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Invited research article

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 O_2 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 $\mu g\ g^{-1}$, 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.

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 ($UO_2(CO_3)_3^{4-}$) with a concentration of around 3.3 $\mu g\ l^{-1}$ (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

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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 μg g^{-1} (Partin et al., 2013). Redox transitions influence the $^{238}U/^{235}U$ 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 (Brennecka 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 μg g^{-1} (Taylor and McLennan, 1995). However, U concentrations of up to 250 μg 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 >20 μg 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 μg 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 km^2 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 km^3 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., 2001; 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 (Fig. 1). Up to nine cores per site were retrieved simultaneously using an uwitec mulitcorer (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 (Fig. 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 11,106–85, Germany) and the pore water