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Rare Earth Elements in Tributaries of Lake Baikal (Siberia, Russia)

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Abstract

REE dissolved in waters from sixty five sampled tributaries of Lake Baikal show diversity in abundances ($\Sigma\text{REE} = 0.02 - 2.16 \mu\text{g/L}$) and distribution patterns ($[\text{La/Yb}]_{\text{N}} = 0.20-5.58$; $[\text{La/Tb}]_{\text{N}} = 0.30-2.59$). Total REE contents vary seasonally and yearly, while REE patterns remain generally similar. The REE patterns in stream waters correlate with those in the drained rocks and hence, seem to be predominantly controlled by watershed lithology. Rivers having small watersheds around Lake Baikal belong to six lithological provinces with different stream-water REE patterns: the Olkha plateau and the ranges of Primorsky, Baikalsky, Barguzin, Ulan-Burgassy, and Khamar-Daban. The Khamar-Daban province, in turn, is lithologically heterogeneous and comprises four subprovinces with different respective patterns of dissolved REE. Rock-water interaction in subsurface aquifers that feed the Baikal inlets provides much stronger lithological control of REE than the weak interaction of short and rapid streams with rocks on the surface. REE fractionation in stream waters show negative Ce anomalies in almost all samples ($\text{Ce}_{\text{anom}} = 0.12-0.97$), except for those of large rivers (Selenga, Turka, Barguzin, Upper Angara, and Kichera). The reason is that the great length, relatively slow current, and the presence of streambed fine alluvium make the water chemistry more uniform and the REE patterns less dependent on local variations in watershed lithology. The sampled tributaries represent a range of physico-chemical and geomorphological conditions which can be used as reference for calibrations in future studies of sediment sources and, possibly, as a valuable tool for mineral exploration.

Key words: rare earth elements (REE), stream waters chemistry, watershed lithology, Lake Baikal, Siberia, Russia

Highlights:

REE dissolved in waters from sixty five sampled tributaries of Lake Baikal show large differences in abundances ($\Sigma\text{REE} = 0.02 - 2.16 \mu\text{g/L}$) and distribution patterns ($[\text{La/Yb}]_{\text{N}} = 0.20-5.58$; $[\text{La/Tb}]_{\text{N}} = 0.30-2.59$).

The REE patterns in stream waters apparently depend on watershed lithology.

Six lithological provinces with different stream-water REE patterns have been distinguished.

REE patterns in stream waters all contain negative Ce anomalies ($\text{Ce}_{\text{anom}} = 0.12-0.97$), in contrast to patterns found in the large tributaries (Selenga, Turka, Barguzin, Upper Angara, and Kichera).

1. Introduction

Rare earth elements (REE), with their unique chemical properties as a group, have been extensively used as powerful tracers of fundamental geochemical processes in surficial and subsurface waters (Dia et al., 2000; Elderfield, 1990; Goldstein and Jacobsen, 1988; Johannesson et al., 1997; Meybeck, 1987; Négrel et al., 1993; Noack et al., 2014; Sholkovitz, 1995; Sholkovitz et al., 1999; Smedley, 1991; Stille et al., 2006). There are three main criteria for REE suitability as geochemical tracers: (i) their absolute abundances (ii) the degree of fractionation (e.g. $[\text{La/Tb}]_{\text{N}}$ and $[\text{La/Yb}]_{\text{N}}$ ratios), and (iii) anomalies in normalised REE patterns. The latter mainly refers to the cerium anomaly

(Ce_{anom}) that can arise in water because Ce, unlike the other trivalent REE, can easily oxidize to Ce (IV) under normal Earth surface conditions, which is less mobile and more easily adsorbs onto suspended particles (e.g. Bau, 1999; De Baar et al., 1988; De Carlo et al., 1998; Leybourne, Johannesson, 2008; Loges et al., 2012; Ohta, Kawabe, 2001; Pourret et al., 2008; Smedley, 1991).

