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New insights into the formation and burial of Fe/Mn accumulations in Lake Baikal sediments

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ABSTRACT

Lake Baikal is the deepest and oldest lake on Earth. Extraordinary features of the lake are manganese and iron-enriched layers and crusts occurring at different depths within the sediment. They can be broadly subdivided into an upper accumulation at the O_2/Mn(II) redox boundary and one or more layers buried within the reducing part of the sediment. The processes leading to their formation and peculiar distribution within the sediment have remained subject of debate, in particular whether the burial of vast amounts of Mn and Fe-oxides results from a steady-state process or if it is the consequence of singular events, such as changes in sedimentation rate, bottom water oxygen concentrations, or the mass accumulation rate (MAR) of organic carbon (C_{org}), Mn or Fe. We retrieved short cores from the South basin, the North Basin, and Academician Ridge, determined sedimentation rates, contents of C_{org}, Mn and Fe, and estimated pore-water fluxes from concentration profiles of O_2, NO_3^-, Mn(II), Fe(II), SO_4^{2-} and CH_4. A consistent picture emerged from the data showing that the upper Fe/Mn layer formed at the lower end of the oxygen penetration depth as a dynamic pattern, moving upward with the growing sediment. Thereby, reductive dissolution of Mn(IV) occurred at the lower margin. Upward diffusing Mn(II) was oxidized with O_2 forming the upper boundary of the Fe/Mn accumulation. The buried Fe/Mn layers were immobilized within the sediment and underwent slow reductive dissolution mainly driven by the anaerobic oxidation of CH_4. The process leading to the detachment of the 'active' Fe/Mn layer from the top redox interface is not unambiguously clear. However, we suggest 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.

1. Introduction

Lake Baikal is the deepest and most voluminous lake on Earth with a maximum depth of 1637 m and a surface area of 31,700 km^2. Lake Baikal is also very ancient with an estimated age of 30–40 million years, which lead to a sedimentary deposit of over 7 km bearing a tremendous archive of past environmental changes, mainly for the paleoclimate (Kuzmin et al., 1997; Grachev et al., 1998; Kashiwaya et al., 2001). Its size and the fact that it lies in the tectonic rift zone between Europe and Asia have prompted some researchers to consider Lake Baikal as an example for early stage ocean formation (e.g. Granina et al., 2010), and the occurrence of the Baikal freshwater seal as part of a unique and rich biosphere makes this perspective even more palpable. However, these mainly physical characteristics are not the only parameters which make this giant lake 'oceanic' when we consider that the water column is pervasively oxic with a constant chemical composition (Kozhov, 1963; Falkner et al., 1991) down to the bottom with an oxygen penetration depth of more than 5 cm into the sediment (Martin et al., 1998), leading to a dominant oxic stage of diagenesis. Furthermore, primary productivity is limited by phosphate availability causing the oligotrophic character of Lake Baikal (Müller et al., 2005).

However, a striking and rather unique feature of the sedimentary record in Lake Baikal is represented by the formation of iron and manganese layers within the sediment, spreading over large parts of the lake. They occur predominantly as Fe- and Mn-oxides (within this manuscript, the term oxide is used summarily and includes true oxides as well as hydroxides and oxyhydroxides) in distinct layers or accumulations and are found in the deeper plains of the lake basins. The general pattern of such an accumulation zone is always a prominent black layer of Mn-oxide above a thin ochre layer of Fe-oxide. At sites where sedimentation rates are small most often two or even more of these banded layers occur within the top 60 to 80 cm. The upper layer is always right below the O_2/Mn(II) redox boundary

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while the lower one is buried within the reducing, older sediment. Granina et al. (2004) correlated the magnitude and sediment depth of Fe/Mn layers at several sites and estimated their age to be several decades at high sedimentation sites and up to several thousand years at Academician Ridge and the North Basin (Deike et al., 1997; Müller et al., 2002). Ancient relics of such layers and crusts are also found much deeper in the sediment, some at more than 2-m depth, with an estimated age between 65,000 and 85,000 years (Deike et al., 1997; Mats et al., 2000; Granina et al., 2003, 2004). Other Fe- and to a lesser extent Mn-enriched horizons have been described at depths of several hundreds of meters (Sapota et al., 2006).

While the Mn and Fe cycling in the sediments of Lake Baikal certainly exhibits an unusual character, sedimentary succession including intervals strongly enriched in Mn and/or Fe have been found in other lacustrine and marine environments. For example in some settings of the Great Lakes (Rossmann and Callender, 1968; Richardson and Nealson, 1989), Loch Lomond in Scotland (Farmer and Lovell, 1984, 1986), the Arctic Ocean, where they are likely linked to glacial cycles and fluctuations in organic carbon (C_{org}) sedimentation (Gobeil et al., 2001; Katsev et al., 2006; März et al., 2011), and the Amazon deep-sea fan, possibly due to non-steady-state diagenesis involving a decrease in sedimentation and C_{org} accumulation rates (Kasten et al., 1998).

It has been hypothesized that the peculiar character of Mn- and Fe-rich layers in the sediments of Lake Baikal might reflect global paleoclimate changes. Granina et al. (1993) and Deike et al. (1997) proposed that ancient Fe/Mn crusts formed during the transition from glacial to interglacial periods, after high glacial melt–water discharge but before high biological productivity. Other researchers, such as Mats et al. (2000), suggested that some of the buried Fe/Mn crusts might have been submerged by tectonic events and acted as a source for further diagenetic redistribution of Mn and Fe in the sediments.

