Th + Np rinse		Oxalic Rinse	U rinse		
Reagents	3 M HNO3		3 M HNO3			11 M HCl	5 M HCl + 0.1 M Oxalic		5 M HCl	0.5 M HCl		
Number of column volume (2 mL)	1 - 5	6 - 10	11 - 15	16 - 20	21 - 25	26 - 28	29 - 33	34 - 38	39 - 43	44 - 48	49 - 53	54 - 58
Element												
Na	91.49	8.32	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.14	0.05	<0.01	b.d.l.	<0.01
Mg	90.76	8.62	0.09	0.05	0.04	0.14	0.08	0.04	0.05	0.10	0.03	<0.01
Al	91.22	8.59	0.01	b.d.l.	b.d.l.	0.04	0.01	<0.01	0.02	0.09	<0.01	<0.01
Ca	89.73	8.46	b.d.l.	b.d.l.	b.d.l.	0.29	0.53	0.71	0.07	0.17	<0.01	0.04
Sc	72.92	27.03	0.05	b.d.l.	b.d.l.	b.d.l.	b.d.l.	<0.01	<0.01	b.d.l.	b.d.l.	b.d.l.
Ti	89.03	8.43	0.09	0.04	0.03	0.06	0.98	1.02	0.24	0.08	<0.01	0.01
Fe	90.81	8.57	0.05	0.01	<0.01	0.03	0.03	0.01	<0.01	0.39	0.05	0.04
Ni	91.17	8.75	0.04	0.01	<0.01	<0.01	<0.01	b.d.l.	b.d.l.	0.01	b.d.l.	<0.01
Y	87.51	12.44	0.05	<0.01	<0.01	<0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Zr	59.88	27.83	10.37	1.44	0.21	0.13	b.d.l.	0.01	0.02	0.05	0.05	<0.01
Sn	90.89	8.55	0.12	0.08	0.06	0.06	0.05	0.04	b.d.l.	0.14	b.d.l.	b.d.l.
La	90.28	9.65	0.04	<0.01	<0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02	b.d.l.	b.d.l.
Yb	87.35	12.58	0.04	<0.01	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02	0.01	b.d.l.
Hf	85.28	14.30	0.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03	0.13	0.12	0.10	0.02
Th	0.03	<0.01	<0.01	0.03	0.11	0.06	99.15	0.17	0.40	0.04	<0.01	<0.01
U	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.08	0.22	0.46	98.91	0.18	0.09

^a For each element, collected values are normalized to the fraction collected from loading to the end of the elution. The collected fraction is typically more than 97 % of the calculated fraction passed onto the column.

Table 3
Chromatographic extraction protocol of U on U/TEVA. Column volume (cv) = 2 mL. Modified from Weyer et al. (2008)

Step	Acid type	Volume	Comment
Cleaning	0.05 M HCl	20 mL	
Conditioning	3 M HNO ₃	6 mL	
Sample loading	3 M HNO ₃	10 mL	
Matrix rinse	3 M HNO ₃	40 mL	Elution of matrix, except U, Th, Np
Conversion to HCl	11 M HCl	6 mL	
Th rinse	5 M HCl + 0.1 M oxalic	20 mL	Elution of Th
Oxalic acid rinse	5 M HCl	10 mL	
Elution	0.05 M HCl	25 mL	U is recovered

Table 4
Faraday collector configurations and method specifications for U isotopic measurements on MC-ICPMS in low resolution

	Configuration						Focus	Dispersion	Uptake Time	Acquisition Time	Rinse Time
	L2	L1	Axial	H1	H2	H3					
Resistor (W)	10 ¹¹	10 ¹¹	SEM	10 ¹¹	10 ¹¹	10 ¹¹					
Main	-	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	²³⁸ U	-1.5 V	0 V	90 sec	210 sec	> 210 sec
Sem/F calibration	-	-	²³⁶ U	²³⁸ U	-	-	-1.5 V	0 V	90 sec	210 sec	> 210 sec

^a The "main" sequence is used to measure the samples and the bracketings standards.

^b The "Sem/F calibration" sequence was used weekly to determine the conversion factor from counts per seconds (cps) to volts on the SEM.