The presence and distribution patterns of dissolved REE in aquatic systems has been traditionally attributed to weathering of the substratum (e.g., Armand et al., 2015; Aubert et al., 2001; Braun et al., 1998; Dia et al., 2000; Négrel et al., 2000; Tweed et al., 2006; Viers et al., 2000) or to anthropogenic influence (e.g., Hissler et al., 2016; Klaver et al., 2014; Kulaksız and Bau, 2013; Nozaki et al., 2000; Zhang and Liu, 2004). Direct links between the REE patterns of dissolved load and bedrock are poorly manifested in data from streams within large catchments (e.g. Dupré et al., 1996; Elderfield et al., 1990; Gaillardet et al., 1997; Sholkovitz et al., 1999; Viers et al., 1997; Yang et al., 2002; Zhang et al., 1998) because of integrated effects of chemical and physical weathering over vast areas. On the other hand, REE patterns including europium anomalies (Eu_{anom}) in stream waters of small catchments generally correlate well with watershed lithology (e.g. Leybourne and Johannesson, 2008; Steinmann and Stille, 2008; Stille et al., 2006; Tricca et al., 1999). Many recent studies of tropical, boreal, and temperate-climate rivers have clearly demonstrated that REEs are commonly transported in large part along with Fe-rich and/or organic colloids (e.g. Åström and Corin, 2003; Braun et al., 1998; Dupré et al., 1999; Ilina et al., 2016; Ingri et al., 2000; Pokrovsky and Schott, 2002; Pokrovsky et al., 2006; Stolpe et al., 2013; Vasyukova et al., 2010; Viers et al., 1997). REE fractionation in stream waters varies with contents of total organic carbon (TOC), Fe, Mn, and Al, as well as with other physico-chemical parameters such as Eh, pH, and ionic strength (García et al., 2007; Goldstein and Jacobsen, 1988; Keasler and Loveland, 1982; Li and Byrne 1997; Pokrovsky and Schott, 2002; Pourret, 2007; Sholkovitz, 1995; Tricca et al., 1999). The REE behavior in streamwaters also depends on several landscape factors such as topography, climate, and vegetation (Armand et al., 2014; Ilina et al., 2016 and references therein).

Thus, total REE abundances and their distribution in stream waters depend on (1) watershed lithology; (2) stream hydrology; (3) climate; (4) groundwater chemistry and physics (Fe, Mn, Al, and TOC; Eh and pH); landscape (5) and (6) anthropogenic impact. There were attempts to estimate the contributions of specific factors, especially watershed lithology, for relatively small (e.g. Tricca et al., 1999; Vasyukova et al., 2010) or large (e.g. Armand et al., 2014; García et al., 2007; Xu, Han, 2009; Ingri et al., 2000; Pokrovsky et al., 2006) river systems. The tributaries of Lake Baikal appear to be advantageous targets in this respect, for the following reasons: they totally cover an area of 700 × 150 km, but most of them are as short as 10-50 km and have watershed areas limited to a few hundreds of square km; they all occur within the same boreal zone of strongly continental climate and are nearly pristine and thus free from climate and anthropogenic influence; and, most importantly, the Baikal drainage basin has an extremely diverse lithology consisting of Archean to Cenozoic igneous, sedimentary, and metamorphic rocks. Previously, the REE behaviour was investigated only in particulate matter of several large rivers: Selenga and Barguzin by Bobrov et al. (2001) and Selenga, Buguldeika, and Goloustnaya by Lomonosov (2001).

In this paper we report results from sixty five tributaries of Lake Baikal. Sampling was carried out during a brief period of 14 days in 2007, at the average water level and under similar weather conditions, providing a snapshot of dissolved REE inputs. Later, in 2008 through 2015, repeated or multiple sampling of several streams showed stable REE contents in some of them but variable in others.

2. Physiography and geomorphology of the Baikal drainage basin

Fluvial input accounts for more than 70% of dissolved and particulate loads brought into Lake Baikal (Rusinek et al., 2012). The lake receives waters from a 557,000 km² area in southern East Siberia and North Mongolia. However, the catchment area of all the smaller streams, excluding the Selenga, the largest tributary, and the four next largest rivers, is ten times smaller.

The Baikal basin is flanked by the Primorsky and Baikalsky ranges in the west, the Barguzin and Ulan-Burgassy Ranges in the east, and the Khamar-Daban Range in the south; the Sharyzhalgai uplift (Olkha Plateau), an inlier of the Siberian craton basement, borders the lake in the southwest (Fig. 1a). The area is a zone of ongoing tectonic activity, with numerous active faults marked by cold and hot springs.

