Uranium isotope cycling on the highly productive Peruvian margin

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ABSTRACT

Uranium isotopes (δ238U values) in ancient sedimentary rocks (shales, carbonate rocks) are widely used as a tool to reconstruct paleo-redox conditions, but the behaviour of U isotopes under modern non-sulfidic anoxic vs. oxic conditions remains poorly constrained. We present U concentration and isotope data for modern sediments from the Peruvian margin, a highly productive open ocean environment with a range of redox conditions. To investigate U in different host fractions of the sediment (reactive, silicate, and HNO3-soluble fraction), we conducted a series of sequential extractions. Detrital-corrected authigenic U isotope compositions (δ238U auth) in sediments deposited beneath anoxic water column show little deviation from the dissolved seawater U source, while anoxically deposited sediments have δ238U auth values that are up to 0.4‰ heavier compared to seawater δ238U. Under anoxic, non-euxinic conditions, the U isotope offset between sediment and seawater is larger compared with oxic, but significantly smaller when compared with euxinic conditions from the literature. The results from sequential extractions show that the reactive sediment fraction records more pronounced differences in δ238U Reactive than δ238U auth values depending on the oxidation state of the overlying water column. Furthermore, we found a strong correlation between total organic carbon (TOC) and both U concentrations (U auth) and δ238U auth values (R² = 0.70 and 0.94, respectively) at the persistently anoxic site that we examined. These correlations can be caused by several processes including U isotope fractionation during microbially-mediated U reduction at the sediment-water interface (diffusive U input), during sorption onto and/or incorporation into organic matter in the water column (particulate U input) and diagenetic redistribution of U, or a combination of these processes. Our data show that several factors can influence δ238U values including oxidation state of U, the presence or absence of hydrogen sulfide and organic matter. These findings add new constraints to the degree of U isotope fractionation associated with U incorporation into sediments in different low-oxygen environments, thus aiding in interpretation of ancient paleo-redox conditions from U isotope data.

1. Introduction

The oceans underwent substantial changes in their redox state from the Archean Eon to the present (e.g. Diamond and Lyons, 2018), and they are bound to change in the future (e.g., deoxygenation; Keeling et al., 2010; Schmidtke et al., 2017). Reconstructing the extent of ocean anoxia in the past will reveal important information for future predictions. Trace metals such as Mo, V, Cr, and U are powerful tools to record redox changes in marine environments, because their solubility decreases under reducing conditions. However, reducing conditions are not only controlled by dissolved oxygen in seawater, but are also coupled to the rate of organic carbon (Corg) rain to and burial in the sediment, processes that can be mutually connected. It is therefore essential to investigate the full range of parameters that can affect such redox-sensitive trace metals. Hexavalent U in oxic seawater occurs as the stable uranyl carbonate.
ion (UO$_2$CO$_3$), or as Ca/Mg-UO$_2$CO$_3$ complexes, at concentrations between 13 and 14 molm kg$^{-1}$ (Ku et al., 1977; Langmuir, 1978; Endrizzi and Rao, 2014). It behaves conservatively with a long residence time of around 200,000 to 400,000 years (Ku et al., 1977). The major source for U in seawater is riverine input, where U is mobilised from the continental crust during oxidative weathering, and soluble U(VI) is transported to the oceans (Dunk et al., 2002). Anoxic sediments are the main sink for U. Other sinks, such as biogenic carbonates, as well as weathering of basalts at mid-ocean ridges, also play a role (Dunk et al., 2002).

Uranium can also be sequestered in sediments as carbonate fluorapatite (CFA), the initial mineral phase of phosphorites (Arning et al., 2009). Under suboxic or anoxic conditions in the sediments, U is removed from porewater via reduction to U(IV) and subsequently replenished by diffusion across the sediment-water interface (e.g. Klinkhammer and Palmer, 1991; Weyer et al., 2008). Reduction of U can take place abiotically or can be mediated by sulfate or Fe reducing bacteria or other (e.g. Rademacher et al., 2006; Basu et al., 2014; Stirling et al., 2015; Stylo et al., 2015; Basu et al., 2020). After reduction to U(IV), U precipitates inorganically as U(IV)-UO$_2$ but can also be present as non-crystalline solid phase as observed for lacustrine environments (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Stetten et al., 2018). In contrast to Mo, U shows less affinity for shuttling to the sediment with Fe and Mn (oxyhydroxides (Algeo and Tribovillard, 2009; Scholz et al., 2017). Instead, incorporation into organic particles has been recognised as a mechanism for U delivery to the sediment, especially in high productivity environments such as the Peruvian margin (Anderson et al., 1989a; McManus et al., 2006; Zheng et al., 2002a).

In the water column, U uptake by organisms or sorption onto their surfaces in the surface waters allows transport of particulate non-lithogenic U (PNU) to the sediment (Anderson et al., 1989b). Diffusive accumulation of U at the sediment-water interface and input of U with particulate organic material can take place in the same setting and are difficult to distinguish. The accumulation of U in sediments can be elevated under reducing conditions (e.g. Black Sea), but also where the C$_{org}$ rain and burial rates are high (e.g. Peruvian margin; Zheng et al., 2002b; McManus et al., 2005). Under oxic conditions, PNU is near-quantitatively remobilised before burial (Zheng et al., 2002a). In contrast, under anoxic conditions, U can be preserved and contribute up to 70% of the total authigenic U in sediments. Uranium transport to the sediment can be linked with sinking organic matter in a range of marine environments. Sedimentary U concentrations are therefore being used as a proxy for surface ocean productivity or C$_{org}$ burial rate (e.g. Anderson et al., 1989a; Kumar et al., 1995; Chase et al., 2001; Zheng et al., 2002b; McManus et al., 2006). Other studies, however, have suggested that bottom water oxygen is the primary control of authigenic U accumulation (Francois et al., 1993; Hayes et al., 2014; Abshire et al., 2020).

While U concentrations in sediments have been widely accepted as both a redox and productivity proxy, changes in stable U isotope ratios ($^{238}$U/$^{235}$U, expressed as $\delta^{238}$U) are mostly interpreted to reflect redox conditions (reviewed by Lau et al., 2019). The most abundant isotopes of U are the primordial $^{238}$U and $^{235}$U isotopes, with half-lives of 4.5 and 0.7 billion years, respectively. Even though these two isotopes are not stable, given their long half-lives for decay, variations of $^{238}$U/$^{235}$U are largely the result of chemical reactions rather than radioactive decay (Weyer et al., 2008). The daughter isotope of $^{238}$U, $^{234}$U, has a half-life of 248,000 years. The ratio of $^{234}$U/$^{238}$U ($\delta^{234}$U) shows large variations caused by biological, biological and radiogenic processes (Kigoshi, 1971). For example, during weathering $^{234}$U is preferentially released from the solid to the dissolved phase, eventually leading to a $^{234}$U value of seawater (147%), which is higher than secular equilibrium (Chen et al., 1986; Henderson, 2002; Andersen et al., 2010). The $\delta^{234}$U value of sediments can be used to estimate detrital and authigenic components of the sediment, with seawater-like $^{234}$U values indicating authigenic U as the dominant component (Anderson et al., 2010; Andersen et al., 2014). Variations of $^{238}$U/$^{236}$U are induced by nuclear volume isotope fractionation, whereby the heavy $^{238}$U isotope is enriched in the reduced U(IV) species (Bigeleisen, 1996; Fuji et al., 2006; Schäuble, 2007). The $\delta^{238}$U composition of seawater is $-0.39 \pm 0.02\%$ (2SD) and is thought to have been invariant over the past 600,000 years (Andersen et al., 2014; Tissot and Dauphas, 2015). Primary abiotic and biogenic Ca carbonates have been shown to incorporate seawater dissolved U with only minor isotope fractionation (0 to 0.1%), while modern marine carbonate sediments documented $\delta^{238}$U values $\approx 0.3\%$ higher than modern seawater due to pore water U(III) reductions during diagenesis (Stirling et al., 2007; Weyer et al., 2008; Romaniello et al., 2013; Chen et al., 2016; Chen et al., 2018a; Chen et al., 2018b). In contrast, U isotope fractionation up to 0.8% ($\delta^{238}$U$_{sediment-seawater}$) is thought to be caused by redox changes occurring during U reduction in porewater prior to accumulation in the sediment (e.g. Weyer et al., 2008). In agreement with the nuclear volume effect (Bigeleisen, 1996; Schäuble, 2007), the highest $\delta^{238}$U values are found in reducing sediments (Weyer et al., 2008). Incorporation of U into primary Ca carbonates does not involve U redox changes and thus, isotope fractionation is minimal under most circumstances (Romaniello et al., 2013; Chen et al., 2016). Uranium sorption onto Fe- or Mn-crusts favours lighter U isotopes, leading to lower $\delta^{238}$U values in the crusts relative to the seawater source (Brennecka et al., 2011; Goto et al., 2014; Wang et al., 2016). Ranges of U isotope fractionation factors in microbial reduction experiments are large ($\delta^{234}$U$_{U(IV)}$/235U$_{U(IV)}$, up to 1%) and confirm results from reducing sediments (Basu et al., 2014; Stirling et al., 2015; Stylo et al., 2015). Additionally, U reduction associated with organic matter in surface seawater (sorption on or uptake into organics) induces significant isotope fractionation (Brennecka et al., 2011; Basu et al., 2014; Holmden et al., 2015; Stirling et al., 2015; Stylo et al., 2015; Basu et al., 2020). For example, the U isotope offset $\Delta^{238}$U$_{plankton-seawater}$ resulted in $-0.79\%$ (Holmden et al., 2015). Sorption of U onto particle surfaces can induce both positive and negative U isotope fractionation (e.g. Rademacher et al., 2006; Brennecka et al., 2011; Basu et al., 2014; Basu et al., 2020). Although the processes fractionating U isotopes during sorption on and uptake into organic matter are largely unconstrained, they were recently found to be governed by both the mechanism and the rate of reduction (Basu et al., 2020). A two-step process was suggested, involving 1) sorption of U(VI) on particles or diffusive transport to reduction site and 2) enzymatic reduction to U(IV) (Holmden et al., 2015; Basu et al., 2020).

