Elevated uranium concentrations in Lake Baikal sediments: burial and early diagenesis

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Abstract

The water column of Lake Baikal (Siberia) is pervasively oxic and O₂ penetrates several cm into the sediment, followed by distinct layers of Fe/Mn oxide that undergo reductive-dissolution/oxidative-precipitation cycles. Uranium (U) contents of the oxic surface sediment layers were ~15 µg g⁻¹, which is unparalleled in oxygenated lakes. To understand the processes leading to this enrichment we investigated the geochemical composition of the particulate matter and pore water of four sediment cores from different locations in the lake and performed mass balance calculations based on sediment mass accumulation rates and published loads from major tributaries. The comparison of loads and export of U in Lake Baikal suggested that current estimates of loads are too low by a factor of about 3 compared to sediment mass accumulation rates. Peak loads during spring ice melt in tributaries that are difficult to monitor and quantify might be the main cause for the deviation. The high U concentrations in the lake sediments originated from the scavenging of U in the water column through association with settling organic particles and particulate Fe(III)- and, to a lesser extent, Mn(IV)-oxides. We outline the hypothesis that two distinct U phases, lithogenic and non-lithogenic U reach the lake sediment and that authigenic U is subsequently formed under reducing conditions within the sediment. In some cores we found that most U was remobilized during the degradation of organic matter, in particular within the top oxygenated layer of the sediment. Significant enrichments prevailed due to U adsorption to and/or co-precipitation with Fe-oxides. When Fe-oxides and, to a lesser extent, Mn-oxides were reductively dissolved, they released U to the pore water, leading to peak dissolved U concentrations in the anoxic sediment, which in turn, precipitated as authigenic U under predominantly sulphate-reducing conditions. The onset of the accumulation of authigenic U coincided with the formation of distinct Fe/Mn oxide layers above. We argue that the resilience of Fe-oxides (especially crystalline goethite and hematite), in association with phosphate, even within reducing (but non-sulfidic) sediments support the burial of substantial amounts of U.

Keywords: Uranium diagenesis; Lake Baikal; trace elements; Fe- and Mn-oxides; biogeochemical cycling in lacustrine surface sediments and pore water

1. Introduction

On Earth's surface environment, uranium (U), a radioactive metal from the actinide series, primarily occurs in two redox states with distinctly different physico-chemical characteristics. Under oxic conditions, such as in modern seawater, U is predominantly present as soluble and stable U(VI) carbonate complex ($\text{UO}_2(\text{CO}_3)_3^{4-}$) with a concentration of around $3.3 \mu\text{g l}^{-1}$ (14 nM) and exhibits conservative behaviour with a high oceanic residence time of 0.3 to 0.6 million years (Ku et al., 1977; Dunk et al., 2002). U concentrations in freshwater lakes are usually about one or two orders of magnitude lower than in the ocean (e.g. Falkner et al., 1997; Nagao et al., 2002; Chappaz et al., 2010; Li et al., 2011), depending on the lithology of the lake's watershed (Palmer and Edmond, 1993; Windom et al., 2000; Dunk et al., 2002; Andersen et al., 2016). The largest single sink for U in the ocean is by diffusion across the sediment-water interface into organic-rich, oxygen-depleted sediments (Anderson et al., 1989; Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993; Morford and Emerson, 1999). Here it can be reduced to U(IV) at sedimentary redox conditions near those for the conversion of Fe(III) to Fe(II) (Ginder-Vogel et al., 2006), and precipitate either as uraninite (UO_2), U_3O_7 or U_3O_8 (e.g. Klinkhammer and Palmer, 1991; Crusius et al., 1996) or as a monomeric U(IV) species that readily associates with phosphate or carbonate functional groups (e.g. Bargar et al., 2013; Morin et al., 2016). Thereby, microbially mediated reduction of aqueous U(VI) to sparingly soluble U(IV) is considered to be the most important process controlling the biogeochemical cycling of U in the subsurface (Williams et al., 2013; Bargar et al., 2013). In Phanerozoic times, where significantly higher atmospheric and oceanic O_2 concentrations allowed for a more pronounced role of oxygen in the U cycle, this may have been responsible for U contents in black shale of well above $100 \mu\text{g g}^{-1}$ (Partin et al., 2013).. Redox transitions influence the $^{238}\text{U}/^{235}\text{U}$ isotope ratio, which makes sedimentary U an important redox tracer due to the distinctly different geochemical behaviour of the reduced and oxidized species, and the long residence time in the ocean (Brennecke et al., 2011; Andersen et al., 2016). A detailed understanding of the processes involved in the accumulation of U in the sediment and during early diagenesis is thus required.

In addition, uranium is associated with particulate matter in the water column, termed particulate non-lithogenic U (PNU; Anderson, 1982), either in the form of organic complexes (Knauss and Ku, 1983; Hirose and Sugimura, 1991) or co-precipitated with Mn- and Fe-oxides (Duff et al., 2002; Dunk et al., 2002; Cumberland et al., 2016). In well-oxygenated marine and lacustrine sediments, U concentrations typically remain in the range found within the Earth's crust, i.e. around $2.8 \mu\text{g g}^{-1}$ (Taylor and McLennan, 1995). However, U concentrations of up to $250 \mu\text{g g}^{-1}$ may be present in phosphatic rocks, and fine-grained sedimentary rocks typically contain more U than coarser-grained rocks due to the presence of clays and organic matter to which U adsorbs (e.g. Bird, 2012).

Oligotrophic (nutrient poor) and pervasively oxic Lake Baikal (Siberia, Russia) is the largest lake on Earth by volume and harbours about 20% of the world's available freshwater resources. Its watershed is dominated by granitoid rocks (Fagel et al., 2007), which, compared to other contemporary lacustrine environments, contribute to a comparatively elevated average U concentration of 420 ng l^{-1} in the water column (Falkner et al., 1991, 1997). However, despite high O_2 concentrations down to the lake bottom and into the top sediment layer, it has been shown that sedimentary U contents can reach more than $20 \mu\text{g g}^{-1}$ (Petrov et al., 1999; Zhmodik et al., 2003, 2005; Chebykin et al., 2004, 2007; Goldberg et al., 2005), i.e. about 5 times higher than the rocks of Lake Baikal's watershed (Jahn et al., 2009; Litvinovsky et al., 2011). These U concentrations are also far higher than observed in other freshwater lake sediments where they typically range from 0.5 to $5 \mu\text{g g}^{-1}$ (e.g. Markich, 2002). Mass balance calculations result in a U residence time of about 160 years in the water column, compared to 400 years for Lake Baikal's water mass (Falkner et al., 1997), suggesting that a significant portion of U is removed into, and permanently buried within the sediment. This is striking when considering that the residence time of U in the ocean exceeds the one for its water by about two magnitudes.

In this manuscript, we investigate and discuss the transport and settling of U in the sediment, and processes of remobilization and final sequestration during early sediment diagenesis leading to the high sediment content of U. The present study represents the third project on the diagenetic

evolution and elemental composition of Lake Baikal sediments and pore water based on the same sediment cores (Och et al., 2012; Och et al., 2014).