All Baikal inlets are located within a single climate zone in the continent interior, i.e. highland taiga terrain, and feed from atmospheric precipitation and groundwaters. The groundwater contribution to the budget of different streams varies from over 50% to below 20% (Pissarsky, 1987). The precipitation inputs vary considerably over the area due to elevation contrasts. Mean air temperatures are about -19°C over the cold season (January - February) and about $+11^{\circ}\text{C}$ in August. Most of rivers drain Precambrian and Paleozoic metamorphic, sedimentary, and igneous rocks within small watersheds (Table 1). The small streams, which altogether contribute less than 20% of the total water inflow, flow in the immediate vicinity of Lake Baikal. The five largest rivers (Selenga, Upper Angara, Kichera, Barguzin, and Turka), which catch waters from the great Baikal drainage basin, provide most of the fluvial input: Selenga ($\sim 50\%$), Upper Angara and Kichera together ($\sim 20\%$), Barguzin (7%), and Turka ($\sim 2\%$) (Rusinek et al., 2012).

The rivers with small catchments belong to six provinces with different geomorphological and lithological features (Fig. 1a), and the five large tributaries, though being geographically dispersed, form a separate group (Table 1). The streams of the six watershed provinces originate from 800 to 2800 m high mountains around Lake Baikal:

Olkha Plateau: elevations 800 m asl or lower; rivers are short (mostly 10-20 km), with small watersheds and swampy sources;

Primorsky Range: 800-1000 m asl; rivers are 70-120 km long and drain areas of 1000-2000 km²;

Baikalsky Range: at least 1700 m asl; rivers are mostly 5 to 20 km, with watersheds of a few hundreds of km² or less, except for the northernmost rivers (Kurkula, Slyudyanka, Rel, and Tyia) which form in geomorphological settings similar to those of the Primorsky range;

Barguzin Range: 1800-2100 m asl; river lengths from 20 to 100 km and watershed areas from 60 to 2000 km²;

Ulan-Burgassy Range: 800-1300 m asl, gently dipping; rivers vary in length (10-80 km) and watershed area;

Khamar-Daban Range: 1500-2800 m high; rugged terrain in the west and smoother topography (within 1500 m asl) in the east; rivers are mostly no longer than 50 km except for the Snezhnaya exceeding 100 km; watersheds are mostly from 60 to 900 km², exceeding 1000 km² only in the Snezhnaya and Utulik rivers.

Most of the small Baikal tributaries are very rapid, due to large elevation contrasts, and deposit very little or no fine alluvium, even at their mouths where they slow down.

3. Watershed lithology

The Lake Baikal drainage basin consists of rock complexes of different ages and lithologies.

The watershed provinces differ in lithology (Fig. 2B, Table 1) from one another but can be assumed lithologically homogeneous within their limits, except for the Khamar-Daban province.

Olkha Plateau: the watershed lithology includes Archean and Paleoproterozoic granulite- or less often amphibolite-facies gneisses, and mafic granulites; minor amounts of marbles and quartzites, as well as Early Precambrian granites, numerous pegmatite veins, scarce ultramafic intrusions and mafic dikes of the Sharyzhalgai basement inlier (Melnikov et al., 1994).

Primorsky Range: Paleoproterozoic metamorphic clastic sediments, craton-margin granites (Primorsky complex), and the Neoproterozoic clastic and carbonate sediments of the Baikal Group (Melnikov et al., 1994). Carbonates enclose phosphorite lenses and bear complex-ore mineralization. The Goloustnaya River in the southern part of the province drains mostly Neoproterozoic rocks while the Buguldeika, Sarma, and Anga in its north flow through Paleoproterozoic rocks. The Early

Precambrian Sharyzhalgai rocks are exposed in the bank of the Kotinka River in the southern end of the range, and Mesozoic conglomerates crop out a short distance away.

Baikalsky Range: mainly felsic, mafic and less often intermediate rocks of the Paleoproterozoic North Baikal volcano-plutonic belt (Donskaya et al., 2008, 2009). The Kurkula, Slyudyanka, Rel, and Tyia rivers in the northern part of the range drain mainly Paleoproterozoic granites and amphibolite-facies volcanoclastics, as well as low-grade Neoproterozoic clastic-carbonate sediments and volcanoclastic rocks of the Baikal-Muya terrane. Neoproterozoic carbonates host Pb-Zn mineralization (Sklyarov et al., 2015), as well as sporadic lenses or thin layers of phosphorites.