To accurately interpret the cause of $\delta^{238}$U variability in ancient sedimentary rocks, studies on $\delta^{238}$U values in modern marine environments with fine-grained sediments are necessary (Stirling et al., 2007; Weyer et al., 2008; Andersen et al., 2014a; Holmden et al., 2015; Noordmann et al., 2015; Stirling et al., 2015; Hinojosa et al., 2016; Rolison John et al., 2017). Andersen et al. (2014a) present a model where U isotope compositions of modern sediments up to 1.2% higher than seawater indicate anoxic or euxinic seawater conditions, whereas values similar to seawater suggest oxic conditions. Under fully sulfidic conditions in porewaters and above, reduction of U diffusing into the porewater is thought to be fast, leading to a large U isotope fractionation of up to 1.2% (Andersen et al., 2014a). If the bottom water isoxic and oxygen penetrates the upper porewater, the distance between the sediment-water interface and the zone of U reduction increases (Andersen et al., 2014a). As a result, the measured isotope fractionation decreases (Clark and Johnson, 2008).

Uranium isotope offsets between sediment and seawater are also proposed to be associated with biological processes (possibly in the lower water) other than microbial Fe or sulfate reduction (Holmden et al., 2015; Hinojosa et al., 2016; Rolison John et al., 2017). Chen et al. (2014a) present a model where U isotope compositions of modern sediments up to 1.2% higher than seawater indicate anoxic or euxinic seawater conditions, whereas values similar to seawater suggest oxic conditions. Under fully sulfidic conditions in porewaters and above, reduction of U diffusing into the porewater is thought to be fast, leading to a large U isotope fractionation of up to 1.2% (Andersen et al., 2014a). If the bottom water isoxic and oxygen penetrates the upper porewater, the distance between the sediment-water interface and the zone of U reduction increases (Andersen et al., 2014a). As a result, the measured isotope fractionation decreases (Clark and Johnson, 2008).
sediment (e.g. McManus et al., 2006). However, the relationship between U isotope fractionation and (sinking) organic matter has received little attention for interpretations of δ²³⁸U values in the sedimentary rock record.

This contribution focuses on quantifying U isotope variations in a modernoxic to anoxic, non-euxinic environment with a high C-org burial rate. We contribute U isotope data of bulk sediments and sequential extractions from a highly productive open ocean environment (Peruvian margin), along with U concentration data measured on the same sample aliquots. Our data complement previous publications investigating U concentrations and isotope compositions on the Peruvian margin (e.g. Scholz et al., 2011; Cole et al., 2020). These studies are complemented with δ²³⁸U data of sediment samples of up to 28 cm sediment depth, including results from sequential extractions and phosphorites. The insights from our data set are crucial to better understand pathways of U from the water column to the sediment and to reconstruct changes in the global ocean.

2. Methods

2.1. Study area

The Peruvian margin is a well-characterised open marine environment with oxic to anoxic (non-sulfidic) bottom water conditions and high productivity (Table 1, Fig. 1) and is commonly used as a modern analogue for anoxic environments where organic-rich mud sediments are deposited (e.g. Scholz et al., 2017; Scholz, 2018). At the Peruvian margin, upwelling is induced by northwestward blowing winds. This leads to high rates of primary productivity, high export production, and a C-org burial rate of 6.8 mmol m⁻² d⁻¹ (mean rate on the total margin (0 to 1000 m depth); Dale et al., 2015). The fine-grained sediments on the Peruvian margin contain up to 20 wt% total organic carbon (TOC), biogenic silica and authigenic phosphate minerals, e.g. carbonate fluoroapatite (Krissek et al., 1980; Reimers and Suess, 1983; Froelich et al., 1988; Bönning et al., 2004; Gutiérrez et al., 2008).

The core of the oxygen minimum zone (OMZ) becomes anoxic due to the intense degradation of organic material (OM) in the water column (Molina-Cruz, 1977; Brockmann et al., 1980; Gutiérrez et al., 2008; Thadrum et al., 2012). The water column on the Peruvian margin is not euxinic, contrasting anoxic, euxinic basins such as the notably restricted Black Sea (Anderson et al., 1989a). Our sample set consists of sediment samples from six short (< 50 cm) cores spanning a transect from the oxic shelf through the OMZ to below the OMZ (Fig. 1a). Within the OMZ, the bottom water oxygen is below detection limit in three cores from the shelf to slope (BIG005, MUC29, MUC19; bottom water oxygen data from Scholz et al., 2011). The stations BIG005 and MUC29 sporadically experience exposure to low-oxygen bottom water (Levin et al., 2002), but conditions were anoxic when the samples were collected. Below the lower redoxcline, bottom water oxygen increases from 2 to 39.9 μM between cores MUC41, MUC25 and MUC15 (Scholz et al., 2011). Fig. 1b illustrates the OMZ based on oxygen data from GP16, a transect 1°S of our stations (US GEOTRACES; Moffett and German, 2018; Schlitzer et al., 2018). At our study sites, hydrogen sulfide (H₂S) concentrations in the porewaters are insufficient to build up at or above the sediment-water interface most of the time (e.g. Scholz et al., 2011). At the time of sampling, only two stations (MUC19 and MUC29) had H₂S concentrations above detection limit (≈ 2 μM). These increases in H₂S occurred below sediment depths of 10 cm (MUC19) and 20 cm (MUC29), respectively (Scholz et al., 2011). Hence, the majority of the sediment samples investigated here are non-sulfidic and all samples were deposited in a non-euxinic environment. The core MUC41 was only sampled for phosphorites.

2.2. Sediment sampling

Sediment cores from the Peruvian margin were retrieved using a multi corer (MUC) or obtained from benthic lander deployments (Biogeochemical Observatory, BIGO) in 2008 during the M77–1 and M77–2 cruises of RV Meteor (Scholz et al., 2011). Subsamples (1–5 cm slices) of the sediment cores were taken in an argon-flushed glove bag.

2.3. Uranium concentration and isotope analysis

2.3.1. Uranium separation

To provide a detailed geochemical insight into the composition of the sediments, U concentrations and isotope compositions were analysed on bulk samples as well as on separated fractions (reactive, silicate and organic and pyrite fraction) using a sequential extraction (Huerta-Díaz and Morse, 1990; Bruggmann et al., 2019). These data complement previously published analyses of U concentrations in sediments and porewater on the Peruvian margin (e.g. Scholz et al., 2011).