2. Environmental setting

Lake Baikal is situated on an active continental rift that separates the Siberian craton in the northwest from the Mongolian-Transbaikalian belt in the southeast (see Fig. 1; Hutchinson et al., 1992; Moore et al., 1997; Logatchev, 2003). The onset of the rifting dates to the Oligocene (34 – 23 Ma; Mats and Perepelova, 2011). While the lake remained free of permanent ice cover throughout the Pleistocene epoch (Kashiwaya et al., 2001), it freezes over for four to five months a year (December to May). Following the ice break up and snow melt around May, a short term increase in terrigenous input is observed (Heim et al., 2005; Zakharova et al., 2005). Most of Lake Baikal's catchment of about 557'000 km² is sparsely populated and, hence, suffers little anthropogenic contamination. A major U enrichment plant situated by the Angara River, the lake's only outflow, about 40 km downstream of Irkutsk, was only established in the mid-twentieth century and is unlikely to have a major impact on sedimentary U in Lake Baikal (e.g. Khlopkov, 2008; Moore et al., 2009). However, major U mining operations are located in the eastern transbaikalian region (Ischukova, 1997; Brunello et al., 2006; Laverov et al., 2009). One of the latter is the Khiagda ore field in the Vitim uranium district about 140 km north of Chita, whereby mineralization occurs within fluvial sediments in paleovalleys of relatively narrow tributaries (e.g. Doynikova et al., 2014). The Vitim U district, however, is located outside the watershed of Lake Baikal (see Fig. S1 in the supplementary information). Nonetheless, we cannot exclude that other U ore deposits, which may have an influence on U delivery to Lake Baikal, occur within the watershed, particularly in the Mongolian part.

The total riverine water input to the lake amounts to about 58 km³ a⁻¹ (Votintsev et al., 1965; Falkner et al., 1997). All the rivers together carry approximately 3780 kt of suspended particulate matter per year (Vologina and Sturm, 2009). The largest river is the Selenga, which contributes 50% of the water

and about 75% of the particle load to the lake. The input of fluvial suspended particles southwards from the Selenga Delta is about twice as high as that to the north (Granina et al., 2000, 2004; Müller et al., 2005). The second and third largest rivers, the Upper Angara and the Barguzin, contribute to 20% and 7% of the water, 15% and 6% of the particle load, respectively. The Aeolian contributions account for about 6% of the total particulate matter supply to the lake (Agafonov, 1990; Lomonosov et al., 1995; Granina et al., 2000; Fagel et al., 2007).

In summary, 40% of the total terrigenous matter delivered to the lake goes to the South Basin, 32% to the Central Basin and 28% to the North Basin (Vologina and Sturm, 2009), which constitutes an overall balanced input. However, according to Table 1, about 90% of total dissolved U introduced into the lake, around 46 tons per year, comes from the Selenga River (Edgington et al., 1996; Falkner et al., 1997), which also delivers around 18 tons U per year contained in particulate matter (calculated using data by Bobrov et al., 2001).

3. Methods and Materials

3.1. Sampling sites and core description

Sediment cores were collected during an expedition between June 25 and July 2, 2010 at stations A-D from water depths of about 1400 m, 490 m, 380 m and 900 m respectively (Figure 1). Up to nine cores per site were retrieved simultaneously using an uwitec multicorer (www.uwitec.at). Unfortunately, the multi-coring device was lost at station D in the North Basin, and cores had to be retrieved individually one by one. Hence, some geochemical profiles from station D can be slightly out of alignment due to the vessel drifting during coring (see also Och et al., 2012).

All cores are mainly composed of biogenic-terrigenous mud whereby diatom remains represent an important component (Figure 2; see also Och et al., 2012). In addition, turbidite deposits have been observed in core A and D. No indications for bioturbation were apparent in either core. The oxidized zone, indicated by different shades of brown including oxidized crusts, can be discontinuous, i.e.

disrupted by reduced, grey sediments, which is most visible in cores A and C. The depicted core segments of the surface sediment represent deposition of about 200 years for cores A and C, 360 years for core B and roughly 500 years for core D.

3.2. Sample treatment and ICP-MS analysis

The procedures of sampling and analysis are given in detail in Och et al. (2014). In short, the sediment cores were sectioned in slices of 5 to 15 mm thickness with an uwitec piston extruder on site, transferred to filter holders of 70 mm diameter with 0.45 µm membrane filters (cellulose acetate, Sartorius 11106-85, Germany) and the porewater extracted with a vacuum flask. Aliquots were acidified with 5 µl HNO₃ (conc. suprapure, Sigma Aldrich) for trace element analyses. The remaining sediment was freeze-dried 7 to 10 days after retrieval, ground in an agate mortar and digested with Aqua Regia in a microwave system MLS START (Milestone Inc., USA). Three reference lake sediments from the Canadian Certified Reference Material Project were used for quality control. All digestions were performed in duplicate and results presented as averages. Samples were analysed against ICP element standards (Merck and Alfa Aesar) by inductively coupled plasma mass spectrometry (ICP-MS) using a high resolution magnetic sector field instrument Element 2 (Thermo Scientific, Germany) with Rhodium as an internal standard. The reproducibility varied with the element concentration, i.e. ca. 20% for contents in the sub ppb range and ca. 5% for contents above 100 ppb.

3.3. Sequential iron extraction

Sedimentary Fe speciation was determined using a modified version of the sequential extraction technique by Poulton and Canfield (2005). Around 80-85 mg of freeze-dried, ground samples were subjected to a 0.5 N HCl extraction for 1 hour. This released amorphous to weakly crystalline hydrous ferric oxides (e.g. ferrihydrite, lepidocrocite) plus any Fe(II) associated with particle surfaces, Fe-carbonates, -phosphates or -monosulphides (Thamdrup et al., 1994; Zegeye et al., 2012; Goldberg et al., 2012). Directly after the extraction, Fe(II) in the extraction solution was determined using ferrozine and a UV/Vis spectrophotometer (Thermo Genesys 6) at a wavelength of 562 nm (Stookey,

1970). The remaining extraction solution was analysed for total extracted Fe(II+III) using an atomic adsorption spectrometer (AAS Varian SpectrAA 400), and Fe(III) was calculated as the difference between Fe(II) and total extracted Fe. Crystalline ferric oxyhydroxides (e.g. goethite, hematite) were extracted using a 2 hour sodium dithionite extraction, and magnetite was determined via a 6 hour sodium oxalate extraction, both followed by Fe analysis via AAS.