Unlike the western shore of Lake Baikal where Precambrian rocks prevail, the lithology of the eastern shore mostly consists of Late Paleozoic igneous rocks: the Anga-Vitim granite batholith and co-magmatic volcanics (Litvinovsky et al., 2011; Tsygankov et al., 2010). Other rocks are much less abundant or almost lacking from the *Barguzin Range* watershed. The same Late Paleozoic granitoids are found in the *Ulan-Burgassy Range* as well, while Early Paleozoic gneisses, amphibolites, and marbles of the Olkhon terrane occur along the Baikal shore.

The Khamar-Daban Range comprises several lithological subprovinces (Fig. 2): (I) mostly Late Paleozoic granites; less abundant Early Paleozoic granites and gabbro; the Early Cretaceous Selenga metamorphic core complex (MCC) (Litvinovsky et al., 2011; Mazukabzov et al., 2011); (II) the detachment zone of the Selenga MCC; (III) clastic and volcanic rocks metamorphosed mostly in the Early Paleozoic; less abundant Early Paleozoic granites and gabbro (Skol'nik et al., 2011, 2016; Vasil'ev et al., 1981); (IV) mainly clastic and carbonate sediments metamorphosed in high-grade (granulite- and amphibolite) facies in the Early Paleozoic in the westernmost part (Melnikov et al., 1994; Vasil'ev et al., 1981). Carbonate sediments host apatite-rich beds of metamorphic phosphorites (Vasil'ev et al., 1981).

Cenozoic alluvium reaches notable amounts only in the watersheds of large rivers (Selenga, Barguzin, Upper Angara, and Kichera). Quaternary fluvioglacial lacustrine and palustrine deposits occur in the lower reaches of rivers in the Barguzin and Ulan-Burgassy provinces, as well as some rivers in the eastern Khamar-Daban province.

4. Sampling and analytical methods

Water samples from sixty five tributaries of Lake Baikal (Fig. 1A; Table 1) were collected between the 10th and 23rd July of 2007. In some rivers, another sampling campaign was carried out at a later time (2013, 2014). The streams were sampled in their lowermost reaches, in places of most rapid flow, from water depths 0.2 – 0.5 m.

Water temperature, pH, Eh, and dissolved oxygen were taken directly while sampling in the field. Temperature and pH were measured using an *HI – 8314 HANNA* pH/mV/C° meter with an HI 1230 plastic pH electrode, to the precision 0.02 (pH) and 0.1 (T), pre-calibrated against pH = 6.86 and 9.18 waters. Dissolved oxygen and oxygen saturation were measured with an *Oakton DO – 100* meter with a resolution of 0.01 mg/L and 1σ error ± 1.5%.

Major anions (HCO_3^- , Cl^- , SO_4^{2-} , F^-) in water samples collected into 1.5 L plastic bottles were determined at the Chemical Laboratory of the Institute of Geochemistry (Irkutsk) following the standard analytical procedures for fresh water (Lurje, 1971): colorimetry for SiO_2 and F^- , titration for $\text{HCO}_3^- + \text{CO}_3^{2-}$ (Alk) and Cl^- , and turbimetry for SO_4^{2-} . Unfiltered samples were collected for organic carbon measurements into glass bottles, and were analyzed on a *DRB 200* reactor and a *HACH DR/890* colorimeter (USA).

For analysis of element concentrations, water was collected into 50 ml HDPE sample bottles, pre-cleaned in 0.1M HCl and rinsed in *Milli-Q* deionized water. The sampled water was filtered in the field through *Sartorius Minisart* acetate-cellulose syringe filters, 0.45 μm pore-size, 25 mm in diameter. The bottled samples were immediately acidified with *MERK* ultrapure nitric acid (to pH = 1.5), sealed with *Parafilm* paraffin and stored cool (at 4°C) for three weeks before analysis. Possible contamination during sampling and filtering was checked against blank samples preconditioned using the standard

procedure. The concentrations of all elements in the replica samples were either below or commensurate with the detection limits.

The trace-element compositions of stream waters were determined by ICP-MS on a high-resolution *Finnigan Element-2* mass spectrometer at the Baikal Shared Analytical Center (Irkutsk). The spectrometer was calibrated using SPEX CLMS-1, 2, 3 multielement standard solutions (USA). The instrument time drift and signal fluctuations during spectrometry were monitored against an internal standard (Rh with the final concentration of 2 µg/L). The spectra were recorded at low (LR-300), medium (MR-4000), and high (HR-10000) nominal mass $M/\Delta M$ resolutions depending on interference of the element spectra. The following isotopes of REE were monitored during the ICP-MS measurement in order to minimize isobaric interferences: ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{162}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{171}Yb , ^{175}Lu . All solutions were made using deionized water ($18.2\text{ M}\Omega\text{ cm}^{-1}$) purified with a *Millipore-ELIX-3* system (France).