2.3.1.1. Bulk. A sample size of approximately 20–100 mg was chosen to achieve a total U amount of approximately 500 ng U. Samples were incinerated in ceramic vessels to oxidise organic matter and digested following the standard procedure for mud sediments using concentrated HF and aqua regia (e.g. Bruggmann et al., 2019).

2.3.1.2. Sequential extraction. Sequential extraction was conducted following procedures adapted from Scholz et al. (2007) and Huerta-Díaz and Morse (1990). The following phases were targeted by our sequential extraction scheme:

2.3.1.3. Reactive fraction. Samples were shaken in 15 ml 0.5 M HCl at room temperature for 1 h. The supernatant after centrifugation comprises the sample with amorphous Fe- and Mn-oxhydroxides, carbonates, hydrous aluminosilicates, and Fe monosulfides.

2.3.1.4. Silicate fraction. Two washing steps with MilliQ (MQ) were conducted after HCl extraction of the reactive fraction and each rinse solution was discarded. These steps were followed by addition of 1 ml concentrated HF. The HF was dried down and another 1 ml concentrated HNO₃ (30 ml) and 0.1 M HCl (10 ml), centrifuged, and decanted. The supernatant of the subsequent washing step (50 ml MQ) was added to the decanted solutions, altogether comprising U associated with clay and silicate minerals.

2.3.1.5. HNO₃-soluble fraction. The residue was treated with 2 ml concentrated HNO₃ and ultrasonicated for 15 min and evaporated to dryness. This fraction contains U associated with organic matter and pyrite.

2.3.1.6. Phosphorites. Phosphorites from MUC41 were washed with MQ, 0.1 M HCl and MQ to remove particles prior to crushing with an agate mill (mortar/pestle). Samples were weighed (approximately 30–100 mg) and leached with 0.05 M HCl (shaking table, 1 h) to remove

Table 1

| Station        | Longitude  | Latitude | Water depth (m) | BW O₂ (μM) |
|----------------|------------|----------|----------------|------------|
| BIG005         | 77°47.7’W  | 11°00.0’S | 85             | < LD       |
| MUC29          | 77°56.6’W  | 11°00.0’S | 145            | < LD       |
| MUC19          | 78°10.0’W  | 11°00.0’S | 319            | < LD       |
| MUC41          | 78°20.9’W  | 11°00.0’S | 510            | 2          |
| MUC25          | 78°25.6’W  | 11°00.0’S | 697            | 12.1       |
| MUC15          | 78°30.0’W  | 11°00.0’S | 930            | 39.9       |

BW = bottom water.
carbonate. Subsequently, the phosphorite samples were dissolved using aqua regia.

All samples were treated with a mixture of 1 ml concentrated HNO₃ and 100 μl H₂O₂ to remove residual organic material. If samples were not completely dissolved, an additional step using reversed aqua regia as well as another HNO₃:H₂O₂ step (2 ml:0.4 ml, cap and let react overnight) were applied. If necessary, 2.5 ml of 70% perchloric acid was added to the HNO₃:H₂O₂ mixture, capped and cooked at 180 °C for 6–8 h and subsequently evaporated.

2.3.1.7. Concentration analysis. Samples were redissolved in 0.3 M HNO₃ and aliquots (50 μl, diluted to 5 ml) were taken for concentration analysis with inductively-coupled plasma mass spectrometry (ICP-MS), using the iCap-Q ICP-MS Thermo Fisher at Arizona State University (ASU). The precision of U concentrations of repeatedly analysed standard solutions was ±2% (n = 11).

2.3.1.8. Chromatographic separation. Prior to chromatographic separation, samples were adequately spiked with a 233U:238U double-spike to reach a spike:sample ratio of ~0.03 (Weyer et al., 2008; Chen et al., 2016), evaporated and re-dissolved in 5 ml 3 N HNO₃. A sample of pre-dissolved rock standard (black shale SDo-1), as well as two CRM145, were processed over the columns along with the samples.

The column chemistry was conducted following Andersen et al. (2004), Romainiello et al. (2013), and Chen et al. (2016). Anion columns (BioRad) were loaded with 0.8 ml UTEVA resin (Eichrom). The resin was pre-cleaned with 4 times 2.5 ml 0.05 M HCl and preconditioned with 3 times 0.8 ml 3 M HNO₃. The sample was then added to the column, and matrix elements were eluted with 5 times 2 ml 3 M HNO₃. Subsequently, 3 times 0.8 ml 10 M HCl was loaded onto the column and Th was eluted using 3 times 0.8 ml of a mixture of 5 M HCl and 0.05 M oxalic acid. To remove the oxalic acid, 3 times 0.8 ml 5 M HCl was added to the column. Finally, U was eluted and collected using 7 ml 0.05 M HCl (1 + 1 + 1 + 2 + 2 ml).

To remove organic residue from the columns, samples were treated with a mixture of concentrated HNO₃ and 30% H₂O₂ (2 ml + 300 μl, respectively), capped and heated for 3–4 h, evaporated and re-dissolved in 2 ml 3 M HNO₃ before repeating the column chemistry for further purification.

2.3.2. Isotope analysis

After the chromatographic separation of U, U isotopes were analysed using a multi-collector ICP-MS (MC-ICP-MS, Thermo Scientific Neptune) at ASU. The samples were re-dissolved in 0.3 M HNO₃ to achieve a U concentration of ~ 50 ppb and injected into the MC-ICP-MS using an Apex-Q desolvation introduction system. The ion beams of U isotopes (233U, 234U, 235U, 236U, and 238U) were analysed in Faraday cups connected to resistors with 10¹² or 10¹¹ Ω (238U) at a typical ion beam of ~ 30 V for 238U.

The results are reported as shown in Eqs. 1 and 2 as δ238U and δ234U in permille (‰) with the precision indicated as two standard error (± 2SD) of replicate runs. The number of runs is indicated in brackets, duplicates or triplicates of samples are stated as n.

\[\delta^{238}U = \left( \frac{^{238}U}{^{235}U} \right)_{\text{sample}} \left( \frac{^{238}U_{\text{CRM}145}}{^{235}U_{\text{CRM}145}} \right)_{\text{CRM}145} - 1 \times 1000\]

\[\delta^{234}U = \left( \frac{^{234}U}{^{238}U} \right)_{\text{sample}} \left( \frac{^{234}U_{\text{CRM}145}}{^{238}U_{\text{CRM}145}} \right)_{\text{CRM}145} - 1 \times 1000\]

The certified standard CRM 145 shows a reproducibility of δ238U and δ234U values of replicate analysis of ± 0.07‰ and ± 3.6‰, respectively (2 SD, n = 11). The average U isotope composition of the Devonian Shale USGS standard reference material SDo-1 was -0.07 ± 0.06‰ (2SD, n = 7), which is within error of published values for this standard (e.g. Abshire et al., 2020).

2.3.3. Corrections for detrital and U

To investigate the influence of marine environmental conditions on U concentrations and isotope compositions in sediments, we calculated the authigenic fraction of U that has interacted with seawater rather than U contained in unreactive terrigenous sediment components. Bulk U concentrations and δ238U values of replicate analysis of δ238U and δ234U values of replicate analysis of δ238U and δ234U are calculated using Al as an indicator of δ238U for the unreactive detrital (det) sediment fraction (e.g. Tribouvillard et al., 2006).

\[U_{\text{auth}} = U_{\text{sample}} - \left( \frac{U}{Al} \right)_{\text{det}} \times A_{\text{sample}}\]

Authigenic U isotope compositions were calculated using the detrital correction equation (Eqs. 4 and 5). We used (U/Al)det = 1.8 × 10⁻⁵ and δ238Udet = -0.3‰ to correct for detrital contributions, as the δ238Udet value is thought to be similar to the continental crust (McManus et al., 2006; Weyer et al., 2008; Andersen et al., 2014a).

\[\delta^{238}U_{\text{auth}} = \frac{\delta^{238}U_{\text{sample}} - \delta^{238}U_{\text{det}} \times f_{\text{det}}}{1 - f_{\text{det}}}\]

\[f_{\text{det}} = \frac{A_{\text{sample}} \times \left( \frac{U}{Al} \right)_{\text{det}}}{U_{\text{sample}}}\]

Isotope offsets between seawater and authigenic U in the sediments were calculated using
Δ^{238}U = δ^{238}U_{auth} − δ^{238}U_{seawater} \tag{6}

with the typical seawater value (δ^{238}U_{seawater, global} = −0.39‰; Andersen et al., 2014a)

3. Results

3.1. U concentrations

Under oxic conditions below the OMZ, sedimentary U_{auth} concentrations range between 6.05 and 11.55 ppm (Fig. 2a, Table 2), with δ_{fact} ranging between 0.02 and 0.32. The reactive fractions at the oxic stations contain between 4.84 and 2.94 ppm U (Fig. 3a, Table 3). The HNO_{3}-soluble fraction contains very little U (as low as 0.06 ppm in BIGO05). The phosphorites contain highly variable U concentrations (6.80 to 73.8 ppm). In the anoxic cores (BIGO05, MUC29, MUC19), U_{auth} concentrations range between 2.34 and 19.46 ppm.