3.4. Uranium speciation and flux calculations

Thermodynamic equilibrium calculations of dissolved U species were performed using the software ChemEQL (Müller, 1996: www.eawag.ch/en/departement/surf/projects/chemeql). We applied equilibrium constants compiled by Chappaz et al. (2010) and used concentrations of Ca^{2+} , UO_2^{2+} and HCO_3^- typically found in Lake Baikal sediment pore waters (Pogodaeva et al., 2007; Torres et al., 2014). Sorption of UO_2^{2+} and UO_2CO_3 to Fe-oxide surfaces was modelled considering two types of sorbing sites, weak and strong with complexation constants selected by Chappaz et al. (2010), and electrostatic interaction was calculated with the Generalized Two Layer Model suggested by Dzombak and Morel (1990). Humic substances, which can play an important role in U speciation in sediment pore waters (e.g. Markich, 2002; Cumberland et al., 2016), were not considered in the present study. Areal pore water fluxes (J_{sed}) were determined from concentration gradients (dC/dx) applying Fick's first law of diffusion (see also Schulz, 2006):

$$J_{\text{Sed}} = \phi * D_{\text{Sed}} * \frac{dC}{dx} \quad (1)$$

$$D_{\text{Sed}} = \frac{D^0}{\phi * F} \quad (2)$$

where D_{Sed} is the effective diffusion constant in the sediment, ϕ the porosity calculated according to Och et al. (2012), and F the formation factor (Berner, 1980), which is approximated by $F = \phi^{-1.81}$ (Maerki et al., 2004). Molecular diffusion coefficients (D^0) for the dissolved U species dominant in freshwater environments, such as UO_2CO_3 and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, can be approximated using the equation from Schwarzenbach et al. (1993):

$$D^0 = \frac{2.7 \times 10^{-4}}{M^{0.71}} \quad (3)$$

where M represents the molecular mass. As a result, D^0 at 25°C is $4.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for UO_2CO_3 , and $3.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (see also Zheng et al., 2002b; McManus et al., 2005; Chappaz et al., 2010). After adjusting for 5°C with the Stokes-Einstein relation (Li and Gregory, 1974):

$$\frac{D_{25^\circ\text{C}}^0}{D_{5^\circ\text{C}}^0} = \frac{\eta_{5^\circ\text{C}}^0}{\eta_{25^\circ\text{C}}^0} \times \frac{298.15}{278.15} = 1.81 \quad (4)$$

where η stands for the temperature-dependent viscosity of water, D^0 values diminish to $2.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for UO_2CO_3 , and to $1.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$. In the present study, these values will be considered for calculation of maximum and minimum diffusive fluxes, respectively.

3.5. Lithogenic, non-lithogenic and authigenic uranium

In modern surface environments it is appropriate to differentiate between three different U pools based on their origin and formation: (1) lithogenic U, which represents U bound to minerals of the predominantly granitoid rocks occurring in the catchment of Lake Baikal, i.e. the Mongolian-Transbaikalian Belt (MTB); (2) non-lithogenic U comprising U scavenged by particulate matter in the water column; and (3) authigenic U precipitated in the sediment due to diagenetic processes. While granites contain about $4 \mu\text{g g}^{-1}$ U on average (e.g. Condie, 1993), the granitoid rocks in the MTB have U contents averaging $3.4 \pm 1.7 \mu\text{g g}^{-1}$ ($n = 27$; Litvinovsky et al., 2011). However, normalization with the immobile element Al reveals average U/Al ratios of 4.4×10^{-5} (w/w), more than twice the lithogenic average (e.g. Rudnick and Gao, 2004; see also Och et al., 2014) and significantly higher than average granite (ca. 3×10^{-5} ; Condie, 1993). Normalization with the equally conservative element Sc (e.g. De Groot, 1995, Audry et al., 2004) yields U/Sc ratios of about 1 for the MTB granitoid rocks, which is comparable to average granite. Due to the very large watershed of Lake Baikal we assume this ratio to be more or less constant within lithogenic particles settling in Lake Baikal. In addition, contrary to cores B to D, the Al concentration profile through core A shows very high variability and is rather different from the Sc profile, leading to spurious correlations between

various other elements for as yet unknown reasons (see Och et al., 2014). Hence, in order to gain consistency among all studied cores, we calculated the relative abundance of lithogenic U relative to Sc according to the equations:

$$U_L + U_{NL} = U_M \quad (5)$$

$$U_L = Sc_M \times \frac{U}{Sc_L} \quad (6)$$

The subscript NL denotes the non-lithogenic fraction, the subscript M stands for measured values and $(U/Sc)_L$ is the average lithogenic ratio found in granitoid rocks of the MTB (0.97). The authigenic U fraction, U_{auth} , which will be more amply discussed later, is part of non-lithogenic U but is explicitly formed within the sediment and will be estimated based on the U_{NL} and pore water U profiles.

4. Results

4.1. Oxygen in the sediment and particulate Mn and Fe profiles

In the present study, the sediment penetration depth of O_2 is taken into account (see Fig. 2), which has been measured and discussed for the same cores in Och et al. (2012). Bottom O_2 concentrations were between 11.5 and 13.2 mg l⁻¹. The upper Fe/Mn layers or crusts likely form at the lower end of the oxygen penetration depth as a dynamic pattern, moving upwards with the growing sediment. Thereby, reductive dissolution of Mn(IV) occurs at the lower margin, and upward diffusing Mn(II) is oxidised with O_2 . The buried, lower Fe/Mn layers were immobilized within the sediment and undergo slow reductive dissolution mainly driven by the anaerobic oxidation of CH_4 . Och et al. (2012) suggested a cyclic pattern where the burial of a Fe/Mn layer is accompanied by the generation of a new enrichment at the O_2 /Mn(II) redox boundary, which is subsequently nourished by the slowly dissolving old layer. The distribution of Mn(IV), Fe(III), total organic carbon (TOC) and total sulphur (TS) in the sediment cores from the same publication are used in this study for a better

understanding of the biogeochemical cycling of major and trace metals that potentially affect the distribution of U (see Fig. 2).

4.2. Uranium speciation

Thermodynamic equilibrium calculations with ChemEQL considering a pH between 6 and 8, typical for Lake Baikal sediment pore water (Maerki et al., 2006), suggested that the main U species expected in the pore waters were UO_2CO_3 and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, with some $\text{UO}_2(\text{CO}_3)_2^{2-}$ (see Fig. 3a), i.e. (Ca)- $\text{UO}_2\text{-CO}_3$ complexes. The redox potential Eh within Lake Baikal sediments is not explicitly known but can be approximated using concentrations of pore water Fe(II) using the equation:

$$\log[\text{Fe}^{2+}] = -\frac{1}{0.059} \times \text{Eh} - 1.8 \quad (7)$$

Thereby, $\text{pE} = 16.9 \text{ Eh}$ (see Fig. 3). Besides pH and Eh, pore water Ca^{2+} and HCO_3^- concentrations are the relevant parameters. It has been shown that Ca^{2+} and HCO_3^- can significantly lower the reduction potential due to the formation of Ca- $\text{UO}_2\text{-CO}_3$ complexes and that may hinder bacterial reduction of U(VI) (Phillips et al., 1995; Brooks et al., 2003; Fox et al., 2006; Stewart et al., 2010). In the pore water analysed for the present study, Ca^{2+} concentrations were mainly in the range of 12 to 25 mg l^{-1} (0.3 to 0.6 mmol l^{-1} ; Pogodaeva et al., 2007). HCO_3^- concentrations were measured (or calculated) in previous studies and ranged between 30 and 100 mg l^{-1} , i.e. 0.5 and 1.6 mmol l^{-1} , within the uppermost 50 cm of the sediments, and typically increased to more than 100 mg l^{-1} downcore from the sediment-water interface (Maerki et al., 2006; Pogodaeva et al., 2007). However, when including adsorption reactions between Fe-oxides and U as shown in Figure 3b (Davis, 2001; Chappaz et al., 2010), the formation of $(\text{FeO})_2=\text{UO}_2\text{CO}_3^{2-}$ complexes becomes prevalent at lower pH and successively replaces Ca- $\text{UO}_2\text{-CO}_3$ with increasing sorption sites.