Table 5 Summary of U isotopic compositions and concentrations of geostandards measured in this study																								
From double spike data reduction										rom sample-standard bracketing not using the double spike														
Sample	Material	Mass Resin digested # (mg)	n		95 Cl		95 Cl		Conc. (μ g/g)	2 SD	95 Cl		95 Cl		Conc. (μ g/g)	z	Source							
			$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$			$\delta^{235}\text{U}/^{238}\text{U}$	$\delta^{235}\text{U}/^{238}\text{U}$												
ROCKS																								
AGV-1	Andesite	*** SEM	✓	2	126.63	9	-0.16	0.05	29.2	0.3	-10.6	0.3	1.89	0.01	3.3%	-0.21	0.19	36.9	0.3	-3.5	0.4	1.92	0.15	(1)
AGV-2	Andesite	*** Far.	✓	2	128.5	9	-0.18	0.09	31.9	8.7	-7.9	8.3	1.87	0.01	3.3%	-0.23	0.08	39.4	8.6	-1.0	8.2	1.88	0.16	(1)
Arizo-1	Basalt	*** SEM		2	174.4	9	-0.27	0.04	39.0	0.5	-1.0	0.5	1.39	0.01	3.3%	-0.22	0.13	41.5	0.5	0.4	0.6	1.4	***	(2)
BCR-1	Basalt	*** SEM		2	138.45	9	-0.26	0.05	39.0	0.3	-1.1	0.3	1.68	0.01	3.4%	-0.33	0.19	50.2	0.3	9.3	0.4	1.75	***	(3)
BCR-2	Basalt	* Far.		2	302.03	9	-0.23	0.05	45.3	6.7	5.0	6.5	1.64	0.01	3.4%	-0.21	0.10	43.8	6.7	3.0	6.3	1.69	0.19	(1)
BCR-2 rep.	Basalt	** Far.		2	150.3	9	-0.24	0.06	45.1	5.7	4.8	5.5	1.68	0.01	3.0%	-0.30	0.05	41.8	5.7	1.3	5.4	1.69	0.19	(1)
BCR-2 rep.	Basalt	*** Far.		2	142.68	3	-0.24	0.11	39.2	11.6	-0.9	11.2	1.67	0.01	3.3%	-0.27	0.33	43.4	11.6	2.9	11.2	1.69	0.19	(1)
BCR-2 rep. bef	Basalt	*** SEM		2	144.05	9	-0.26	0.05	39.7	0.2	-0.3	0.2	1.67	0.01	3.3%	-0.31	0.06	47.3	0.2	6.6	0.2	1.69	0.19	(1)
BCR-2 rep. aft	Basalt	*** SEM		2	144.27	9	-0.26	0.05	40.2	0.2	0.1	0.2	1.66	0.01	3.4%	-0.30	0.06	48.5	0.2	7.7	0.2	1.69	0.19	(1)
BCR-2 rep.	Basalt	*** SEM		2	143.2	9	-0.26	0.03	40.9	0.7	0.8	0.7	1.66	0.01	3.4%	-0.23	0.12	49.1	0.7	8.1	0.7	1.69	0.19	(1)
BCR-2 rep.	Basalt	*** SEM		2	144.4	9	-0.26	0.04	41.1	0.5	1.0	0.5	1.70	0.01	3.3%	-0.32	0.09	47.5	2.6	6.7	2.5	1.69	0.19	(1)
BE-N	Basalt	* Far.		2	98.13	9	-0.30	0.04	38.8	3.9	-1.2	3.8	2.41	0.01	1.8%	-0.26	0.07	-16.1	3.9	-53.8	3.7	2.4	0.18	(3)
BE-N rep.	Basalt	*** SEM		2	102.2	9	-0.33	0.05	37.9	0.5	-2.0	0.5	2.47	0.02	3.1%	-0.32	0.07	33.1	0.5	-7.0	0.4	2.4	0.18	(3)
BHVO-2	Basalt	** Far.		2	571.8	9	-0.32	0.06	38.5	6.1	-1.5	5.8	0.40	0.00	3.6%	-0.34	0.08	54.5	6.0	13.4	5.8	0.42	***	(3)
BX-N	Bauxite	*** SEM		2	30.7	9	-0.34	0.05	44.9	0.3	4.8	0.3	9.15	0.06	3.1%	-0.32	0.12	44.6	0.3	4.0	0.3	8.8	***	(3)
BX-N rep.	Bauxite	*** SEM		2	28.8	9	-0.30	0.04	46.1	0.3	5.8	0.3	9.04	0.07	3.0%	-0.32	0.13	40.5	0.3	0.6	0.4	8.8	***	(3)