All stations show an increase in U_{auth} with depth from 2.34–9.23 ppm at the surface to 3.66–11.55 ppm at depth. The increase is most pronounced at the most anoxic station MUC19, where concentrations reach a maximum of 19.46 ppm at 4 cm depth. At MUC19, however, concentrations decrease again with depth, reaching a value of 6.39 ppm at 30 cm depth, which is in the same range as the remaining stations.

In the sequentially extracted near-surface samples, the highest U_{auth} concentrations are found in the reactive fraction of MUC19 (24.29 ppm; Fig. 3a, Table 3), and the reactive fractions of the anoxic stations (BIGO05, MUC29 and MUC19) overall show concentrations of between 1.65 and 24.29 ppm. The concentrations of the reactive fractions compare well with calculated U_{auth} concentrations, for example in MUC19, where the reactive fraction shows a U concentration of 24.29 ppm, compared with a U_{auth} of 19.46 ppm.

3.2. U isotope compositions

The detrital-corrected δ^{238}U_{auth} values are within error of the bulk δ^{238}U values (Table 2). Samples from the oxic stations (MUC25 and MUC15) span a tight range of authigenic U isotope compositions from −0.34 to −0.25‰ (Fig. 2b, Table 2). Uranium isotope offsets (Δ^{238}U_{auth-seawater}) between sediments (δ^{238}U_{auth}) and seawater are around 0.1‰ under oxic conditions (Table 2). Reactive fractions of samples towards the deepest portion of the OMZ (MUC25) and below the OMZ (MUC15) are −0.43‰ and −0.35‰, respectively. Due to the low contribution of the HNO_{3}-soluble fraction to the total U, and analytical limitations, HNO_{3}-soluble fractions were not analysed for U isotope compositions. The δ^{238}U values of HF extracts typically range around −0.25 ± 0.07‰ (2SD). The phosphorite nodules show the lowest δ^{238}U values from −0.80‰ to −0.47‰.

Bulk δ^{234}U values in sediments are lighter than seawater δ^{234}U values (147‰; e.g. Andersen et al., 2010), showing values of 106‰ or lower in oxic sediments (Fig. 2c). The sequential extractions of sediments deposited under oxic conditions show a large range of δ^{234}U values between 49‰ and 134‰, with the reactive fraction recording δ^{234}U values close to seawater. The silicate fraction shows a clear offset from the δ^{234}U_{seawater} value (BIGO05: 104‰, MUC29: 107‰), except for MUC19. The phosphorite nodules show δ^{234}U values from −57‰ to 42‰.

Anoxic cores show a range of δ^{238}U_{auth} values (−0.33 to 0.01‰; Fig. 2b, Table 2), with the highest δ^{238}U_{auth} value found in a sample from MUC19 at 3.5 cm sediment depth. At this sediment depth, the H_{2}S concentration is below detection limit. The Δ^{238}U_{auth-seawater} values range up to 0.49‰ under anoxic and typically non-sulfidic conditions (Table 2). The reactive fractions of the sequentially extracted sediment samples from the permanent OMZ and the shelf range from −0.20 to −0.04‰ (Fig. 3b). The silicate fraction of the sample from the permanent OMZ (MUC19) is higher compared with other silicate fractions (−0.06‰). Analyses of bulk δ^{234}U values of Peruvian margin sediments show that all samples from the core of the permanent OMZ (MUC 19) are between 130 and 147‰, very close to seawater (Fig. 2c). The reactive fraction of anoxic samples consistently records seawater-like δ^{234}U values (147‰). The silicate fraction from the permanent OMZ is higher compared with other silicate fractions (135‰).

4. Discussion

4.1. Comparison of samples from oxic and anoxic stations

At most sites investigated in this study, authigenic U is accumulating, as suggested by the increasing solid U concentrations with depth (Fig. 2a). Authigenic U concentrations in the shallowest stations (BIGO05 and MUC29) are the lowest of the five sites analysed, consistent with fluctuating bottom water oxygen concentrations that can cause U accumulation as well as U remobilisation. At these sites, porewater U (U_{pw}) concentrations increase in the surface sediment, which was attributed to episodes of oxygenation, during which U can be reoxidised and recycled across the benthic boundary (Zheng et al., 2002a, 2002b; Gutiérrez et al., 2008; Scholz et al., 2011). Most sites show U_{auth}
Table 2