4.3. Nonlithogenic and authigenic uranium formation

Figure 4 shows the percentages of the U_L and U_{NL} fractions, and an estimate for authigenic uranium, U_{auth} , based on the premise that U_{NL} derived from settling particles either remained unreactive or

decreased with age/depth of the sediment through either reductive dissolution of oxidized host phases or its release through the degradation of organic matter. At the sediment-water interface, U_{NL} made up for 65 % of U_M in core C, up to 85 % in core D, and ca. 75 % in cores A and B. In core A from the Southern Basin, and core C from the Academician Ridge, the application of equation (6) indicated complete remobilization of U_{NL} at depth. However, as the calculated minima for U_{NL} in core A and C were below zero with -0.15 and $-1.7 \mu\text{g g}^{-1}$, respectively, these estimates have to be considered with some caution. While the former lies well within an analytical error of the Sc and/or U concentrations of less than 2%, the latter either results from an analytical error of up to 20% or illustrates the incidence of slightly varying U/Sc ratios in the inputs to Lake Baikal through time.

4.4. Core A

In the sediments of core A (Fig. 2), U_{NL} contents declined rapidly from $16.5 \mu\text{g g}^{-1}$ below the sediment-water interface and remained relatively constant (between 8.8 and $9.6 \mu\text{g g}^{-1}$ down to the upper Fe/Mn accumulation, followed by a steep decrease down to about $5 \mu\text{g g}^{-1}$. Between both Fe/Mn enrichments, a single U_{NL} peak of $12 \mu\text{g g}^{-1}$ was observed at 5 to 6 cm depth with a concomitant maximum in pore water U of $9 \mu\text{g l}^{-1}$. In addition, there were minor peaks of pore water Fe(II) and Mn(II) at the same depth, framed by two higher peaks concomitant with the Fe-oxide layers. Below the buried Fe-oxide layer, however, pore water U decreased to below $1.5 \mu\text{g l}^{-1}$. This minimum coincided with low pore water Fe(II) concentrations and steeply increasing TS contents decoupled from the TOC profile. At the bottom of the core, pore water U increased again in concert with Fe(II) concentrations. U_{auth} was likely formed where maximum peaks of U_{NL} were observed, i.e. between 5 and 6 cm and around 11 cm depth, where it accounted for up to 20% of total particulate U. The U_{auth} enrichment at ca. 11 cm depth was further indicated by diffusive fluxes of dissolved U from above and below the enrichment.

4.5. Core B

In core B (Fig. 2), U_{NL} contents were constant at $\sim 11 \mu\text{g g}^{-1}$ within the uppermost 12 cm of the sediment, then decreased to a minimum of $<6 \mu\text{g g}^{-1}$ within the buried Mn-oxide layer followed by a steep increase to a maximum of $\sim 18 \mu\text{g g}^{-1}$ right below the Fe-oxide peak at 21 cm. Lower values occurred towards the bottom of the core. The maximum accumulation of U_{NL} was concomitant with a peak in pore water Fe and right above a decrease in SO_4^{2-} . Pore water U concentrations were below $2.5 \mu\text{g l}^{-1}$ down to the buried Fe-oxide enrichment, and reached peak concentrations of $13.5 \mu\text{g l}^{-1}$ at 22.5 cm. The pore water U peak coincided with the maximum dissolved Mn concentration of 6 mg l^{-1} . An U_{auth} enrichment likely occurred below the buried Mn/Fe-oxide layer at 20 - 25 cm depth, accounting for up to 20% of total particulate U.

4.6. Core C

Core C exhibited clear boundaries between grey and brown intervals visualizing relative amounts of oxidized Fe (see Fig. 2 and 5), and hence indicated more pronounced redox gradients as compared to most of core B. U_{NL} contents were $\sim 10 \mu\text{g g}^{-1}$ down to the upper Mn-oxide accumulation at 5.5 cm, and decreased within the Fe-oxide layer below to $\sim 6 \mu\text{g g}^{-1}$. The subsequent U_{NL} peak of $12 \mu\text{g g}^{-1}$ at 12 cm was located between the two major Fe/Mn accumulations. Deeper in the sediments, U_{NL} contents according to eq. (6) steeply decreased and became ultimately non-existent within the buried Fe/Mn-oxide enrichment before increasing again to $5.5 \mu\text{g g}^{-1}$ at the bottom of the core. As in core B, high pore water U concentrations prevailed at the depth of elevated U_{NL} (and/or U_{auth}) contents below the Fe/Mn-oxide enrichment, where decreasing SO_4^{2-} concentrations indicated sulphate-reducing conditions. Pore water U concentrations were generally $<3 \mu\text{g l}^{-1}$ except for three prominent peaks above the upper Mn-oxide enrichment and on top and below the buried Fe/Mn accumulations. The hypothesized U_{auth} content of up to 50% of the total particulate U at the bottom of the core was concomitant with decreasing pore water Fe(II) and Mn(II) concentrations.

4.7. Core D

In core D, U_{NL} contents were comparatively high in the top 8 cm of the core, with $\sim 13 \mu\text{g g}^{-1}$ down to the upper, minor Fe-oxide accumulation. Deeper in the sediments, U_{NL} decreased steeply down to $\sim 3 \mu\text{g g}^{-1}$, with generally low contents interrupted only by a peak at 14 cm, and even lower values of $\sim 0.5 \mu\text{g g}^{-1}$ within the buried Fe/Mn enrichment. Pore water U concentrations remained $< 2.5 \mu\text{g l}^{-1}$ from the upper Fe/Mn layer down to the U_{NL} peak at 14 cm. Within the deeper sediments, including the buried Fe/Mn layer, an increasing but unsteady trend was observed, reaching pore water U concentration of $> 7 \mu\text{g l}^{-1}$ at the bottom of the core, where high TS contents occurred. This pore water U flux was directed upwards to the U_{NL} peak at 14 cm where SO_4^{2-} concentrations were at their minimum, indicating that the accumulation likely consisted of U_{auth} . Varying contents of U_{auth} could be expected further down the core, possibly reaching more than 50% of total particulate U.