BSK-1	Bottom Sed.	*** SEM		2	81.39	9	-0.18	0.06	96.1	0.3	53.9	0.3	2.63	0.02	3.7%	-0.14	0.17	116.7	0.3	72.6	0.4	3	***	(4)
COQ-1	Carbonatite	** Far.		2	24.8	9	-0.35	0.06	20.4	5.7	-18.8	5.5	9.07	0.10	3.7%	-0.37	0.05	41.5	5.7	1.0	5.4	11	0.60	(1)
COQ-1 rep.	Carbonatite	*** SEM		2	28.2	9	-0.31	0.05	26.4	0.5	-13.1	0.5	12.04	0.13	2.3%	-0.29	0.07	-5.6	0.5	-43.8	0.4	11	0.60	(1)
CLB-1	Coal	** Far.		2	409.2	9	-0.32	0.06	53.7	6.1	13.2	5.8	0.50	0.00	3.7%	-0.35	0.08	72.0	6.0	30.1	5.8	0.55	***	(1)
CVE-1	Coal	*** Far.		2	801.1	7	-0.26	0.10	42.2	9.8	3.0	9.4	0.75	0.00	2.5%	-0.24	0.09	20.8	9.8	-18.8	9.3			
W-2	Dabase	*** Far.		2	453.58	9	-0.34	0.09	42.4	8.7	2.3	8.3	0.49	0.00	3.5%	-0.37	0.08	57.5	8.6	16.4	8.2	0.53	***	(1)
DR-N	Diorite	*** SEM		2	162.9	9	-0.32	0.06	41.3	5.0	1.2	4.8	1.56	0.01	3.2%	-0.41	0.20	38.4	5.0	-2.0	4.7	1.53	0.13	(5)
WS-E	Dolerite	** Far.		2	370.17	9	-0.22	0.09	45.0	8.7	4.7	8.3	0.62	0.00	3.4%	-0.26	0.08	56.8	8.6	15.8	8.2	0.85	***	(3)
AC-E	Granite	* Far.	✓	2	109	9	-0.25	0.05	-7.2	6.7	-45.5	6.5	4.41	0.02	3.2%	-0.38	0.10	-12.8	6.7	-50.6	6.3	4.6	***	(3)
GA	Granite	* Far.	✓	2	100.28	9	-0.25	0.06	-13.7	4.8	-51.8	4.6	4.58	0.02	3.7%	-0.42	0.09	-3.1	4.8	-41.3	4.6	5	0.50	(3)
GS-N	Granite	*** Far.	✓	2	34.5	9	-0.33	0.07	8.4	6.3	-30.5	6.0	7.73	0.07	3.0%	-0.30	0.06	4.5	6.3	-34.3	6.0	7.5	***	(3)
G-2	Granite	*** SEM	✓	2	137.36	9	-0.11	0.10	33.4	0.3	-6.6	0.3	1.86	0.01	3.1%	-0.17	0.17	34.2	0.3	-6.1	0.4	1.76	***	(3)
G-3	Granite	*** Far.	✓	2	136.9	9	-0.19	0.07	47.0	10.1	6.5	9.7	3.08	0.02	1.9%	-0.09	0.06	5.2	10.0	-33.8	9.6	2.3	0.30	(6)
GSP-1	Granodiorite	*** SEM	✓	2	97.52	8	-0.04	0.05	15.0	0.3	-24.3	0.3	2.37	0.01	3.8%	-0.11	0.13	27.3	0.3	-12.6	0.3	2.54	***	(3)
GSP-2	Granodiorite	*** SEM	✓	2	101.05	9	0.17	0.06	18.6	0.3	-21.1	0.3	2.44	0.02	3.3%	0.12	0.17	23.4	0.3	-16.7	0.4	2.4	0.19	(1)
JG-1	Granodiorite	*** SEM	✓	2	63.63	8	-0.29	0.05	24.1	0.3	-15.3	0.3	4.00	0.02	3.2%	-0.28	0.13	25.9	0.3	-13.7	0.3	3.93	0.07	(7)
SDC-1	Mica-Schist	*** Far.	✓	2	78.4	9	-0.30	0.09	34.7	8.7	-5.2	8.3	2.85	0.02	3.6%	-0.32	0.08	51.0	8.6	10.2	8.2	2.43	0.14	(8)
SDC-1 rep.	Mica-Schist	*** SEM		2	42.8	9	-0.26	0.04	36.3	0.5	-3.7	0.5			3.8%	-0.20	0.06	53.7	0.5	12.5	0.5	2.43	0.14	(8)
NDO-H-1	Mn-Nodule	* Far.		2	34.6	9	-0.53	0.07	128.5	6.3	85.5	6.1	6.93	0.07	3.1%	-0.59	0.07	128.0	6.3	83.6	6.0	7	0.07	(9)
NKT-1	Nephelinite	*** SEM		2	107	9	-0.29	0.08	40.0	0.7	0.0	0.6	2.15	0.02	3.4%	-0.32	0.09	45.6	0.7	4.8	0.5	2.275	0.00	(10)
RGM-2	Rhyolite	*** Far.	✓	2	46.5	9	-0.31	0.09	43.8	8.7	3.6	8.3	5.61	0.05	3.0%	-0.33	0.08	41.4	8.6	1.1	8.2	5.8	0.50	RGM-1 USGS