| Station   | Sediment depth (cm) | δ²³⁸Uauth (‰) | SD | δ²³⁴Uauth (‰) | SD | n | TOC (wt %) | Al (ppm) | U (ppm) | U/Al | Uauth (‰) | fnet | δ²³⁸Uauth (‰) | Δ²³⁸U (‰) | U/PNU(%) |
|-----------|---------------------|---------------|----|---------------|----|---|------------|----------|----------|------|------------|------|-------------|-----------|----------|
| BIGO05    | 5                   | −0.31         | 0.07 | 76            | 3   | 3 | 3.9        | 52,145   | 3.28     | 0.063 | 2.34        | 0.29 | −0.32       | 0.07      | 28        |
|           | 3                   | −0.31         | 0.07 | 62            | 1   | 2 | 3.3        | 64,289   | 3.69     | 0.057 | 2.53        | 0.31 | −0.31       | 0.08      | 22        |
|           | 5                   | −0.32         | 0.04 | 50            | 4   | 4 | 3.2        | 70,421   | 3.94     | 0.056 | 2.67        | 0.32 | −0.33       | 0.06      | 20        |
|           | 10                  | −0.26         | 0.12 | 55            | 3   | 3 | 2.3        | 69,837   | 4.92     | 0.070 | 3.66        | 0.26 | −0.25       | 0.14      | 11        |
| MUC29     | 0.5                 | −0.23         | 0.07 | 108           | 3   | 3 | 7.6        | 45,998   | 4.44     | 0.097 | 3.62        | 0.18 | −0.22       | 0.17      | 36        |
|           | 3.5                 | −0.18         | 0.07 | 120           | 3   | 1 | 7.9        | 50,872   | 7.89     | 0.155 | 6.97        | 0.12 | −0.17       | 0.22      | 19        |
|           | 11                  | −0.17         | 0.08 | 119           | 4   | 2 | 8.7        | 47,757   | 7.26     | 0.152 | 6.40        | 0.12 | −0.15       | 0.24      | 23        |
|           | 28                  | −0.29         | 0.08 | 115           | 0   | 2 | 7.1        | 50,481   | 7.29     | 0.144 | 6.38        | 0.12 | −0.28       | 0.11      | 19        |
| MUC19     | 0.5                 | −0.32         | 0.07 | 130           | 1   | 2 | 10.7       | 32,647   | 9.82     | 0.301 | 9.23        | 0.06 | −0.32       | 0.07      | 20        |
|           | 3.5                 | 0.00          | 0.01 | 147           | 2   | 4 | 17.3       | 21,498   | 19.84    | 0.923 | 19.5        | 0.02 | 0.01        | 0.40      | 15        |
|           | 11                  | −0.16         | 0.03 | 141           | 3   | 4 | 15.4       | 17,855   | 12.00    | 0.672 | 11.7        | 0.03 | −0.16       | 0.23      | 22        |
|           | 20                  | −0.25         | 0.03 | 135           | 3   | 4 | 12.5       | 22,682   | 7.24     | 0.319 | 6.83        | 0.06 | −0.25       | 0.14      | 31        |
|           | 29                  | −0.28         | 0.06 | 125           | 1   | 4 | 12.6       | 21,434   | 6.77     | 0.316 | 6.39        | 0.06 | −0.28       | 0.11      | 34        |
| MUC41     | surface             | −0.52         | 0.03 | −57           | 7   | 4 | 30.28      | 73.83    | −0.08    | 0.80        | 0.41 |
|           | surface             | −0.47         | 0.06 | −21           | 1   | 4 | 73.83      | 73.83    | −0.08    | 0.80        | 0.41 |
|           | surface             | −0.80         | 0.12 | 41            | 2   | 4 | 6.80       | 6.80     | −0.41    | 0.80        | 0.41 |
| MUC25     | 0.5                 | −0.27         | 0.09 | 84            | 3   | 4 | 6.7        | 36,375   | 7.44     | 0.205 | 6.79        | 0.09 | −0.27       | 0.12      | 17        |
|           | 3.5                 | −0.33         | 0.10 | 90            | 3   | 5 | 6.7        | 39,599   | 9.29     | 0.235 | 8.58        | 0.08 | −0.34       | 0.05      | 13        |
|           | 9                   | −0.25         | 0.04 | 96            | 3   | 3 | 6.8        | 37,367   | 9.53     | 0.255 | 8.86        | 0.07 | −0.25       | 0.14      | 13        |
|           | 16                  | −0.29         | 0.04 | 99            | 3   | 5 | 5.6        | 45,324   | 11.49    | 0.254 | 10.68       | 0.07 | −0.29       | 0.10      | 9         |
|           | 28                  | −0.33         | 0.08 | 106           | 1   | 4 | 5.5        | 45,412   | 10.38    | 0.228 | 9.56        | 0.08 | −0.33       | 0.06      | 10        |
| MUC15     | 0.5                 | −0.30         | 0.09 | 62            | 1   | 3 | 5.2        | 41,407   | 9.11     | 0.220 | 8.36        | 0.08 | −0.30       | 0.09      | 10        |
|           | 3.5                 | −0.27         | 0.06 | 85            | 4   | 4 | 4.4        | 39,503   | 7.06     | 0.171 | 6.05        | 0.11 | −0.26       | 0.13      | 12        |
|           | 9                   | −0.27         | 0.07 | 71            | 1   | 4 | 4.1        | 41,971   | 11.14    | 0.265 | 10.28       | 0.07 | −0.27       | 0.12      | 7         |
|           | 16                  | −0.32         | 0.02 | 67            | 3   | 3 | 30.28      | 32,214   | 12.24    | 0.320 | 11.55       | 0.06 | −0.32       | 0.32      | 32        |

*U/PNU* is calculated based on the data from Holmden et al. (2015), using a U/PNU/TOC ratio of 0.17 ppm/wt%.
in/on particulate matter in the water column is added while particles are settling (i.e. scavenged) as live plankton contributes settling particles, likely through sorption. We calculate a U authen/sediment depth) from each of our site on the Peruvian margin. The circles indicate the U concentration measured in bulk samples. The U concentration of the HNO$_3$-leachable fraction in BIGO05 is lower than the thickness of the lines of the bar. Plot b) shows U isotope compositions of sequential extractions for the same samples. The blue horizontal bar indicates the global seawater δ$^{238}$U value.

Additional data (TOC, sequential extraction) that support a second mechanism of (isotopically heavy) U delivery to the sediment which is discussed below.

### 4.2. Diffusive and particulate input

The reduction of U in the surface sediment under anoxic conditions is generally accepted as the main mechanism driving U accumulation in sediments (e.g. Klinkhammer and Palmer, 1991). However, U can also be transported to the sediment by particles (e.g. Anderson et al., 1989b; Zheng et al., 2002a). Across the Peruvian margin, diffusion of U into the sediment alone cannot explain the U accumulation (Scholz et al., 2011). Indeed, authigenic U mass accumulation rates (MAR) and benthic fluxes suggest that diffusion of U is typically not sufficient to supply authigenic U in our sediments (Scholz et al., 2011).

In the sediment samples in the persistently anoxic core (MUC19) with the highest TOC content (up to 17.3 wt%; Scholz et al., 2011), we observe a good correlation between $U_{auth}$ concentrations and TOC ($R^2 = 0.70$; Fig. 4a). Two possible pathways can explain this positive correlation: 1) Efficient U reduction mediated by microorganisms directly below the sediment-water interface of organic-rich sediments, and 2) shuttling of U to the sediment with sinking organic matter, e.g. PNU. A positive correlation between TOC and $\delta^{238}$U$_{auth}$ values as in the MUC19 core ($R^2 = 0.94$; Fig. 4b) was previously observed under anoxic conditions on the Namibian continental margin (Abshire et al., 2020). This correlation suggests that microbially reduced U is fractionated towards heavier isotope compositions. However, we cannot exclude particulate U input in the MUC19 core based on our data set.

In most of our stations, the benthic diffusive fluxes of U cannot account for the corresponding MAR of U, indicating that diffusive U accumulation is not the only pathway of U delivery to the sediment (Scholz et al., 2011). Organic matter such as plankton has very low U concentrations, indicating that only a small proportion of U is incorporated into the organisms (Holmden et al., 2015). Instead, these authors suggest that the U in/on particulate matter in the water column is added while particles are settling (i.e. scavenged) as live plankton contributes very little to the U in sediment traps (2%). Uranium associated with organic matter or inorganic particles settling through the water column is fractionated by a two-step mechanism (Holmden et al., 2015; Basu et al., 2020). This mechanism includes 1) sorption of U onto settling organic particles and 2) reduction of U(VI) to U(IV) inducing a positive fractionation.

To investigate whether delivery of U through organic particles can contribute U with elevated isotope composition (relative to seawater), we turn to the data of Holmden et al. (2015) from the oxygen-deficient Saanich Inlet. Their sediment trap data reveal that U is incorporated into settling particles, likely through sorption. We calculate a $U_{PNU/TOC}$ ratio of 0.17 ppm/wt% based on their data, using their sediment trap U concentrations and seawater U fractions ($f_{seawater}$) to calculate $U_{PNU}$ (Tables 2 and 4). Applying this ratio to our sediment U and TOC data, we estimate that up to 36% of U at our anoxic sites (BIGO09, MUC19 and

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**Table 3**

Sequential extraction data for one surface sediment sample (0.5 or 3.5 cm sediment depth) from each site.

| Fraction       | Sediment depth | U (ppm) | $\delta^{238}$U (%) | 2SD | $\delta^{234}$U (%) | 2SD | n |
|----------------|----------------|---------|---------------------|-----|---------------------|-----|---|
| reactive       | 0.5            | 1.65    | -0.20               | 0.12| 147                 | 9   | 3 |
| reactive       | 3.5            | 4.35    | -0.09               | 0.02| 147                 | 11  | 4 |
| reactive       | 3.5            | 24.3    | -0.04               | 0.04| 147                 | 9   | 4 |
| reactive       | 3.5            | 2.48    | -0.43               | 0.02| 134                 | 1   | 3 |
| reactive       | 3.5            | 3.18    | -0.25               | 0.12| 49                  | 3   | 4 |
| reactive       | 3.5            | 9.29    | -0.33               |     |                     |     |   |
| reactive       | 3.5            | 2.94    | -0.35               | 0.06| 132                 | 1   | 3 |
| reactive       | 3.5            | 3.03    | -0.21               | 0.04| 63                  | 6   | 4 |
| reactive       | 3.5            | 0.19    |                     |     |                     |     |   |
| reactive       | 3.5            | 6.16    |                     |     |                     |     |   |
| reactive       | 3.5            | 6.76    | -0.27               |     |                     |     |   |
local detrital especially for anoxic sediments. through PNU may constitute a sizable proportion of authigenic U, derived from PNU (Table 2). These estimates confirm that U delivered to the U isotope composition of PNU in Saanich Inlet samples. Isotope mass balance using data from Holmden et al. (2015) to calculate the U isotope composition of PNU in Saanich Inlet samples. Table 4