4.8. Iron speciation

Iron speciation analysis for the characterization of mineral Fe phases in the sediment cores A, C and partially in core B (Fig. 5), indicated that sedimentary Fe-oxides were composed of about 50% crystalline Fe-oxides [e.g. hematite (Fe_2O_3) and goethite (FeOOH)], 35% amorphous Fe-oxides [e.g. ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$)] and about 15% magnetite (Fe_3O_4). It also suggested that the brown color of the sediment, indicating Fe(III), was visible if there were at least 1.5 wt% of Fe (oxyhydr)oxides (including hematite, goethite and ferrihydrite). Fe(II), which is involved in the formation of Fe-monosulphides, Fe-carbonates and Fe-phosphates in sedimentary environments, remained below 2‰ throughout all sections of the core. The highest Fe(II) concentrations were found at the bottom of core A where high TS contents had been observed (see Fig. 2), suggesting the presence of Fe-sulphides. This Fe(II) peak was concomitant with a minor peak in U_{NL} and minimum pore water U concentrations. Phosphorus concentrations correlated well with total Fe and/or amorphous Fe-oxides whereby the P/Fe ratio was increased within the Fe-oxide enriched layers.

5. Discussion

5.1. Mass balance and U accumulation in sediments

We estimated the deposition rate of U in the sediments of Lake Baikal based on a mass balance using U loads reported in previous studies (Edgington et al., 1991, 1996; Falkner et al., 1997; Bobrov et al., 2001). In addition, there is an aeolian component, accounting for about 6% of the total particulate input (Lomonosov et al., 1995; Granina et al., 2000; Fagel et al., 2007), which is enriched in U with a concentration of $\sim 6 \mu\text{g g}^{-1}$ (Bobrov et al., 2001), adding over a ton of particulate U per year. Assuming that the particulate load leaving the lake through the Angara River is negligible, about 55 t U are permanently buried in the sediment annually (see Table 1). Averaged over the surface area of the lake ($31'722 \text{ km}^2$), this translates to a mass accumulation rate (MAR) for U of $\sim 1.75 \text{ mg m}^{-2} \text{ a}^{-1}$. Considering the sedimentation rates established for cores A to D (0.05 to 0.09 cm a^{-1} ; Och et al., 2012), and assuming a sediment density of 2.6 g cm^{-3} , U contents of $\sim 1.2 \mu\text{g g}^{-1}$ are thus expected. Contents may be higher in the south basin than in the north and central basins as the bulk of particulate lithogenic U is mainly deposited in the South Basin and within the Selenga Delta (Vologina and Sturm, 2009). Nonetheless, the estimated $1.2 \mu\text{g g}^{-1}$ were far below the values expected for the upper continental crust ($2.8 \mu\text{g g}^{-1}$; Taylor and McLennan, 1995), and even further below the average U content in the granitoid rocks of the Mongolian-Transbaikalian Belt adjacent to the eastern shore of Lake Baikal (ca. $3.4 \mu\text{g g}^{-1}$; Jahn et al., 2009; Litvinovsky et al., 2011).

Based on these mass balance considerations alone, Lake Baikal sediments would be expected to be depleted in U relative to the upper continental crust. However, U contents measured in the present study average $13 \mu\text{g g}^{-1}$ with maxima of $>20 \mu\text{g g}^{-1}$ in the surface sediment, which is in accordance with previous studies (e.g. Chebykin et al., 2007). This discrepancy may be caused by the highly variable sedimentation rates that are difficult to determine precisely and, which on the Academician Ridge, can be as low as 0.002 cm a^{-1} (Edgington et al., 1991; Appleby et al., 1998; Vologina et al., 2000, 2003; Granina et al., 2004 and references therein; Müller et al., 2005; Watanabe et al., 2009; Vologina and Sturm, 2009; Morgenstern et al., 2013). Alternatively, the mass budget calculations presented above are based on load data that must be considered with caution. Samples for the estimation of riverine U load were collected during summer, when the lake and its tributaries were

more easily accessible for sampling. The peak input of terrigenous material occurs in May after the ice break-up and major snow melt (Edgington et al., 1996; Falkner et al., 1997; Bobrov et al., 2001). Hence, we suspect that a more extensive sampling campaign throughout the year might provide the missing load and begin to close the gap in the dataset for U input into the lake.

5.2. Uranium deposition

In the present study we discuss the processes governing dissolution and precipitation of U bearing particles and minerals between the water column and the deeper sediments. In this context, substantial sedimentary U enrichments may result from either (1) diffusive U flux from the bottom water into the sediment (Klinkhammer and Palmer, 1991; Chaillou et al., 2002; McManus et al., 2005; Morford et al., 2009a, b), (2) accumulation of U associated with particulate organic matter, so-called non-lithogenic or bio-authigenic U (Anderson, 1982; Knauss and Ku, 1983; Anderson et al., 1998; Zheng et al., 2002a; McManus et al., 2005), (3) the association of U with other settling particles, such as Fe(III)- and Mn(IV)-oxides (Hsi and Langmuir, 1985; Barnes and Cochran, 1993; Sani et al., 2004), or (4) a combination of all the above. As reported by Chebykin et al. (2010), the scavenging of U by particulate matter occurs in the water column of Lake Baikal, as U is significantly enriched in pelagic suspended matter in comparison with riverine material. This is likely due to a decrease in the concentration of dissolved complexing agents as rivers enter the lake (Edgington et al., 1996, 1997), exemplified by a several fold decrease in dissolved organic matter between riverine and lacustrine water masses (Yoshioka et al., 2002).

Good correlation between U_{NL} and the export flux of organic carbon to the sediment has been shown for marine (Anderson et al., 1998; Zheng et al., 2002b; McManus et al., 2005) and lacustrine environments (Chappaz et al., 2010). This suggests that particulate non-lithogenic U (PNU) associated with settling organic matter might play an important role for U scavenging in aquatic systems. Moreover, Zheng et al. (2002a) found that up to 70% of deposited PNU were buried within anoxic marine sediments. In the present study, the profiles of $U_{NL-auth}$, i.e. non-lithogenic U without

estimated, newly added authigenic U (see Fig. 4), and total organic carbon (TOC) did not correlate well along the analysed depth profile except for a short interval between the uppermost few centimetres and the uppermost Fe/Mn accumulations in cores A and D and to a lesser extent in core C. This is not necessarily surprising since correlation between U and organic matter concentrations can vary significantly within natural samples (Cumberland et al., 1016). However, a broadly positive covariation between the MARs of U_{NL} and TOC, although based on a very limited dataset, is consistent with association of U with settling organic matter to some degree (see Fig. 6). C/N ratios within the uppermost (oxic) sediment layer negatively correlated with the MAR of U_{NL} . As lower C/N values suggest a higher contribution from allochthonous organic matter (e.g. Meyers and Ishiwatari, 1993), the negative relationship with U_{NL} MARs suggests that the association of U with organic matter, if at all, primarily occurred in the lake and not in the watershed. Hence, that ambiguous connection between the $U_{NL-auth}$ and TOC profiles possibly arose from the greater proportion of allochthonous organic matter in the lake as opposed to the ocean. Regarding a potential association of biosiliceous phytoplankton with U_{NL} , longer sediment cores from Lake Baikal showed that elevated U concentrations were concomitant with higher counts of diatoms (Gavshin et al., 1994; Edgington et al., 1996; Goldberg et al., 2005), and it was hypothesized that U accumulated in diatom frustules. This was, however, rejected by Goldberg et al. (1998), and the similarity in the profiles of U and diatom counts was compellingly accounted for by the effects of glacial-interglacial cycles on both riverine input and primary productivity (Edgington et al., 1996; 1997; Chebykin et al., 2004). Furthermore, it was previously suggested that some U in the water column of Lake Baikal adsorbed onto particulate surfaces such as Fe-hydroxide coatings (Edgington et al., 1996; Falkner et al., 1997; see also Chebykin et al., 2010). However, we did not find a correlation between the MARs of Fe and U calculated from the concentrations at the top of the analysed sediment cores, and the respective geochemical profiles suggested that the association between Fe and U might be secondary.