The generation of the accumulation layers must be the result of a complex interplay of the mass accumulation rate (MAR) of C_{org} (gC m^{-2} y^{-1}), the sedimentation rate (mm y^{-1}), oxygen supply of the bottom water, and the sequence of diagenetic redox reactions and molecular diffusion of substances within the sediment pore water. However, it is still unclear which factors could cause the frequently observed burial of the active layers at the top redox interface.

We discuss in detail the mineralogical–chemical composition of the Fe and Mn phases, the intimately linked diagenetic processes and mechanisms that produced these major metal accumulations in the sediments, quantify fluxes and estimate timescales of their 'lifecycle'. The possible causes for the burial are reviewed and discussed in light of the detailed physical–chemical analysis of five sediment cores from different locations across Lake Baikal.

2. Sampling location

Lake Baikal, with a length of 640 km and a volume of 23,600 km^3 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 fold belt in the southeast (Hutchinson et al., 1992; Moore et al., 1997; Mats and Perepelova, 2011). Lake Baikal can be described as an asymmetric half-graben with steep border-fault margins on the northwestern side and more gradual ramp margins on the southeastern side (e.g. Colman et al., 2003; Vanneste et al., 2003). The onset of the rifting can be dated back to the Oligocene (34–23 Ma) and today stretches over 1600 km from northern Mongolia in the southwest to the Aldan shield (Yakutia) in the northeast (Mats and Perepelova, 2011 and references therein). This 'proto-ocean,' as mentioned in the introduction, is the deepest and probably the oldest lake on Earth and contains the world's largest freshwater resource (~20%; salinity 0.76‰). Most of its catchment of about 540,000 km^2 and over 350 tributaries is sparsely populated and hence, suffers little anthropogenic contamination. 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 southward from the Selenga Delta is about twice as high as that to the north (Granina et al., 2004). Together with the Barguzin and Turka Rivers, these major tributaries contribute 80% of the suspended particles and about 57% of the particulate C_{org} input while the Upper Angara River in the north supplies about 15% of the total suspended sediments entering the lake (Müller et al., 2005). Lake Baikal can be divided into three basins, the Southern Basin, with a maximum depth of 1420 m, the Central Basin, with the greatest depth of 1640 m, and the Northern Basin, with a depth of over 900 m (see Fig. 1; Vologina and Sturm, 2009). The Selenga Delta on top of the Bugul'deika Isthmus separates the Southern Basin from the Central Basin while the Academician Ridge, which rises to a depth of about 250 m, lies between the Central and the North Basin, both elevations being situated on fault-controlled accommodation zones. Large, flat basin plains, permitting undisturbed accumulation of pelagic sediments, form the deepest part of all three basins. However, occasionally occurring slope instabilities generate turbidity currents and trigger the deposition of turbidite layers and the topography of underwater ridges shows unevenly rough surfaces, caused by vertical fault tectonics (Colman et al., 2003; Charlet et al., 2005). The topography of underwater ridges shows unevenly rough surfaces, caused by vertical fault tectonics (Colman et al., 2003; Charlet et al., 2005). The Academician Ridge is isolated from terrigenous sources of particulate material and affected by strong northward directed water currents caused by the local hydrological conditions (e.g. Hohmann et al., 1997). The lake is dimictic whereby the South basin freezes over between January and May and the North Basin between December and June. The spring and autumn overturn and the annual deep-water renewal cause the oligotrophic water column of the lake to be well oxygenated down to the sediment surface (Wüest et al., 2005).

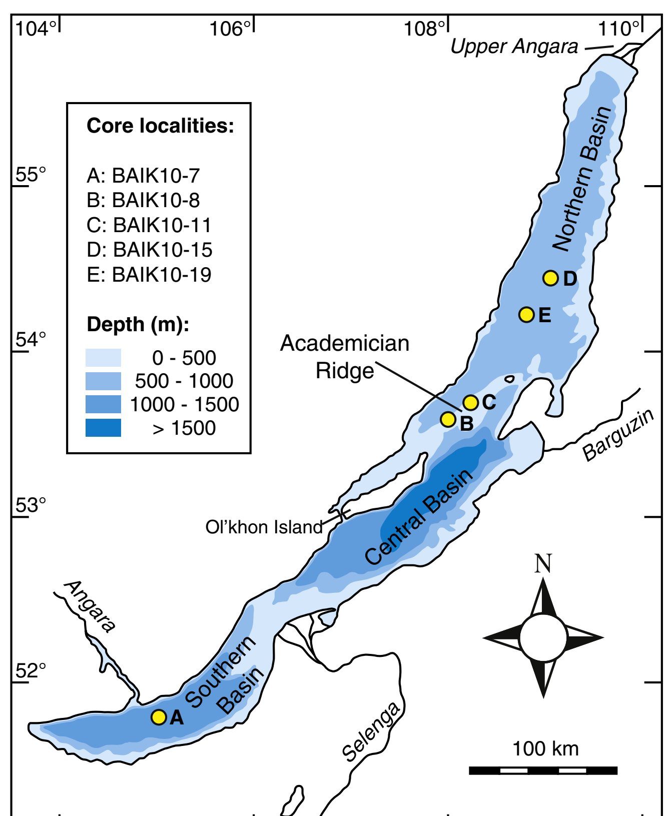

Fig. 1. Map of Lake Baikal in Siberia. Yellow circles depict coring sites.