SBC-1	Shale	*** SEM		2	49	8	-0.26	0.05	35.6	0.7	-4.3	0.6	5.63	0.03	5.5%	-0.35	0.07	117.5	1.5	73.5	1.4	5.7	***	(11)
SBC-1 rep.	Shale	*** SEM		2	11.5	5	-0.25	0.06	24.4	0.4	-15.1	0.4	5.51	0.11	24.0%	-0.53	0.06	726.1	2.2	663.1	2.1	5.7	***	(11)
SDO-1	Shale	*** SEM		2	6.5	9	-0.07	0.05	40.6	0.2	0.3	0.2	43.58	1.50	3.3%	-0.12	0.08	49.6	1.6	8.6	1.5	48.8	6.50	(1)
SDO-1 rep.	Shale	*** SEM		2	5.4	9	-0.06	0.04	41.0	0.6	0.7	0.6	43.90	1.83	3.3%	-0.09	0.07	49.6	0.8	8.6	0.8	48.8	6.50	(1)
SDO-1 rep.	Shale	*** SEM		2	5	8	-0.11	0.05	40.8	0.6	0.5	0.6	41.61	1.96	4.0%	-0.06	0.05	73.3	3.5	30.9	3.3	48.8	6.50	(1)
SGR-1	Shale	* Far.		2	92.99	9	-0.17	0.05	44.8	6.7	4.5	6.5	5.24	0.02	3.4%	-0.08	0.10	43.8	6.7	2.9	6.3	5.4	0.40	(1)
SGR-1 rep.	Shale	** Far.		2	53.1	9	-0.22	0.07	36.7	6.3	-3.3	6.1	5.03	0.04	3.2%	-0.25	0.07	37.8	6.3	-2.6	6.0	5.4	0.40	(1)
SGR-1 rep.	Shale	** Far.		2	48.9	9	-0.18	0.07	42.8	6.3	2.5	6.1	4.76	0.04	3.5%	-0.22	0.07	55.5	6.3	14.2	6.0	5.4	0.40	(1)
SONE-1	Soil	*** SEM		2	118.8	9	-0.32	0.06	-40.7	0.3	-77.7	0.3	3.34	0.02	2.0%	-0.34	0.17	-79.3	0.3	-113.1	0.4			
STM-2	Syenite	*** SEM		2	27.8	9	-0.34	0.06	38.8	5.0	-1.2	4.8	8.06	0.09	3.6%	-0.39	0.20	48.9	5.0	8.0	4.7	9.06	***	(3)
ISH-G	Trachyte	*** SEM		2	30.9	9	-0.27	0.08	39.8	0.7	-0.2	0.6	9.11	0.09	2.8%	-0.31	0.09	24.7	0.7	-15.1	0.5	8.8	***	(3)
MDO-G	Trachyte	*** SEM		2	40.1	9	-0.34	0.05	34.3	4.5	-5.4	4.3	6.27	0.04	3.1%	-0.39	0.18	30.4	4.5	-9.6	4.2	6.3	***	(12)
MINERALS																								
AL-1	Albite	*** SEM		2	43.4	9	-0.25	0.06	-58.0	5.0	-34.4	4.8	5.77	0.05	3.2%	-0.33	0.20	-60.3	5.0	-95.8	4.7	5.8	***	(3)
DT-N	Dixite	*** SEM		2	108.8	9	-0.26	0.04	24.3	0.6	-15.2	0.6	2.21	0.02	3.3%	-0.27	0.07	33.0	0.8	-7.1	0.8	2.3	0.43	(3)
GL-O	Glaucanite	*** Far.		2	297.46	9	-0.38	0.07	63.0	6.3	22.2	6.0	0.81	0.01	3.3%	-0.39	0.06	68.6	6.3	27.1	6.0	0.80	***	(3)
Mica_Mg	Mica (phlogopite)	*** SEM		2	1615.88	9	-0.50	0.06	22.2	0.3	-17.0	0.3	0.14	0.00	3.4%	-0.69	0.17	32.4	0.3	-7.3	0.4	0.15	***	(3)
Mica_Fe	Mica (biotite)	*** SEM		2	3.48	9	-0.30	0.05	62.0	0.3	21.2	0.3	87.88	0.35	2.8%	-0.35	0.12	44.5	0.3	4.0	0.3	80	8	(12)
SONE-1	Soil	*** SEM		2	118.8	9	-0.32	0.06	-40.7	0.3	-77.7	0.3	3.34	0.02	2.0%	-0.34	0.17	-79.3	0.3	-113.1	0.4			
STM-2	Syenite	*** SEM		2	27.8	9	-0.34	0.06	38.8	5.0	-1.2	4.8	8.06	0.09	3.6%	-0.39	0.20	48.9	5.0	8.0	4.7	9.06	***	(3)
ISH-G	Trachyte	*** SEM		2	30.9	9	-0.27	0.08	39.8	0.7	-0.2	0.6	9.11	0.09	2.8%	-0.31	0.09	24.7	0.7	-15.1	0.5	8.8	***	(3)
MDO-G	Trachyte	*** SEM		2	40.1	9	-0.34	0.05	34.3	4.5	-5													