The analytical results were checked against NIST CertiPUR IQC-026, X, XII certified multi-element standard solutions (USA), and against standard samples for REE. Our measurements were in good agreement with the certified values, generally within an error of <10 % (except for less accurate Tm and Lu determinations with 23% and 25% errors, respectively).

5. Results

5.1. Major ions

The measured parameters (pH, $T^{\circ}\text{C}$, O_2), TOC, and contents of major and some trace elements are summarized in Table 1S (see supplementary information). All water samples are transparent, oxygenated, and mainly have a Ca bicarbonate chemistry, except for those of three streams flowing from the Baikalsky Range foothills (Elokhin, Small Cheremshan, and Big Cheremshan) where SO_4^{2-} constitutes 70-90 % of total anions. The relative percentages of SO_4^{2-} are also high in some streams in the Khamar-Daban province (Pereyomnaya, Anosovka, Vydrennaya (50-60%) and Osinovka (75%) rivers). The contents of Cl^- ions do not exceed 1.62 mg/l. The cations are mostly Ca^{2+} (from 44 to 85%). Some streams flowing from the Baikalsky and Primorsky ranges have highly magnesian waters: 40-50% and 30-40%, respectively. The concentrations of Na and K ions are, respectively, in the ranges 0.34 – 5.36 mg/l and 0.11 – 1.67 mg/l. The major-ion compositions we obtained for the sampled stream waters generally agree with the earlier data of years-long continuous monitoring synthesized by Votintsev et al. (1965). The contents of total dissolved solids (TDS) are the lowest (12 – 27 mg/l) in stream waters of the Baikalsky Range province and the highest (87–279 mg/l) in those sourced at the Primorsky Range foothills. Total organic carbon (TOC) reaches 9.5-19.7 mg/l only in streams of the Olkha plateau but is within 1.5 – 4.8 mg/l in all other samples, which is close to that in the Baikal water: 2.86 - 3.46 mg/l (Tarasova and Mescherikova, 1992).

The measured pH values are in the range 7.1 – 8.6 in most of water samples and slightly below 7 in those of few streams that drain granitic terrains (the Angara-Vitim batholith and granites of the Khamar-Daban Range).

5.2. Rare earth elements

REE abundances and fractionation patterns recorded in the $[\text{La}/\text{Yb}]_{\text{N}}$, $[\text{Tb}/\text{Yb}]_{\text{N}}$, and $[\text{La}/\text{Tb}]_{\text{N}}$ as well as Ce and Eu anomalies ($\text{Ce}_{\text{anom}} = 2(\text{Ce}/\text{Ce}^*)/(\text{La}/\text{La}^* + \text{Pr}/\text{Pr}^*)$ and $\text{Eu}_{\text{anom}} = 2(\text{Eu}/\text{Eu}^*)/(\text{Sm}/\text{Sm}^* + \text{Gd}/\text{Gd}^*)$), where Ce^* , La^* , Pr^* , Eu^* , Sm^* , and Gd^* represent the content of the respective REE in Post-Archean Australian Shale (PAAS) (Taylor and McLennan, 1985)) in the sampled stream waters are listed in Table 2S (see supplementary information).

REE abundances in the Baikal tributaries vary from 0.02 to 2.16 µg/L. As noted above, the sampled streams belong to six provinces while the *five large rivers* Selenga, Barguzin, Upper Angara, Kichera, and Turka jointly form a separate (seventh) group of the great Baikal catchment occupying 90% of the total watershed area. REE patterns in the Selenga, the largest tributary, are similar to those

in the Amazon River and in some large rivers worldwide (Fig. 2). In general, while the large rivers of the World show a wide variability in REE contents (see Fig. 2b), they all display a relative enrichment in heavy REE (HREE). The Selenga sample shows a minor negative Ce anomaly ($Ce_{anom} = 0.84$), a positive Eu anomaly ($Eu_{anom} = 1.18$), and light REE (LREE) depletion ($[La/Yb]_N = 0.73$). The negative Ce anomaly is more prominent in the other large rivers ($Ce_{anom} = 0.68-0.88$) and the positive Eu anomaly reaches 1.40 in two northern streams, while total REE contents are two or three times higher than in the Selenga River. The REE patterns of these rivers show minor HREE depletion, with $[La/Yb]_N = 1.31-2.47$.

