



## Rare earth elements in the sediments of Lake Baikal



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### ABSTRACT

Lake Baikal is the deepest and probably oldest lake on Earth. Its water column is pervasively oxic and sedimentation rates are very low which leads to the formation of a dynamic iron (Fe) and manganese (Mn) enrichment below the Mn(II)/O<sub>2</sub> boundary. These often massive accumulations can be buried within the reducing part of the sediments and give rise to complex and cryptic redox cycles. The mobility of rare earth elements (REEs) is influenced by the dissolution and reduction dynamics of the ferromanganese oxides. The present study offers an overview of the REE chemistry in Lake Baikal and its catchment area and more specifically REE distribution in five 11- to 26-cm-long sediment cores situated across the lake at different water depths. We analysed and discussed normalised REE patterns and their consequential cerium (Ce) anomalies. While particulate REE concentrations are mainly influenced by processes above or near the surface of Lake Baikal, such as the development of a widespread negative Ce anomaly, processes occurring during early diagenesis in the sediment are most reflected in pore water REEs. The dissolution of ferromanganese oxides at the Mn(II)/O<sub>2</sub> boundary remobilizes significant amounts of REE into the pore water whereby some are likely adsorbed onto colloidal Fe oxides. However, besides the tendency of Ce being associated with Mn-oxides, pore water REEs fractionate predominantly around the buried Fe/Mn accumulation where light REEs preferentially adsorb onto Fe-oxides.

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### 1. Introduction

Lake Baikal is situated within the region of Siberia, Russia, and is the deepest, most voluminous and probably the oldest lake on Earth. Because it lies in the tectonic rift zone between Europe and Asia, some researchers consider Lake Baikal as an example for early stage ocean formation (e.g. Crane et al., 1991; Granina et al., 2010). In addition, like most of the ocean, the water column of Lake Baikal is pervasively oxic with a constant chemical composition down to the bottom (Kozhov, 1963; Falkner et al., 1991). Furthermore, primary productivity is limited by phosphate availability causing the oligotrophic character of the lake (Müller et al., 2005). This, combined with very low sedimentation rates (Edgington et al., 1991; Appleby et al., 1998; Vologina and Sturm, 2009; Watanabe et al., 2009; Och et al., 2012), leads oxygen to penetrate deeply into the sediment causing massive iron (Fe) and manganese (Mn) oxide accumulations whereby Fe and Mn concentrations often exceed 10% (of dry bulk sediment; e.g. Granina et al., 2004). These enrichments are involved in a dynamic redox cycling underneath the Mn(II)/O<sub>2</sub> boundary until, because of a yet unexplained process, their reductive dissolution slows down and burial within the anoxic

part of the sediment ensues (Granina et al., 1993; Deike et al., 1997; Granina et al., 2004; Sapota et al., 2006; Och et al., 2012). The burial of Fe- and Mn-oxide layers, however, leads to the emergence of complicated redox interactions throughout the zone of early diagenesis, i.e. the surface sediment, and influences the biogeochemical cycling of trace elements (e.g. Müller et al., 2002), including the rare earth elements (REEs; Owen and Mackin, 1980; Elderfield and Sholkovitz, 1987; De Carlo and Green, 2002; Duncan and Shaw, 2003; Haley et al., 2004; Caetano et al., 2009).

Over the last few decades and in particular after analytical difficulties have been overcome, REEs have gained importance as powerful tracers of chemical processes on the Earth's surface due to their unique geochemical properties. Examples from modern environments include the study of estuaries, ocean circulation and hydrothermal processes (e.g. Klinkhammer et al., 1983; Hoyle et al., 1984; Elderfield et al., 1990; Sholkovitz, 1993; German et al., 1995; Haley et al., 2004). REEs have also been found to be useful and innocuous geochemical analogues for actinide elements (Nugent, 1970; Krauskopf, 1986) and, being critically appraised, can be used for sediment provenance studies (McLennan, 1989; Sholkovitz et al., 1999; Piper and Bau, 2013). The REEs are composed of the 15 metals of the lanthanide series from La to Lu, whereas Pm is not naturally occurring. Even-numbered elements are more abundant than odd-numbered elements (Oddo–Harkins Rule; Schmitt et al., 1963) and hence, each REE is commonly normalised