| Sample        | Depth (m) | TOC (wt%) | U (ppm) | δ²³⁸U (‰) | 2SE | fₜₕ | 1 - fₜₕ | U_PNU (ppm) | U_PNU/TOC (ppm/ wt%) | δ²³⁸U_PNU (‰) | Δ²³⁸U_PNU-SW (‰) |
|---------------|-----------|-----------|---------|-----------|-----|-----|---------|-------------|----------------------|----------------|------------------|
| January/February |          |           |         |           |     |     |         |             |                      |                |                  |
| Shallow       | 50        | 7.10      | 2.04    | −0.52     | 0.21| 0.79| 0.43    | 0.06        | 0.65                 | 1.10            |                  |
| Mid           | 115       | 4.90      | 1.67    | −0.66     | 0.01| 0.19| 0.81    | 0.32        | 0.06                 | 0.06            | 0.51             |
| Deep          | 180       | 4.70      | 1.96    | −0.58     | 0.10| 0.27| 0.73    | 0.53        | 0.11                 | 0.10            | 0.55             |
| March         |           |           |         |           |     |     |         |             |                      |                |                  |
| Deep          | 180       | 3.60      | 2.10    | −0.29     | 0.42| 0.58| 0.88    | 0.25        | 0.46                 | 0.91            |                  |
| April         |           |           |         |           |     |     |         |             |                      |                |                  |
| Mid           | 115       | 3.80      | 1.98    | −0.51     | 0.16| 0.41| 0.59    | 0.81        | 0.21                 | −0.05           | 0.40             |
| Deep          | 180       | 4.10      | 2.90    | −0.56     | 0.23| 0.42| 0.58    | 1.22        | 0.30                 | −0.19           | 0.26             |
| Average ± 2SD |          |           |         |           |     |     |         |             |                      | 0.17 ± 0.20    | 0.17 ± 0.63     | 0.62 ± 0.63     |

SW = seawater; fₜₕ represents the seawater-derived U fraction, δ²³⁸U_PNU is calculated using 1 − fₜₕ and δ²³⁸U_detrital value of −0.83 ± 0.12 (2σ); δ²³⁸U value of seawater endmember: −0.45 ± 0.06 (2σ). MUC29), and 7 to 17% at the oxic sites (MUC25 and MUC15) may be derived from PNU (Table 2). These estimates confirm that U delivered through PNU may constitute a sizable proportion of authigenic U, especially for anoxic sediments.

Next, we use an isotope mass balance to calculate the U isotope composition of PNU in the Saanich Inlet samples (Eq. 4). Based on the local detrital δ²³⁸U value and measured bulk U isotope composition of sediment trap samples, we calculate an average δ²³⁸U value for PNU (δ²³⁸U_PNU) of 0.17 ± 0.63‰ (2SD; Table 4). Note that the isotope composition of the detrital component in the Saanich Inlet sediments is unusual light (−0.83‰), which the authors attribute to fractionation of U during soil processes and weathering, where altered minerals preferentially retain the lighter U isotopes (Holmden et al., 2015). Compared to the U isotope composition of −0.45‰ for Saanich Inlet seawater, our calculations suggest that U incorporation into settling particles can deliver PNU that is similar to or heavier than the seawater source. The average isotope offset between PNU and seawater (Δ²³⁸U_PNU-seawater) is 0.62 ± 0.63‰ (2SD), which is similar to the isotope effect determined for the Black Sea water column based on dissolved U isotope compositions (Romaniello, 2012). Further, the isotope offset is in the range of experimentally determined isotope fractionation effects of microbial U (VI) reduction (Basu et al., 2014; Stirling et al., 2015). It has been speculated that U reduction occurs in settling particles within the water column (e.g. Anderson et al., 1989a; Rolison et al., 2017). In support, under reducing lacustrine conditions, progressive accumulation of isotopically heavy U in sinking particles with water depth was recently described (Chen et al., 2021). These authors attribute this trend to U(VI) reduction. We note, however, that direct measurements of U redox speciation in the Black Sea water column did not provide any evidence for U(VI) reduction, despite the presence of free H₂S (Anderson et al., 1989a). Also, the highest Δ²³⁸U_PNU-seawater for the Saanich Inlet (1.10‰) was calculated for the surface sediment trap (Table 4), well above the redoxcline (Holmden et al., 2015), thus making a reductive pathway for U uptake unlikely in this sample.

Alternatively, isotope fractionation may occur during sorption onto phytoplankton. However, studies of marine and freshwater phytoplankton suggest that U(VI) sorbed onto living surface plankton fractions in the opposite direction (Δ²³⁸U_plankton-seawater = −0.79‰ for marine and −0.23% for freshwater plankton; Holmden et al., 2015; Chen et al., 2020) than is implied by the deeper sediment trap PNU in the Saanich Inlet. The mechanism for the uptake and elevated U isotope composition in sinking particles on the Peruvian margin, therefore, remains speculative and warrants further investigation that must include direct determination of U redox speciation in dissolved and particulate U phases.

Uranium that settles to the sediment with organic particles is redistributed during early diagenesis under oxic conditions (Zheng et al., 2002a). Within anoxic sediment, early diagenesis leads to degradation of organic matter, releasing both surface-bound and incorporated U into the porewater (Scholz et al., 2011). With the subsequent microbial reduction and precipitation of Uₐ₅₈⁸, U initially associated with organic matter is diagenetically redistributed into an authigenic host fraction.
The reduction of U induces a fractionation of U, leading to preferential enrichment of isotopically heavy U in the authigenic phase. Our data support the hypothesis that input of PNU with sinking organic matter plays an important role in the delivery of U to the sediments (Scholz et al., 2011). Further, we hypothesise that U reduction during early diagenetic redistribution into permanent mineral phases such as uraninite ultimately determines the isotope composition of buried Uauth. This reduction process is more important in organic-rich compared to organic-poor sediments.

While our dataset supports the idea that both diffusive and particulate U input affect the sediment U isotope mass budget, we cannot separate the U isotope fractionation effects of diffusive and particulate U input. Our data suggest that both of these processes seem to favour the incorporation of isotopically heavy U into the sediment. However, diffusive vs. particulate U input may lead to differences in the U isotope composition of the sediment, as previously suggested for the Mo isotope system (Eroglu et al., 2020). Although Andersen et al. (2017) suggested that U reduction can take place above the sediment-water interface, this process is poorly constrained in natural environments. Using a transport model, Lau et al. (2020) linked δ238U values in sediments with productivity and, thus, Corg burial rates. Changes in diffusive vs. particulate U input, e.g. linked to changes in sedimentation and Corg rain and burial rates, in the geological past can affect the global U isotope mass budget.

### 4.3. Uranium-hosting sediment fractions

#### 4.3.1. Reactive fraction

Authigenic U may best be represented by the reactive fraction (0.5 M HCl), which includes mineral phases that precipitated directly from the water column or porewater (e.g. Fe- and Mn-oxhydroxides, carbonates, hydrous aluminosilicates, and Fe monosulfides; Huerta-Diaz and Morse, 1990). Additionally, this fraction may also include U leached from particle surfaces, including PNU and U sorbed onto organic matter. An authigenic origin of the reactive fraction in our sequential extracts is supported by the high δ238U values of all five surface samples (142 ± 16 (2SD) ‰) that are very close to the seawater δ238U value (147‰). The δ234U values of the two sediment cores deposited under oxygenated bottom water (MUC25 and MUC15) have slightly lower δ234U values compared to anoxic cores (e.g. MUC19), possibly due to dissolution of CFA during the HCl leach. Low δ234U values in phosphorite nodules –57 ± 7‰ to 42 ± 1‰ at oxic station MUC41 suggest that CFA δ234U isotope compositions deviate significantly from seawater values, despite being an authigenic mineral phase.