In summary, while U was enriched in the lake, the precise carrier phase for U from the water column to the sediment remains unclear and might include a combination of organic matter, Fe-oxides and

clay particles (e.g. Duff et al., 2002). Despite the high O_2 concentrations in the lake and comparatively deep penetration depths into the sediment, U was remobilized very slowly.. This is in contrast to other studies stating that oxidative U remobilization from lake sediments is a very fast process (Cochran et al., 1986; Anderson et al., 1989). Hence, this suggests that high amounts of reactive U are retained in the Baikal sediment long enough for early diagenetic redistribution.

5.3. The diagenetic cycle of uranium

The thickness of the oxic layer of aquatic sediments defines the rate of exchange of dissolved redox-sensitive metal species between the bottom waters and the deeper anoxic sediment. The main rate determining parameters are molecular diffusion gradients, metal release rates following the oxidation of organic matter, and bioturbation. Within the O_2 -containing zone of Baikal sediments, i.e. between the sediment water-interface and the O_2 /Mn(II) redox boundary (see Fig. 2), U_M contents were relatively constant with values of $\sim 15 \mu g g^{-1}$. The uppermost sample of core A containing $>20 \mu g g^{-1}$ U was an exception. While similar U_M contents extended deeper into the sediments and decreased only at or below the upper Fe-oxide enrichment, U_{NL} contents exhibited an overall decrease, although with some variations, from the sediment-water interface down to the buried Fe- (and Mn-) oxide accumulations. The occasional U_{NL} peaks that occurred deeper in the sediment were interpreted to represent sediment layers where U_{auth} was formed (see section 4.3). A common feature in cores A and C was that the buried Fe/Mn enrichments occurred underneath an interval of greyish sediment, indicative of minimal amounts of reducible Fe-oxides (see Fig. 5), whereas cores B and D exhibited brown sediment between both Fe/Mn enrichments (see Fig. 2). In addition, the relatively constant pore water U concentration within the uppermost 15 to 20 cm in cores B and D was below the solubility of U at reducing conditions, i.e. $<2.5 \mu g l^{-1}$ for amorphous $UO_2 \cdot xH_2O$, and $<0.5 \mu g l^{-1}$ for crystal UO_2 at pH >4 (e.g. Rai et al. 1990; Nagao et al., 2002). Hence, it appeared that more dynamic redox cycling with steeper Eh gradients prevailed in core C and particularly in core A, leading to an enhanced remobilization of U associated with Fe-oxides and/or organic matter (Hsi and Langmuir, 1985; Duff et al., 2002; Sherman et al., 2008; Morford et al., 2009a, b). Bioturbation, which

could significantly accelerate the remobilization of U in sediments (Zheng et al., 2002b; Lagauzère et al., 2013), was not observed in cores A to D, and previous studies suggested that it likely has a limited effect on sediment mixing in the deeper parts of Lake Baikal (Martin et al., 2005).

5.4. Uranium remobilization by reductive dissolution of Fe- and Mn-oxides

In the absence of high concentrations of complexing ligands such as carbonate, oxalate, hydroxide, fulvic and humic acids (e.g. Lenhart et al., 2000; Wazne et al., 2003; Guillaumont et al., 2003; Grenthe et al., 2004), dissolved U(VI) readily adsorbs onto and/or co-precipitates with Fe-oxides such as ferrihydrite, hematite and goethite (Hsi and Langmuir, 1985; Waite et al., 1994; Lenhart and Honeyman, 1999; Duff et al., 2002; Wazne et al., 2003; Nico et al., 2009; Kelly, 2010; Vodyanitskii, 2011; Li and Kaplan, 2012; Cumberland et al., 2016) and Mn-oxides (e.g. Al-Attar and Dyer, 2002; Misaelides et al., 2002; Webb et al., 2006; Wang et al., 2012). This can lead to immobilization of U(VI) in the sediment, as demonstrated by the U speciation model outlined in section 4.2, and inhibit further bacterial reduction (Ortiz-Bernad et al., 2004; Boland et al., 2011). Considering the high contents of Fe-oxides in Lake Baikal, U association with Fe-oxide phases might indeed be an important aspect leading to its accumulation and resilience in the sediment under oxic to suboxic conditions. The diagenetic cycles of Fe- and Mn-oxides, on the other hand, are unlikely to exert significant direct influence on the U diagenetic cycle (Klinkhammer and Palmer, 1991), other than the release of U during the reductive dissolution of Fe- and Mn-oxides. The Fe speciation data demonstrated that a coupling of U(VI) to Fe-oxide particles in the water column could be retained within amorphous and especially crystalline Fe-oxides throughout the studied sediment sections. While U(VI) initially adsorbed to e.g. nanoparticulate ferrihydrite in the water column and/or at the sediment surface, the Fe-U coupling might have been stabilized by the transformation to crystalline Fe-oxides. Under the given temperature-pH conditions and disregarding organic complexation, this could have occurred within a few years (Schwertmann et al., 2004). Note, however, that this transformation in Lake Baikal sediments was likely slowed down by the presence of high pore water phosphate concentrations (see section 5.5; Och et al., 2012). The partial preservation and slow

dissolution of these precipitates at depth might explain the high pore water U concentrations within the reducing sediment intervals, even below the buried Fe-oxide layers. This explanation presumes that the reaction kinetics for the reductive precipitation of U_{auth} , i.e. the transformation of U(VI) to U(IV), are slower than for the reductive dissolution of Fe-oxides, sustaining pore water U concentrations above the solubility of solid U(IV) phases. This is likely due to the formation of $Ca-UO_2-CO_3$ complexes, which probably become more significant with depth along with rising HCO_3^- concentrations partially fuelled by the reductive dissolution of Fe- and Mn-oxides.