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to a rock standard in order to obtain a smooth curve from La and Lu (e.g. Piper and Bau, 2013). For the present study, we used the Post-Archean Australian Shale (PAAS; McLennan, 1989). Other reference materials, such as the North American Shale Composite (NASC; Gromet et al., 1984) or the Upper Continental Crust (UCC; Taylor and McLennan, 1995), are also frequently used and generally result in comparable values (Dubinin, 2004; Piper and Bau, 2013). In addition, and in particular for the study of igneous rocks, REE concentrations are also often normalised to chondrite values, which correspond to the inferred composition of the mantle (e.g. Jarvis and Jarvis, 1985).

The REEs form stable trivalent ions of comparable size which leads to very similar physical and chemical properties within the group. This is due to the gradual contraction of ionic radii with increasing atomic number, the so-called lanthanide contraction. Furthermore, the behaviour of REE in the aqueous environment is more significantly governed by electrostatic rather than covalent bonding, whereby electrostatic interactions depend on the ionic radius (e.g. Kim et al., 1991). This can lead to fractionations between light, middle and heavy REEs, for example in estuaries where riverine freshwater mixes with seawater (e.g. Sholkovitz, 1993). However, while most of the REEs remain in the +III oxidation state, Ce(III) can be oxidized to Ce(IV) under typical surface conditions and Eu(III) can be reduced to Eu(II) under extremely reducing conditions and/or high temperature (see text below; Sverjensky, 1984; Bau, 1991).

The fractionation of Ce from the other REE is caused by an oxidation reaction which is enabled under conditions similar to the oxidation of Mn(II) to Mn(IV) (Moffett, 1990, 1994; Bau, 1999). Accordingly, Ce(IV) is less soluble than Ce(III) and can therefore be removed from solution and incorporated into authigenic mineral phases (Goldberg, 1961). To quantitatively assess the extent of the Ce fractionation, the Ce anomaly can be calculated as (e.g. Bau and Dulski, 1996):

$$\text{Ce/Ce}^* = \text{Ce}_{\text{PAAS}} / (0.5\text{La}_{\text{PAAS}} + 0.5\text{Pr}_{\text{PAAS}}). \quad (1)$$

Thereby, the subscript PAAS indicates measured concentration normalised to the corresponding PAAS value. However, caution must be applied when using the Ce anomaly as a tracer for environmental processes as Ce depletion does not solely depend on the redox conditions (German and Elderfield, 1990; Shields and Stille, 2001; Piper and Bau, 2013) but also depend on microbial activity that catalyses the oxidation of Ce(III) (Moffett, 1990), as well as the pH (Brookins, 1989; Tricca et al., 1999; Stille et al., 2003), depth (Piepgras and Jacobsen, 1992; German et al., 1995) and age of the water body (German and Elderfield, 1990). In any case, oxidative removal of Ce from seawater is reported to be ubiquitous throughout the oceans (Klinkhammer et al., 1983; De Baar et al., 1985), while it is relatively rare in shallow coastal marine environments and river water (e.g. Seto and Akagi, 2008).

As mentioned above, one reason why the sediments of Lake Baikal are particularly interesting with regard to their REE chemistry is their close interaction with the biogeochemical cycling of Fe and Mn which mainly consists in the adsorption of REE onto Fe- and Mn-oxide surfaces (Goldberg et al., 1963; Koeppenkastrup and De Carlo, 1992; Bau, 1999; Ohta and Kawabe, 2000, 2001; Quinn et al., 2006; Pourret and Davranche, 2013). As a result, ferromanganese nodules and crusts can be highly enriched in REE (Piper, 1974; Elderfield et al., 1981; De Carlo and McMurtry, 1992; Bau et al., 1996; Piper and Bau, 2013). Therefore, the well-developed Fe- and Mn-oxide layers in the sediments of Lake Baikal offer a prime example to further study the relationship between ferromanganese accumulations and REEs. However, due to the very different composition of lacustrine freshwater compared to seawater, some major differences in REE cycling can be expected, in particular with regard to mechanisms depending on the ionic strength (Sholkovitz, 1993; Coppin et al., 2002).