Our δ238U isotope analyses show a clear distinction between δ238U values in sediments deposited under oxic (average – 0.39 ± 0.06 (2SD) ‰, n = 2) versus under anoxic conditions (average – 0.07 ± 0.04 (2SD) ‰, n = 2). The two sediment cores deposited under the highest bottom water oxygen concentrations at our sites (MUC25; 12 µM and MUC15: 40 µM; Table 1) show δ238U values (–0.43 ± 0.02‰ and – 0.33 ± 0.06‰, respectively) close to the seawater δ238U value (–0.39 ± 0.01‰; Andersen et al., 2014a, Tissot and Dauphas, 2015).

Under anoxic bottom water conditions (excluding BIG005), the reactive fraction is clearly fractionated towards higher δ238U values (–0.20‰ or higher) compared with oxic conditions. This distinct difference between oxic and anoxic sites is in agreement with the proposed model that under oxic bottom water conditions, U reduction occurs deeper in the sediment, where the resulting diffusive U flux from bottom water to sediment leads to a small to no isotope offset (Andersen et al., 2014a). Bioturbation at the oxic sites would also contribute to maintaining the supply of U with low U input to the surface cm depth. The isotope compositions of sediments deposited under anoxic vs. oxic conditions show more pronounced differences in the reactive fraction (δ238Ureactive) of the sediment compared with calculations of authigenic U (δ238Uauth), suggesting that the reactive fraction is more accurate in recording the long-term redox conditions of the bottom water than δ238Uauth values.

#### 4.3.2. Silicate fraction

The silicate fraction has in δ238U values (~ –0.25‰) similar to the continental crust (~ –0.3‰; Weyer et al., 2008), except for the sample from the persistent OMZ (MUC19) which has a value of ~–0.06‰. The silicate fraction from this core deviates from the other locations in both δ238U and δ234U values. The δ234U values of the silicate fractions for anoxic site MUC19 display values close to seawater (135 ± 2‰), suggesting that this fraction includes an authigenic mineral phase that was insufficiently removed during the leaching step with 0.5 M HCl. This non-silicate phase may include crystalline Fe-oxide minerals (e.g. goethite and lepidocrocite), which was not dissolved by the relatively mild HCl leach. Previous leaching experiments (Severmann, unpublished data) suggest that HF is an effective solvent for crystalline Fe-oxides, which may have formed from amorphous Fe-oxide precursors. Alternatively, sediments at this site may include a higher proportion of biogenic silica.

#### 4.3.3. HNO3-soluble fraction

The HNO3-soluble fraction supposedly contains U associated with organic matter and pyrite. However, U contained in the HNO3-soluble fraction does not seem to play a major role in the U budget on the Peruvian margin. This can be concluded from several observations. First, the U contained in the HNO3-soluble fraction contributes <3.2% of the Uauth. Second, overall Uauth concentrations and TOC do not show a strong correlation (R² = 0.42), except for a positive correlation for the samples from persistently anoxic conditions (MUC19; R² = 0.70). This correlation for MUC19 is even more prominent when comparing δ238Uauth values and TOC (R² = 0.94). This trend indicates that, despite the low U content of the HNO3-soluble fraction, U isotope compositions under persistently anoxic conditions on the Peruvian margin are strongly influenced by organic matter.

Redistribution of U during early diagenesis, as well as imperfect separation of U during successive leaching steps, can explain the low U concentrations in the HNO3-soluble fraction. Uranium associated with organic matter through surface sorption or incorporation during particle settling (e.g. Holmden et al., 2015) may be incorporated into the authigenic (HCl-leachable) fraction during early diagenetic redistribution. Additionally, during sequential extraction, weak HCl may leach U associated with organic matter. Hence, it is possible that a proportion of U associated with organic matter is actually comprised in the reactive fraction rather than in the HNO3-soluble fraction. In the absence of further testing, we are unable to distinguish between the two options. Given the known role of microbial reduction in fixing authigenic U in anoxic sediments (e.g. Klinkhammer and Palmer, 1991) we prefer the former explanation.

#### 4.3.4. Phosphorites

The isotope composition of U in phosphorites indicates that U in this authigenic mineral phase underwent significant changes during its pathway from seawater to phosphorite, leading to pronounced isotope offsets between seawater and phosphorites (δ238Uphosphate-seawater values of between –0.41 and – 0.08‰; Table 2). The U isotope offsets between seawater and phosphorites can be explained by the formation history of phosphorite nodules during early diagenesis. While U can reach the sediment with sinking organic matter such as PNU, it is unlikely that PNU is buried without further alteration in the sediment. Instead, U is redistributed during early diagenesis and accumulates in phosphorite crusts downslope (e.g. Scholz et al., 2011; Bönig et al., 2004).

In upwelling zones, where the conditions in the surface sediments are subsoxic, P can be released to the dissolved phase at the sediment-water interface (e.g. from organic matter or Fe oxides). Consequently, porewater can be supersaturated in CFA, leading to precipitation of CFA (e.g. Froelich et al., 1988). On the Peruvian margin, CFA can precipitate on the shelf, e.g. in BIG005 or MUC29. Due to the low δ18O of the phosphorites (~0.80% to ~0.47%), we propose that precipitation of
CFA during early diagenesis favours the lighter U isotopes ($^{235}$U over $^{238}$U). Due to (episodically) high-energy conditions, CFA coated grains are eroded and transported downslope, where they are re-deposited (Reimers and Suess, 1983; Glenn and Arthur, 1988; Arning et al., 2009). Under oxic conditions (MUC15 and MUC25), the growth of new CFA layers can continue, leading to the formation of phosphorite crusts (Arning et al., 2009). The δ$^{238}$U values of phosphorites (−57 ± 7‰ to 42 ± 1‰) are clearly offset from the seawater δ$^{238}$U value. Since CFA coated grains formed upslope and were later transported downslope, we assume that the source of U in the phosphorites is older compared with other sediment fractions in the same core and sediment depth. In addition, the negative δ$^{238}$U values suggest that $^{234}$U has been preferentially lost from this mineral phase, likely due to diagenetic overprinting. Post-depositional remobilisation of $^{234}$U suggests that the δ$^{234}$U was also affected by diagenetic overprinting, i.e. that these phases do not represent seawater isotope composition. A significantly older age can explain δ$^{234}$U values close to zero assuming closed system radiogenic ingrowth (Henderson, 2002). Alternatively, $^{234}$U is gradually lost from phosphorites during diagenesis by alpha recoil during their life span, which can cause their low δ$^{234}$U values (Henderson, 2002). The δ$^{234}$U data of sediments other than phosphorites further support redistribution of U. High δ$^{234}$U values similar to seawater in the most anoxic core (MUC19) suggest that U in these samples did not undergo substantial loss of $^{234}$U due to alpha recoil and diagenetic overprinting. This observation indicates that U in this core was less affected by remobilisation (e.g. during the redistribution of U during phosphorite formation) compared with the two other anoxic cores (MUC29 and BIG005). Alternatively, other processes, e.g. particulate U input under persistently anoxic conditions, may have had a stronger impact on U in this sediment core. The δ$^{234}$U values of BIG005 indicate extensive loss of $^{234}$U, possibly due to high rates of U remobilisation under episodically oxic conditions (Seyermann and Thomson, 1998). Moreover, δ$^{234}$U values of bulk sediments deposited under oxic conditions (MUC15 and MUC25) are substantially lower than in the anoxic cores (MUC19 and MUC29), supporting that further upslope, U (preferentially $^{234}$U) is remobilised from the sediment and accumulates downslope.

5. Implications for paleo-reconstructions

Cycling of U on the Peruvian margin is schematically illustrated in Fig. 5, providing a model of U cycling in a modern open marine environment. Under reducing conditions in the OMZ, sedimentary δ$^{238}$U values are higher compared to seawater, with the highest values found under persistently anoxic conditions. Across the Peruvian margin, U accumulates in the sediment both via diffusive and particulate input. The correlation between TOC and δ$^{238}$U values in the permanent OMZ (MUC19) indicates that organic-rich sediments preferentially accumulate isotopically heavy U, through the delivery of organic particles with elevated δ$^{238}$U values combined with U reduction within the sediment mediated by microorganisms. With the degradation of organic matter and regeneration of PNU under oxic conditions, associated (isotopically heavy) U can be released into the porewater, from where it precipitates (upon reduction) and accumulates as authigenic U (Scholz et al., 2011). This reworking mechanism can be observed in our isotope analyses, where heavy U isotopes remain in the reactive fraction of the sediment. Light U isotopes are preferentially incorporated into precipitating CFA grains, which are transported downslope and eventually form phosphorite crusts. In sediments deposited under oxic conditions, the δ$^{238}$Uauth values are similar to typical seawater values, and lower compared with sediments deposited under anoxic, non-euxinic conditions.