Table 6 data seawaters

Table 6																									
Summary of U isotopic compositions and concentrations of seawaters, lake, rivers, coral, oysters and evaporites measured in this study																									
					From double spike data reduction											From sample standard bracketing not using the double spike								Recommended	
				Resin #	Mass digested (g)	n	d ²³⁸ U/ ²³⁵ U	95 CI	d ²³⁴ U/ ²³⁵ U	95 CI	d [²³⁴ U/ ²³⁸ U]	95 CI	Conc. (ng/g)	2 SD	Usp/Usm	p	d ²³⁸ U/ ²³⁵ U	95 CI	d ²³⁴ U/ ²³⁵ U	95 CI	d [²³⁴ U/ ²³⁸ U]	95 CI	Conc. (ng/g)	±	Source
Sample	Material/ Location																								
RIVER																									
Garonne river 2011	France	***	SEM	3	81.366	8	-0.21	0.05	186.9	0.7	141.4	0.6	6.231	0.046	1.6%		-0.19	0.07	131.8	1.5	89.9	1.4	0.69	0.10	(1)
Garonne river 2011 rep	France	***	SEM	3	320.590	5	-0.22	0.06	177.9	0.8	132.7	0.8	0.075	0.001	14.1%		-0.60	0.06	554.1	4.4	492.2	4.2	0.69	0.10	(1)
Garonne river 2012	France	***	SEM	3	326.130	8	-0.24	0.05	236.6	0.7	189.3	0.6	0.602	0.011	1.5%		-0.16	0.07	181.0	1.5	136.7	1.4	0.69	0.10	(1)
Garonne river average							-0.22	0.03									-0.32	0.04							
LAKE																									
Lake Michigan 1	Chicago, USA	***	SEM	2	80.350	3	-0.38	0.13	311.8	0.6	261.9	0.5	0.339	0.002	29.4%		-1.38	0.47	1213.5	0.7	1123.9	1.1	0.30	0.02	(2)
Lake Michigan 1 rep.	Chicago, USA	***	SEM	3	322.460	6	-0.36	0.06	315.3	0.7	265.2	0.6	0.330	0.006	3.1%		-0.38	0.06	311.6	2.0	261.2	1.8	0.30	0.02	(2)
Lake Michigan 2	Indiana dunes, USA	***	SEM	2	80.780	3	-0.34	0.13	309.2	0.6	259.3	0.5	0.352	0.003	26.2%		-1.27	0.47	1100.7	0.7	1016.0	1.1	0.30	0.02	(2)
Lake Michigan 2 rep.	Indiana dunes, USA	***	SEM	3	321.330	6	-0.39	0.06	309.8	0.8	260.0	0.7	0.345	0.006	2.8%		-0.46	0.08	297.9	1.7	248.6	1.6	0.30	0.02	(2)
Lake Michigan average							-0.37	0.04									-0.43	0.05							
EVAPORITES																									
Salt_Gypsum	Santioco	***	SEM	3	3.6758	4	-0.60	0.07	244.4	0.9	197.2	0.9	13.8	1.0	1.5%		-0.56	0.07	187.0	4.9	142.7	4.7			
Salt_Halite	Santioco	***	SEM	3	9.448	4	-0.56	0.07	248.2	0.9	200.8	0.9	6.0	0.6	1.0%		-0.57	0.07	172.8	4.9	129.2	4.7	11	6	(3)
Guerande salt	France	***	SEM	3	8.3506	5	-0.54	0.06	190.1	0.8	144.8	0.8	10.0	0.8	0.9%		-0.48	0.08	105.8	3.4	65.3	3.3	11	6	(3)
Evaporite average							-0.56	0.04									-0.54	0.04							
CORAL																									
Modern coral	Florida, USA	***	SEM	1	0.19837	9	-0.38	0.03	188.2	0.5	142.8	0.5	1.96	0.01	2.5%		-0.37	0.06	163.8	4.3	120.5	4.1			
Modern coral rep.	Florida, USA	***	SEM	1	0.20019	9	-0.39	0.03	188.0	0.4	142.6	0.4	2.00	0.01	2.4%		-0.44	0.05	157.0	3.7	114.1	3.5			
Coral average							-0.39	0.02									-0.41	0.04							
OYSTERS																									
Oyster_Arguin	Arguin, France	***	SEM	2	2.13899	5	-0.34	0.07	141.9	8.0	98.2	7.7	40.70	0.14	20.2%		-1.04	0.34	721.0	7.9	650.9	7.4			
Oyster_Gillardot	Gillardot France	***	SEM	2	2.16178	3	-0.63	0.09	166.1	10.3	121.8	9.9	13.02	0.05	60.7%		-2.85	0.44	2130.5	10.2	1995.7	9.6			
Oyster_Quiberon_7V	Quiberon, France	***	SEM	2	2.10936	3	-0.41	0.11	159.4	8.7	115.1	8.4	15.30	0.05	53.7%		-2.27	0.34	1885.7	8.6	1760.1	8.1			
Oyster_Quiberon	Oyster	***	SEM	2	2.10936	1	-0.51	0.15	162.8	17.9	118.5	17.2	15.30	0.05	53.7%		-2.48	0.77	1889.2	17.7	1766.0	16.6			
Oyster_PeconicBay	Peconic Bay, USA	***	SEM	2	2.0496	6	-0.93	0.06	94.5	7.3	53.2	7.0	46.68	0.16	17.3%		-1.36	0.31	574.4	7.2	512.0	6.8			
Tiki_Oyster	Carbonate	***	Far.	2	1.2536	2	-0.26	0.19	-9.3	18.4	-47.5	17.7	30.98	0.00	40.0%		-1.13	0.17	1255.9	18.3	1165.6	17.4			
SEAWATERS																									
Arguin, France	Atlantic Ocean	***	SEM	3	321.020	9	-0.39	0.04	189.9	0.5	144.5	0.5	3.15	0.01	3.0%		-0.39	0.06	179.5	0.5	135.5	0.5	3.22	0.06	(4)
Miami, FL	Atlantic Ocean	**	Far.	2	80.270	9	-0.35	0.06	189.6	5.7	144.2	5.5	2.81	0.02	4.4%		-0.43	0.05	229.7	5.7	183.2	5.4	3.22	0.06	(4)