Based on an extensive dataset of REE concentrations in the sediment and its pore water and aspects of the geo- and hydrodynamics of the

Lake Baikal system, we present a comprehensive study on the REE cycling in Lake Baikal, including REE fractionation from the inflow of its major tributaries to the reducing environment within the sediments. We pay special attention to the pattern of Ce anomalies which are ubiquitous within the lake's sediments and pore waters and investigate how REEs fractionate in concert with the biogeochemical cycling of Fe and Mn. And, due to a relative scarcity of REE studies carried out in lacustrine sediments (Owen and Mackin, 1980; Olivarez et al., 1989; Volkova, 1998; Oliveira et al., 2009) and more specifically Lake Baikal (Tanaka et al., 2007; Baturin and Granina, 2009), we gain a valuable perspective on the REE chemistry in a pristine freshwater environment.

## 2. Lake Baikal, its tributaries and geological setting

Lake Baikal, with a length of 640 km and a volume of 23,600 km<sup>3</sup> is situated on an active continental rift in southeastern Siberia, the Baikal Rift Zone, that separates the Siberian craton in the northwest from the Mongolian–Transbaikalian Belt (MTB) in the southeast (see Fig. 1; Hutchinson et al., 1992; Moore et al., 1997; Logatchev, 2003; Jahn et al., 2009; Mats and Perepelova, 2011). The onset of the rifting can be dated back to the Oligocene (34–23 Ma; Mats and Perepelova, 2011, and references therein) and led to the formation of the deepest and probably the oldest lake on Earth, which is filled with sediments amounting to a thickness of over 7 km, bearing a tremendous archive of past environmental changes (e.g. Deike et al., 1997; Kuzmin et al., 1997; Grachev et al., 1998; Kashiwaya et al., 2001; Prokopenko et al., 2006). The lake remained free of permanent ice cover throughout the Pleistocene epoch (Kashiwaya et al., 2001). However, an ice layer of around 1 m thickness currently prevails during the cold period and starts breaking up in the South Basin in May. The lake remains typically ice-free from June to November. Following the ice break up and snow melt around May, the terrigenous input into the lake firstly increases, but diminishes soon after and returns to very low values (Heim et al., 2005).

Most of Lake Baikal's catchment of about 557,000 km<sup>2</sup> and over 350 tributaries is sparsely populated and hence, suffers little anthropogenic contamination. The total riverine water input to the lake amounts to about 58 km<sup>3</sup> a<sup>-1</sup> (Votintsev et al., 1965; Falkner et al., 1997) whereby 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 75% of the particle load to the lake whereby 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 largest river, the Upper Angara, flows in at the northernmost tip of Lake Baikal and contributes around 20% of the water and 15% of the particle load. The Barguzin River accounts for about 7% of the total riverine input and about 6% of the particle load and drains into the Central Basin.

The composition of the riverine suspended matter greatly differs amongst these three rivers. Whereas the Selenga River is dominated by lithogenic elements, delivering about 80% of all Al entering the lake (Granina et al., 2000), the Barguzin and Upper Angara Rivers have a major impact on the redox-sensitive element budget of the lake. The Upper Angara delivers almost twice as much Fe yearly and the Barguzin supplies more Mn into the lake than the Selenga River (Granina et al., 2000), although the latter exhibits a much more substantial overall sediment discharge (see Table 1). There are no published records on the full REE series in the Baikal tributaries but Granina et al. (2000) reported Ce and Eu riverine fluxes from the Upper Angara that exceed the ones measured in the Selenga River. However, the riverine discharge of elements into the lake varies significantly across the seasons (Heim et al., 2005; see also Zakharova et al., 2005), which influences the REE budget as specifically demonstrated in boreal rivers (Ingri et al., 2000; Stolpe et al., 2013).

While the watershed of the Selenga River accounts for about 80% (c. 450,200 km<sup>2</sup>) of the catchment of Lake Baikal, the Barguzin and

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