Our dataset, investigating the U isotope compositions in modern anoxic and typically non-sulfidic sediments, helps to better constrain the interpretations of U isotope data from the geological record. Reconstructions of the extent of anoxic seafloor typically work with the assumption that the largest effective U isotope fractionations are associated with anoxic sediments (e.g. Zhang et al., 2018). The data from the Peruvian margin show that anoxic sediments do not necessarily record a large offset from seawater. Instead, the offset between sediments and the overlying water column in an anoxic, non-euxinic setting (Δ$^{238}$Uauth-seawater between 0.07 and 0.40‰) is smaller than under euxinic conditions (>0.6‰Basu et al., 2014; Rolison et al., 2017), but larger than under oxic conditions (e.g. Basu et al., 2014). Furthermore, our data indicate that TOC and thus, $^{238}$U in rain and burial rates, also influence the U isotope composition of the sediments. Consequently, large effective U isotope fractionations are not necessarily associated with anoxic conditions in general, but instead, fractionation depends on other factors such as the presence or absence of $\text{H}_2\text{S}$ in and above porewaters, and $\text{C}_{\text{org}}$ rain and burial rates. Nevertheless, euxinic sediments seem to induce the largest degree of U isotope fractionation of all known U sinks, including anoxic, non-sulfidic sediments. Thus, large U isotope fractionation factors in ancient sedimentary rocks are likely recording the extent of euxinia, rather than anoxia in general.

6. Conclusions

We investigated U biogeochemical cycling under a range of redox
conditions in a non-euxinic open ocean environment with high productivity. The δ²³⁸Uauth values in sediments record mixed signals with contributions from organic matter rain from the water column and redox-related processes in the sediments. Particulate and diffusive input of U, both tightly linked to organic matter, can affect U concentrations and their isotope compositions. Our data show that bottom water redox state impacts δ²³⁸Uauth values, although differences between δ²³⁸Uauth values deposited under anoxic and oxic conditions can be small. The results of our sequential extractions show that the reactive sediment fraction is more sensitive to reliably record the redox state of ambient seawater than δ²³⁸Uauth values calculated from major ion chemistry. The applicability of our method to extract the reactive fraction (weak HCl leach) on shales remains to be investigated.

The U isotope offset between anoxic, non-sulfidic sediments and seawater constrained here (<-0.40‰) is smaller compared with the offset observed in euxinic environments, but can be larger than the offset in oxic environments depending on the organic content of the anoxic, non-sulfidic sediments. Thus, large U isotope fractionation factors inferred for anoxic sediments, which inform estimates of ancient ocean anoxia from these redox sensitive records, cannot be univocally applied for all anoxic environments. Instead, the presence or absence of H₂S in and above porewaters, as well as CO₃ rain and burial rates, driving the TOC content of the sediment, also affect U isotope fractionation. These findings allow us to better constrain ancient ocean conditions from the sedimentary U isotope record, further defining the abundance of anoxic ocean conditions in Earth history.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abshire, M.L., Romaniello, S.J., Kuzminov, A.M., Cofrancesco, J., Severmann, S., Riedinger, N., 2020. Uranium isotopes as a proxy for primary depositional redox conditions in organic-rich marine systems. Earth Planet. Sci. Lett. 529, 116079.

Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum – uranium covariation. Chem. Geol. 268, 211–225.

Andersen, M.B., Stirling, C.H., Zimmermann, B., Halliday, A.N., 2010. Precise determination of the open ocean δ²³⁴U/δ²³⁵U composition. Geochim. Geophys. Geosyst. 11, 1–8.

Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W., 2014. A modern framework for the interpretation of δ²³⁴U/δ²³⁵U in studies of ancient ocean redox. Earth Planet. Sci. Lett. 400, 184–194.

Andersen, M.B., Stirling, C.H., Potter, E.K., Halliday, A.N., 2004. Towards epsilon levels using δ²³⁴U/δ²³⁵U in modern seawater. Chem. Geol. 207, 1449–1466.

Clark, S.K., Johnson, T.M., 2008. Effective isotopic fractionation factors for solute removal by reactive sediments: a laboratory. Earth Planet. Sci. Technol. 42, 7850–7855.

Cole, D.B., Planavsky, N.J., Longley, M., Boening, P., Wilkes, D., Wang, X., Swanen, E.D., Witting, C., Loydell, D.K., Baigten, Y., Knudsen, A.C., Speerling, E.A., 2020. Uranium isotope fractionation in non-sulfidic anoxic settings and the global uranium isotope mass balance. Glob. Biogeochem. Cycles 34, 1–22.

Dale, A.W., Sommer, S., Lomnitz, U., Montes, I., 2015. Organic carbon production, mineralisation and preservation on the Bioescescences 12.

Diamond, C.W., Lyons, T.W., 2018. Mid-Proterozoic Redox Evolution and the Possibility of Transient Oxygenation Events, pp. 1–11.

Dunk, R.M., Mills, R.A., Jenkins, W.J., 2002. A reevaluation of the oceanic uranium covariation. Chem. Geol. 268, 211–225.

Endriss, F., Rao, L., 2014. Chemical speciation of uranium(VI) in marine environments: Complexation of calcium and magnesium ions with [UO₂(CO₃)]³⁻ and the effect on the extraction of uranium from seawater. Chem. Geol. 40, 1449–1466.

Erogol, S., Scholz, F., Frank, M., Siebert, C., 2020. Influence of particulate versus diffusive molybdenum supply mechanisms on the molybdenum isotope composition of continental margin sediments. Geochim. Cosmochim. Acta 273, 51–69.

Froelich, P.N., Bacon, M.P., Alabat, M.A., Labeyrie, L.D., 1993. Glacial Interglacial phosphorite crusts off Peru. Mar. Geol. 262, 68–85.

Francois, R., Bacon, M.P., Alabat, M.A., Labeyrie, L.D., 1993. Glacial Interglacial phosphorite crusts off Peru. Mar. Geol. 262, 68–85.

Fujii, Y., Higuchi, N., Haruno, Y., Nomura, M., Suzuki, T., 2006. Temperature dependence of isotope effects in uranium chemical exchange reactions. J. Nucl. Sci. Technol. 43, 400–406.

Glenn, C.R., Arthur, M.A., 1988. Petrology and major element geochemistry of Peru margin phosphorites and associated diagenetic minerals: Authigenesis in modern organic-rich sediments. Mar. Geol. 80, 231–260.

Goto, K.T., Anbar, A.D., Gordon, G.W., Romaniello, S.J., Shimoda, G., Takaya, Y., Tomakura, A., Nozaki, T., Suzuki, K., Machida, S., Hanyu, T., Usui, A., 2014. Uranium isotope systematics of ferromanganese crusts in the Pacific Ocean: Implications for the marine 238U/235U isotope system. Geochim. Cosmochim. Acta 146, 43–58.

Gutiérrez, D., Enríquez, E., Purca, S., Quipizcoa, L., Marquina, R., Flores, G., Graco, M., 2008. Oxygenation episodes on the continental shelf of Central Peru: Remote forcing from a Heinrich event. Prog. Oceanogr. 79, 177–189.

Hayes, C.T., Martínez-García, A., Hasenfratz, A.P., Jaccard, S.L., Hodel, D.A., Sigman, D.M., Haug, G.H., Anderson, R.F., 2014. A stagnation event in the deep South Atlantic during the last interglacial period. Science (80-.) 346, 1514–1517.

Henderson, G.M., 2002. Seawater [235U/238U] during the last 800 thousand years. Earth Planet. Sci. Lett. 199, 97–110.

Hinojosa, J.L., Stirling, C.H., Reid, M.R., Moy, C.M., Wilson, G.S., 2016. Trace metal cycling and 238U/235U in New Zealand’s fjords: Implications for reconstructing global paleoredox conditions in organic-rich sediments. Geochim. Cosmochim. Acta 179, 89–109.