Atlantic Ocean average							-0.38	0.03	189.9	0.5	144.5	0.5					-0.41	0.04	180.0	0.5	136.0	0.5			
Dive 4463 EPR	Pacific Ocean	***	Far.	2	80.140	9	-0.39	0.03	190.5	2.4	145.0	2.3	3.12	0.02	3.0%		-0.40	0.06	185.9	2.4	141.7	2.3	3.22	0.06	(4)
Dive 3961 EPR	Pacific Ocean	***	Far.	2	80.250	9	-0.41	0.05	191.5	4.1	146.1	4.0	3.17	0.02	3.0%		-0.37	0.04	185.2	4.1	141.3	3.9	3.22	0.06	(4)
San Francisco, CA	Pacific Ocean	***	SEM	2	80.280	9	-0.45	0.04	191.7	0.5	146.3	0.5	2.95	0.02	3.3%		-0.40	0.09	191.9	0.5	146.9	0.5	3.22	0.06	(4)
San Francisco, CA rep.	Pacific Ocean	***	SEM	1	80.172	9	-0.38	0.05	192.3	0.4	146.8	0.4	3.03	0.02	3.1%		-0.42	0.08	189.8	3.2	145.4	3.0	3.22	0.06	(4)
San Francisco, CA rep.	Pacific Ocean	***	SEM	2	80.172	9	-0.36	0.05	191.9	0.4	146.4	0.4	3.03	0.02	3.1%		-0.41	0.06	190.9	2.4	146.3	2.2	3.22	0.06	(4)
San Francisco, CA rep.	Pacific Ocean	***	SEM	3	80.172	9	-0.36	0.04	191.3	0.6	145.8	0.6	3.03	0.02	3.1%		-0.36	0.07	189.6	0.8	145.3	0.8	3.22	0.06	(4)
San Francisco, CA rep.	Pacific Ocean	***	SEM	4	80.172	8	-0.41	0.07	190.6	0.5	145.2	0.5	3.03	0.02	3.1%		-0.39	0.07	189.0	0.7	144.7	0.6	3.22	0.06	(4)
San Francisco, CA rep.	Pacific Ocean	***	SEM	5	80.172	9	-0.34	0.04	189.5	0.4	144.0	0.4	3.03	0.02	3.1%		-0.33	0.07	183.6	3.4	139.1	3.2	3.22	0.06	(4)
Pacific Ocean average							-0.40	0.02	191.4	0.3	145.9	0.3					-0.38	0.03	191.4	0.5	146.4	0.5			
Cadaques, Spain	Mediterranean Sea	***	SEM	2	80.230	9	-0.40	0.04	192.8	0.6	147.3	0.6	3.43	0.02	2.9%		-0.45	0.13	177.7	0.6	133.4	0.7	3.22	0.06	(4)
Faedra, Crete	Mediterranean Sea	***	SEM	3	160.710	9	-0.39	0.05	197.1	0.6	151.4	0.6	3.48	0.01	2.8%		-0.38	0.06	181.5	1.4	137.4	1.3	3.22	0.06	(4)
Juan-les-Pins, France	Mediterranean Sea	**	Far.	2	80.150	9	-0.36	0.06	187.3	5.7	141.9	5.5	3.16	0.02	3.6%		-0.42	0.05	201.5	5.7	156.3	5.4	3.22	0.06	(4)
Santorini, Greece	Mediterranean Sea	***	SEM	3	159.970	9	-0.39	0.04	189.2	0.5	143.8	0.5	3.42	0.01	2.8%		-0.38	0.06	170.6	0.5	126.9	0.5	3.22	0.06	(4)
Mediterranean Sea average							-0.39	0.02	192.6	0.3	147.1	0.3					-0.40	0.03	174.5	0.4	130.4	0.4			
Galveston 2011, TX	Gulf of Mexico	***	Far.	2	80.320	9	-0.38	0.07	202.3	6.2	156.4	5.9	2.89	0.02	3.3%		-0.38	0.06	206.9	6.1	162.0	5.9	3.22	0.06	(4)
Galveston 2011, TX rep	Gulf of Mexico	***	SEM	2	81.530	9	-0.35	0.05	202.2	0.2	156.3	0.2	2.85	0.01	3.4%		-0.42	0.06	210.7	0.2	165.3	0.2	3.22	0.06	(4)
Galveston 2011, TX rep	Gulf of Mexico	***	SEM	2	80.050	9	-0.36	0.05	202.1	0.3	156.2	0.2	2.80	0.01	3.6%		-0.46	0.17	215.3	0.3	169.7	0.4	3.22	0.06	(4)
Galveston 2012, TX	Gulf of Mexico	***	SEM	3	160.430	8	-0.37	0.05	204.6	0.6	158.6	0.6	2.13	0.01	4.5%		-0.36	0.05	249.7	3.5	202.1	3.3	3.22	0.06	(4)
Gulf of Mexico average							-0.36	0.03	202.3	0.2	156.4	0.2					-0.39	0.03	212.5	0.2	166.6	0.2			
Abu Dhabi, UAE	Persian Gulf	***	SEM	2	160.610	9	-0.34	0.05	187.2	0.5	141.8	0.5	3.93	0.02	2.4%		-0.34	0.07	155.8	0.5	112.8	0.4	3.22	0.06	(4)
Dubai, UAE	Persian Gulf	***	SEM	2	160.270	9	-0.32	0.05	186.2	0.5	140.8	0.5	3.82	0.01	2.5%		-0.29	0.07	157.3	0.5	114.2	0.4	3.22	0.06	(4)
Persian Gulf average							-0.33	0.03	186.7	0.3	141.3	0.3					-0.32	0.05	156.5	0.3	113.5	0.3			
Arcachon, France	Arcachon Bassin	***	Far.	2	80.030	9	-0.30	0.06	195.1	6.7	149.4	6.5	2.98	0.02	3.0%		-0.39	0.19	189.0	6.7	145.4	6.5	3.22	0.06	(4)
Moulleau, France	Arcachon Bassin	***	Far.	1	120.540	8	-0.33	0.06	191.9	8.9	146.3	8.6	3.12	0.01	3.3%		-0.88	0.14	198.1	8.8	154.3	8.5	3.22	0.06	(4)
Moulleau, France	Arcachon Bassin	***	Far.	2	120.540	8	-0.35	0.07	192.9	7.2	147.3	6.9	3.12	0.01	3.3%		-0.42	0.07	199.1	7.2	154.6	6.9	3.22	0.06	(4)
Moulleau, France	Arcachon Bassin	***	Far.	3	120.540	8	-0.37	0.07	187.9	8.1	142.5	7.8	3.12	0.01	3.3%		-0.40	0.06	194.2	8.1	149.9	7.7	3.22	0.06	(4)
Arcachon Bassin average							-0.33	0.05	193.5	4.3	148.3	4.1					-0.58	0.07	190.5	4.3	146.4				