Not only Fe-oxide, but also Mn-oxide surfaces participate in U adsorption and sequestration (Webb et al., 2006; Wang et al., 2012). In the studied cores, the main particulate Mn species birnessite and todorokite (Och et al., 2012) are both known to adsorb U (Misaelides et al., 2002; Al-Attar and Dyer, 2002), but they occurred at far lower contents than Fe-oxides. In addition, they are considered to be much more reactive under reducing conditions than crystalline Fe-oxides (Och et al., 2012), and thus were likely a quantitatively less important carrier phase for U in deeper, reducing sediments of Lake Baikal.

5.5. The relationship between uranium and phosphorus

The affinity of U to be incorporated into phosphate minerals, with the potential to form stable uranyl phosphate minerals (Jerden and Sinha, 2003; Ohnuki et al., 2004; Wellman et al., 2007), can lead to highly elevated U contents (up to $250 \mu g g^{-1}$; Altschuler et al., 1958; Bird, 2012). Indeed, previous geochemical analysis of Lake Baikal sediments showed that intervals enriched in phosphate minerals (especially vivianite) exhibit U concentrations of up to $90 \mu g g^{-1}$ (Zhmodik et al., 2003; 2005; see also Fagel et al., 2005), at least one order of magnitude higher than in most marine sediments (Plank and Langmuir, 1998). Hence, U association with phosphate minerals can further U enrichment. However, the very good correlation between total Fe and P contents ($R^2 > 0.96$, $p < 0.001$; see Fig. 5 and Och et al., 2012) indicates that in the studied cores, most of the P and Fe enrichments result from enrichments of Fe (oxyhydr)oxides with adsorbed phosphate and/or Fe(II)-phosphates like vivianite. While we did not perform detailed mineralogical analyses of these layers, both vivianite and Fe

(oxyhydr)oxides would contribute to the sum of extracted Fe-oxide phases (Fig. 5) and would explain the excellent correlation between sedimentary P and Fe. The preservation of substantial amounts of amorphous Fe (oxyhydr)oxides in the Fe-rich layers (see Fig. 5) despite their usually fast aging and crystallisation kinetics (Schwertmann et al., 2004) can be explained by the inhibition of this transformation if Fe (oxyhydr)oxides contain large amounts of adsorbed P (Galvez et al., 1999; see also März et al., 2012). Hence, while U was released into the pore water upon the dissolution of amorphous Fe-oxides/Fe(III)-phosphates, it was not trapped and enriched by re-adsorption and/or co-precipitation with the same phases. While average P/Fe (wt%/wt%) ratios in the sediment and the MTB rocks were both 0.056 (Litvinowsky et al., 2011), Fe and P were enriched by a factor of 3 in the sediment. It is, therefore, conceivable that Fe and P minerals exerted a stabilizing effect on particulate U.

5.6. Uranium diffusion across the sediment-water interface

The pore water profiles of U showed an increase from the bottom water down to the limit of O₂ penetration (the O₂/Mn(II) redox boundary). This increase was very well correlated with pore water Fe (with R² around or higher than 0.9), indicating that they predominantly occurred in colloidal form (e.g. Lead and Wilkinson, 2006; Cumberland et al., 2016 and references therein). This was confirmed by the analysis of Lake Baikal sediment pore water with a portable capillary electrophoresis instrument, which discriminated colloidal Fe(III) in the measurement (Torres et al., 2014). These experiments showed that Fe detected in 0.45 µm-filtered pore water by atomic absorption spectroscopy was not Fe(II) but rather consisted of Fe(III) colloids that passed through the filter membrane. In order to evaluate whether dissolved U diffused across the sediment-water interface and precipitated as U_{auth} deeper in the reducing part of the sediment, in the form of UO₂, U₃O₇ or U₃O₈ (e.g. Klinkhammer and Palmer, 1991; Crusius et al., 1996; Zheng et al., 2000; Morford et al., 2001, 2009a, b; Chaillou et al., 2002; McManus et al., 2005), we normalized pore water U to Sc, which predominantly occurs in particulate form and is not redox-sensitive (Orians and Merrin, 2009). Figure 2 shows that pore water U/Sc ratios were quite constant downcore and only increased below

the buried Fe/Mn layer in core B and in the reducing zone of core C. Increases in the U/Sc ratio coincided with the presence of authigenic U (see Fig. 2 and 4) indicating the occurrence of diagenetic reactions of U independent of the fate of Sc that lead to precipitation or associations with different mineral phases.

5.7. The authigenic precipitation of uranium

We can divide the core segments into intervals where U was remobilized, e.g. through reductive dissolution of Fe- and/or Mn-oxides, and where U precipitated, most likely through microbial mediation. As mentioned in section 4.3, the overall downward decrease of particulate U was interrupted by peaks that likely represented U_{auth} formation, indicated by the diffusive fluxes directed towards the enrichments (see Fig. 2 and 4). In core B, estimation of the upward diffusive U flux towards the U_{NL}/U_{auth} peak at 21 cm depth using equations (3) to (6) resulted in 1.6 to 2.2 $\text{mg m}^{-2} \text{a}^{-1}$, depending on the ratio of UO_2CO_3 to $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$. The solid phase U dissolution rate at the depth of maximum pore water U, adding up- and downward fluxes, was between 2.5 and 3.5 $\text{mg m}^{-2} \text{a}^{-1}$. Assuming a constant U flux towards the hypothesized U_{auth} enrichment at 20 - 25 cm depth (Fig. 2 and 4), which was estimated to contain 0.15 g m^{-2} , resulted in an accumulation time of 65 - 90 years. In core C, we calculated a pore water U flux of 0.68 - 0.96 $\text{mg m}^{-2} \text{a}^{-1}$ from the peak of $\sim 10 \mu\text{g l}^{-1}$ at 14 cm directed towards the U_{NL} peak at 12 cm. This U_{NL} peak was likely composed of U_{auth} fed by the diffusive U flux (Fig. 2). Hence, assuming an enrichment of U_{auth} between 10-14 cm resulting in a deposition of $\sim 0.14 \text{ g m}^{-2}$ and a constant diffusive flux, the estimated accumulation time here was 140-200 years. Therefore, the timeframes for the enrichments of U_{auth} in cores B and C matched well with the chronology of the burial of the lower, buried Fe/Mn accumulations, i.e. their decoupling from the dynamic redox cycling at the $\text{O}_2/\text{Mn(II)}$ boundary, and the onset of the precipitation of the upper Fe/Mn layer starting more than 200 years ago (Och et al., 2012). This suggests that the diagenetic accumulation of U_{auth} tends to occur once two Fe/Mn oxide layers have formed.