Table 7 crust composition

Table 7
Abundances, masses, U concentrations and isotopic compositions of main types of rocks in the modern continental crust, the modern oceanic crust and the modern whole crust.

Poldervaart 1955							Ronov & Yaroshevsky 1969						
Rock type	% volume	Mass (10 ²⁴ g)	U conc. ^a (ppm)	d ²³⁸ U (‰)	± (‰)	n	Rock type	% volume	Mass (10 ²⁴ g)	U conc. ^a (ppm)	d ²³⁸ U (‰)	± (‰)	n
Continental crust													
Sediments*	0.8	0.12	3	-0.30	0.05	4	Sediments*	1.7	0.35	3	-0.30	0.05	4
Clays**	0.7	0.10	3	-0.35	0.05	7	Clays**	2.8	0.56	3	-0.35	0.05	7
Shales	1.6	0.24	4	-0.24	0.11	3	Shales	2.5	0.51	4	-0.24	0.11	3
Granite/Rhyolite	41.7	6.03	4	-0.34	0.04	17	Granites	14.2	3.07	4	-0.33	0.05	15
							Syenites, nepheline syenites	0.1	0.03	4	-0.31	0.03	6
							Gneisses	29.0	6.29	3.5	-0.26	0.04	1
Granodiorites	19.2	2.83	3	-0.21	0.09	8	Granodiorites, diorites	15.0	3.25	3	-0.25	0.05	16
Diorites/Andesites	8.1	1.24	3	-0.28	0.04	10							
Basalts	27.8	4.24	0.56	-0.29	0.01	43	Basalts, gabbros, amphibolites, eclogites	29.9	7.05	0.56	-0.29	0.01	43
							Dunites, peridotites	0.0	0.01	0.01	-0.08	0.26	1
							Crystalline schists	4.1	0.88	2	-0.26	0.04	2
							Marbles	0.7	0.15	0.2	?		
<i>Continental Crust</i>	<i>100.0</i>	<i>14.80</i>	<i>2.7</i>	<i>-0.30</i>	<i>0.04</i>		<i>Continental Crust</i>	<i>100.0</i>	<i>22.14</i>	<i>2.5</i>	<i>-0.28</i>	<i>0.03</i>	
		²³⁸ U/ ²³⁵ U ratio ^b		137.796	0.005				²³⁸ U/ ²³⁵ U ratio ^b		137.799	0.004	
Modern oceanic crust													
Sediments*	2.2	0.18	3	-0.30	0.05	4	Sediments*	0.9	0.05	3	-0.30	0.05	4
Clays**	12.8	1.05	3	-0.35	0.05	7	Clays**	11.5	0.57	3	-0.35	0.05	7
Diorites	12.3	1.06	3	-0.28	0.04	8							
<i>Basalts[§]</i>							<i>Basalts[§]</i>						
Upper AOC	6.1	0.55	0.4	-0.17	0.03		Upper AOC	7.3	0.49	0.4	-0.17	0.03	
Lower crust	66.6	6.03	0.05	-0.29	0.01	43	Lower crust	80.3	5.37	0.05	-0.29	0.01	43
<i>Oceanic crust</i>	<i>100.0</i>	<i>8.86</i>	<i>0.83</i>	<i>-0.31</i>	<i>0.03</i>		<i>Oceanic crust</i>	<i>100.0</i>	<i>6.46</i>	<i>0.36</i>	<i>-0.33</i>	<i>0.04</i>	
		²³⁸ U/ ²³⁵ U ratio ^b		137.794	0.004				²³⁸ U/ ²³⁵ U ratio ^b		137.792	0.005	
Whole (continental + oceanic) crust													
Sediments*	1.3	0.30	3	-0.30	0.05	4	Sediments*	1.6	0.40	3	-0.30	0.05	4
Clays**	5.1	1.14	3	-0.35	0.05	7	Clays**	4.7	1.13	3	-0.35	0.05	7
Shales	1.0	0.24	4	-0.24	0.11	3	Shales	1.9	0.51	4	-0.24	0.11	3
Granite/Rhyolite	26.7	6.0	4.0	-0.34	0.04	17	Granites	11.0	3.07	4	-0.33	0.05	15
							Syenites, nepheline syenites	0.1	0.03	4	-0.31	0.03	6
							Gneisses	22.4	6.29	3.5	-0.26	0.04	1
Granodiorites	12.3	2.83	3	-0.21	0.09	8	Granodiorites, diorites	11.6	3.25	3	-0.25	0.05	16
Diorites/Andesites	9.6	2.30	3	-0.28	0.04	10							
Basalts	44.0	10.82	0.27	-0.29	0.01	43	Basalts	42.9	12.90	0.34	-0.29	0.01	43
							Dunites, peridotites	0.0	0.01	0.01	-0.08	0.26	1
							Crystalline schists	3.2	0.88	2	-0.26	0.04	2
							Marbles	0.5	0.15	0.2	?		
<i>Whole crust</i>	<i>100.0</i>	<i>23.66</i>	<i>2.0</i>	<i>-0.30</i>	<i>0.03</i>		<i>Whole crust</i>	<i>100.0</i>	<i>28.61</i>	<i>2.0</i>	<i>-0.28</i>	<i>0.03</i>	
		²³⁸ U/ ²³⁵ U ratio ^b		137.795	0.005				²³⁸ U/ ²³⁵ U ratio ^b		137.798	0.004	

* "Sediments" encompasses calcareous sands, siliceous oozes, sandstone and graywacke.
** "Clays and shales" encompasses red clay, carbonates, limestone, shelf sediments and hemipelagic sediments.
§ The structure of the basaltic layer in the modern oceanic crust is taken from Andersen et al. (2015). The crust is assumed to be 6 km deep, with only the top 500 m being strongly altered by low temperature hydrothermal circulation ([U] = 0.4 ppm and high d238U = -0.17‰) and the remaining 5500 m being MORB like ([U] = 0.05 ppm and d238U = -0.29‰).
^a Unless indicated otherwise, concentrations are taken from Rogers and Adams (1969).
^b Absolute ratios are calculated using the ²³⁸U/²³⁵U ratio from Richter et al. (2010) of 137.837.
^c Errors on the crust isotopic composition take into account the 2SD of the isotopic composition of each lithology, and assume a 25% uncertainty on concentration and masses of each lithology. The error on the isotopic composition dominates by almost a factor of 5.

Table 8

Fluxes and isotopic constraints on the modern U budget of the oceans

Sources	$\delta^{238}\text{U}$ (‰)	Fluxes (Mmol/yr)			
		B&C	M&E	Dunk et al.	H&A
Riverine input	-0.24 ^{1,5,3}	42	40	42.0 ± 14.5	46.2
Amazon shelf sediments	?	5.9	6		
Dust (aeolian input)	-0.29 [*]			1.8 ± 1.1	1.3
Submarine groundwater discharge	?			9.3 ± 8.7	
<i>Total</i>		<i>47.9</i>	<i>46</i>	<i>53.1 ± 16.9</i>	<i>47.5</i>
Sinks					
	$D_{\text{Reservoir-SW}}$ (‰)				
Suboxic sediments (continental margin)	0.1 ^{2,3}	11 - 13	12 - 25	15.3 ± 10.6	5.5
Anoxic sediments (organic-rich)	0.6 ⁷	5.5	6	11.6 ± 6.0	12
Oxix sediments:					
deep sea (pelagic red clay, siliceous ; calcareous deep sea sedime	?	3	3		3
pelagic red clay	0.04 ⁹			0.4 ± 0.2	
biogenic carbonates	0.2 ^{1,2,6,7,3}	3		13.3 ± 5.6	3
opaline silica (Biogenic silica)	?			0.6 ± 0.3	
Mn nodules and metalliferous sediments	-0.24 ^{1,2,4,8,3}	5.9	6	1.0 ± 0.8	1
Crustal alteration - high T	0 ^{5,9}	2	2	1.9 ± 1.9	2
Crustal alteration - low T	0.25 ^{5,9}	9.7	10 - 25	3.8 ± 2.7	4
Coastal zone retention***	-0.24 ^{3**}			11.2 ± 5.6	4.2
<i>Total</i>		<i>40 - 43</i>	<i>39 - 67</i>	<i>59.1 ± 14.9</i>	<i>34</i>

Predicted $\delta^{238}\text{U}$ of modern Seawater

<i>Assuming steady state in the modern ocean</i>	-0.412 - -0.408	-0.413 - -0.422	-0.403 ± 0.062	-0.502
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* Crustal composition assumed (see Table 7)

** The main removal process in the coastal zones is adsorption-complexation of U onto Fe-oxyhydroxides/ organic colloids, followed by scavenging and burial on short timescales before U reduction occurs at depth within the sediment (Church et al., 1996; Swarzenski et al., 2004). We make the observation that phases with adsorbed/complexed U have similar isotopic composition (chimney, evaporites, Fe-Mn nodules, Stirling et al., 2007; Weyer et al., 2008; Goto et al., 2014; this study) and hypothesize that the same adsorption-complexation mechanism is at play in these samples and in coastal retention zones, leading to a similar isotopic fractionation.

*** Salt marshes and mangrove swamps.

^a U oceanic budgets from: Barnes and Cochran 1990 (B&C); Morford and Emerson 1999 (M&E); Dunk et al., 2002; Henderson and Anderson 2003 (H&A).^b References: (1) Stirling et al., 2007; (2) Weyer et al., 2008; (3) This study, (4) Brennecke et al., 2011b; (5) Noordmann et al., 2011; (6) Romaniello et al., 2013; (7) Andersen et al., 2014; (8) Goto et al., 2014; (9) Andersen et al., 2015.^c Note that for the anoxic and suboxic reservoirs, the $D_{\text{Reservoir-SW}}$ value is the averaged fractionation expressed in the sediment, which is different from the expected fractionation of ~1.2‰ obtained by *ab initio* calculations (Bigeleisen 1996; Abe et al., 2008) due to coupled U diffusion and reduction below the sediment water interface. (See Andersen et al. (2014) for more details).

Table 9

Isotopic constraints on the amount of anoxia in the modern ocean

	B&C	M&E	Dunk et al.	H&A
F anoxic adjusted (Mmol/yr)	3.9	4.3	10.1	4.1
% of U in anoxic sediments	11%	13%	18%	18%
Ocean floor surface (m ²) ^c	3.6E+14			
Acc. rate of U in anoxic sediments (umol/m ² /yr)	9.2			
Surface covered by anoxic sediments (10 ¹¹ m	4.2	4.7	11.0	4.5
% of ocean floor covered by anoxic sediments	####	####	0.30%	####

^a U oceanic budgets from: Barnes and Cochran 1990 (B&C); Morford and Emerson 1999 (M&E); Dunk et al., 2002; Henderson and Anderson 2003 (H&A).
Keeping all other fluxes constant, the flux of U into anoxic sediments is adjusted so that the isotopic composition predicted by the model matches the one of the open ocean at -0.392 ± 0.005 ‰.

^c Turekian 1969

^d Dunk et al. 2002

Figure 1 Kds

Figure 2 elution curve

Figure 3 Kd comparison

Figure 4 Cones
a)

b)

Figure 5 DS vs SSB

Figure 6 U taxonomy

Figure 7 PbPb UPb

Figure 8 U budgets comparison

Figure 9 U data vs predictions

Figure 10 U cycle

Modern U cycle