The pore water profiles of Fe, Mn and SO_4^{2-} were used to refine the sedimentary redox stratification. All cores exhibited the highest pore water U concentrations within intervals characterized by SO_4^{2-}

reduction, with values clearly exceeding the solubility for amorphous and crystalline UO_2 within anoxic sediment (e.g. Rai et al., 1990; Nagao et al., 2002). Elevated U contents in anoxic sediment, such as those observed between both Fe-oxide accumulations and at the bottom of core A, have been described in marine sediments (Zhorov et al., 1982; Cochran et al., 1986; Anderson et al., 1989; Chaillou et al., 2002; Audry et al., 2006). The presence of dissolved U(VI) in anoxic sediment was frequently attributed to sampling artefacts, such as re-oxygenation of particulate U(IV) to dissolved U(VI) during sampling (e.g. Anderson et al., 1989) or colloidal U (e.g. Chaillou et al., 2002). While the latter probably occurred within the oxic interval of the Lake Baikal cores (see chapter 5.7), the accumulation of U_{auth} close to pore water U maxima suggested that no U(IV) re-oxygenation occurred within the sampled anoxic sediments. Pore water concentrations were truly increased and might originate from rising levels of HCO_3^- generated by the reductive dissolution of Fe- and Mn-oxides, which would increase the solubility of U due to the formation of carbonate complexes.

While it is generally conceivable that Fe-monosulphides reduced dissolved U(VI) to insoluble U(IV) (e.g. Hua and Deng, 2008; Bargar et al., 2013), this is unlikely to be a major mechanism leading to the accumulation of U_{auth} in Lake Baikal sediments. Comparatively high Fe-monosulphide contents around 10 cm depth in core A corresponded to only modest U_{auth} enrichments, while very minor amounts of Fe-monosulphides occurred in core C where we suspect the most pronounced U_{auth} accumulation at 12 cm depth.

6. Conclusions

For a pervasively oxic lacustrine system, the high uranium concentrations in Lake Baikal sediments are, to date, unparalleled. The mass balance considerations outlined in the present study, however, reveal a significant gap regarding the supply of U into the lake and more frequent sampling of the tributaries to Lake Baikal, in particular right after the ice break-up in May, and a better appreciation of uranium deposits situated within the Lake Baikal watershed is needed to deliver a more detailed appreciation of its elemental budget. Nonetheless, the mechanisms leading to much of the U being

retained within the sediment is likely the adsorption within the water column of dissolved U, or rather non-lithogenic U, onto particulate matter such as organic matter and metal oxides. The diagenetic remobilization of U is mainly limited to the release of non-lithogenic U through the oxidation of organic matter, and the reduction of Fe-oxides and, to a lesser extent, Mn-oxides. Most diagenetically removed U likely re-precipitates as authigenic U by bacterial mediation in the sediment that is relatively rich in organic carbon. Therefore, little of this U is delivered back to the water column. However, the abundance of refractory Fe-P-phases within the sediments of Lake Baikal may also play an important role in retaining high U contents despite dynamic redox cycling down to a few decimetres below the sediment-water interface. Admittedly, some important questions remain unanswered regarding elevated sedimentary U concentrations in Lake Baikal. The hypothesis presented here, such as the division into three U pools (U_L , U_{NL} and U_{auth}), will have to be tested through a more thorough sampling of lake water and sediments as well as mineralogical studies where possible. But certainly, future research on the global U cycle in the past and present will have to take into account that even well oxygenated environments can act as a sizeable U sink under certain conditions.

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Figure 1

Map of Lake Baikal, Siberia, and its geological setting (modified after a compilation of Parfenov et al., 2003). The yellow circles indicate the coring sites from the field campaign undertaken in 2010 (Och et al., 2012). The terranes are of Archean to Paleozoic age and include various lithologies while the Precambrian/Paleozoic granitoids are the main constituents of the Mongolian-Transbaikalian belt (MTB) which can contain some mafic rocks (Fagel et al., 2007; Jahn et al., 2009; Litvinovsky et al., 2011).

Figure 2

Geochemical profiles of total U, U_{NL} (according to equation 6), total organic carbon (TOC), total sulphur (TS) and Fe/Sc across the sediment cores A to D and the respective pore water profiles of U, U/Sc, Fe and SO_4^{2-} (see supplementary information; Och et al., 2012). Note that the U_{NL} value indicated by the dashed interval at a depth of 15 cm in core C is to be considered with caution since its calculation resulted in a value significantly below zero, possibly due to analytical errors. The oxygenated interval on top of the sediment is shaded blue and the Fe- and Mn-oxide layers are in light and dark grey respectively. The dominant redox processes are simplified on the right according to Och et al. (2012).

Figure 3

Pourbaix diagrams showing the predominant U phases without (a) and with (b) Fe oxide surfaces. For the construction of latter diagram we used 10 g l^{-1} adsorbent with a surface area of 10 g m^{-2} and $7 \cdot 10^{-5} \text{ mol}$ active surface sites g^{-1} and a ionic strength of 10 mmol l^{-1} . Concentrations of dissolved components were $1 \text{ mmol l}^{-1} \text{ Ca}^{2+}$, $2 \text{ mmol l}^{-1} \text{ HCO}_3^-$, and $10^{-7} \text{ mol l}^{-1} \text{ UO}_2^{2+}$. The shaded intervals represent the pH range (Maerki et al., 2006) and pE, based on pore water concentrations of Fe(II) (equation 6), to be expected in Lake Baikal sediments.

Figure 4

The relative distribution of lithogenic U (U_L) and non-lithogenic U (U_{NL}) according to equation (6) across the four cores analyzed in the present study. Note that the fraction of U_L increases throughout the sediment cores, likely due to its more refractory nature. The fraction of authigenic U (U_{auth}) represents U_{NL} formed through early diagenetic processes and is an estimation based on the assumption that U_{NL} formed within the water column is gradually being remobilized in the sediment and the pore water U fluxes (see Fig. 2).

Figure 5

Iron speciation profiles through cores A and C and an interval in core B as well as the relative fractions of the Fe-oxides and Fe(II) phases are shown. Note that Fe(II) concentrations are given in permil.. The total phosphorus contents in cores A and C are shown on the right together with P/Fe ratios. The particulate and pore water U concentrations are from figure 2 and shown here for guidance; the scale reaches from 0 to 25 ppm for concentrations in the sediment and from 0 to 15 $\mu\text{g l}^{-1}$ in the pore water, respectively.

Figure 6

The profiles of $U_{\text{NL-auth}}$ (as estimated from Fig. 4) and TOC within cores A to D and the covariation patterns as well as the trendlines between mass accumulation rates (MARs) of organic carbon (C_{org}) and average C/N ratios.

Figure 1

Figure 2

Figure 3

Figure 4

A

C

B

D

Figure 5

Figure 6

Table 1: Uranium concentrations and fluxes into Lake Baikal via its largest tributaries.

References: ¹ Falkner et al., 1997, * surface water concentration from Falkner et al., 1997, ²

Calculated using data from Bobrov et al., 2001.

Rivers	Dissolved ¹ :			Particulate ² :		
	Flow (10 ¹² kg a ⁻¹)	U (µg l ⁻¹)	U Flux (tons a ⁻¹)	Particle input (10 ⁹ kg a ⁻¹)	U (ppm)	U Input (tons a ⁻¹)
<i>Inflow:</i>						
Selenga	29.1	1.58	46	2.84	6.4	18.15
Barguzin	3.9	0.54	2.1	0.23	3.2	0.73
Upper Angara	8.3	0.17	1.4			
<i>Outflow:</i>						
Angara	58.3	0.47*	27.8*			