The total REE contents and patterns, as well as some associated characteristics in the stream waters of the six provinces, can be summarized as follows.

Olkha Plateau: REE abundances and patterns are similar in all samples (Tables 3, Fig. 3A). The water of these small rivers is rich in organic matter and shows elevated Σ REE (0.85 $\mu\text{g/L}$ on average, Table 2); the REE patterns are fractionated, with LREE depletion ($[La/Tb]_N = 0.64$); negative Ce anomaly ($Ce_{anom} = 0.66$ on average) and a minor positive Eu anomaly ($Eu_{anom} = 1.20$).

Primorsky Range: generally low REE contents (Σ REE = 0.29 $\mu\text{g/L}$ on average, Table 2) and three subgroups with different REE patterns (Fig. 3B). Samples from the Kotinka River flowing from Mesozoic conglomerates in the south of the province have the highest REE abundances (0.54 $\mu\text{g/L}$), a prominent negative Eu anomaly ($Eu_{anom} = 0.77$), and a slight HREE depletion ($[La/Yb]_N = 1.84$). The samples of the Goloustnaya River, which drains Neoproterozoic clastic and carbonate rocks, show minor HREE depletion, well pronounced middle REE (MREE) enrichment ($[La/Tb]_N = 0.64$, $[Tb/Yb]_N = 1.30$), and weak negative Ce and weak positive Eu anomalies ($Ce_{anom} = 0.83$, $Eu_{anom} = 1.24$). Three rivers that drain Early Proterozoic granite and metamorphic clastic sediments in the northern part of the province show relatively low REE abundances of 0.13-0.31 $\mu\text{g/L}$, LREE depletion ($[La/Yb]_N = 0.57-1.01$), a prominent Ce anomaly ($Ce_{anom} = 0.41-0.72$) and a weak positive Eu anomaly ($Eu_{anom} = 1.15-1.23$), except in the Anga River, where Eu_{anom} is 0.50.

REE abundances in the stream-water samples from the *Baikalsky Range* province vary from 0.08 to 2.16 $\mu\text{g/L}$ (Fig. 3C) and show prominent negative anomalies in Ce and Eu ($Ce_{anom} = 0.35$, $Eu_{anom} = 0.61$ on average, Table 2). The REE patterns fall into two groups: samples from four large rivers in the north of the province show highest REE contents (0.89-2.16 $\mu\text{g/L}$), minor HREE depletion ($[La/Yb]_N = 1.42-2.39$), and prominent negative Ce and Eu anomalies. The other group is more representative, with REE abundances in the range of 0.08 to 0.69 $\mu\text{g/L}$. The samples also show Ce and Eu depletion, but MREE are often relatively high, unlike the former group, especially in the Big Cheremshan River ($[La/Tb]_N = 0.54$); the $[La/Yb]_N$ ratios are from 0.68 to 2.08.

REE concentrations in samples from the *Barguzin Range* province mainly range from 0.05 to 0.39 $\mu\text{g/L}$, with a maximum of up to 0.86 $\mu\text{g/L}$ in the northernmost Frolikha river (Fig. 3D). The REE patterns show HREE depletion ($[La/Yb]_N = 1.02-5.12$) and most of the streams have negative Ce (except for the Tompuda and the Big Chivyrkui) and positive Eu anomalies ($Eu_{anom} = 1.18-1.45$).

Stream waters from the *Ulan-Burgassy Range* province contain 0.08 to 0.42 $\mu\text{g/L}$ REE and have relatively flat REE patterns, slightly depleted in LREE, and no or very small Ce or Eu anomalies (Fig. 3E).

Stream-water samples from the Khamar-Daban province, which show the greatest diversity in REE abundances and distribution patterns, fall into four geographically dispersed subgroups. Subgroup I (easternmost): highly variable REE contents (0.08-0.26 $\mu\text{g/L}$), more or less prominent negative Ce anomalies, and a slight LREE depletion, no Eu anomalies (Fig. 3F). Subgroup II (three rivers): relatively low REE contents of 0.06-0.21 $\mu\text{g/L}$; strong LREE depletion, like in the samples from the Olkha plateau, and moderate MREE enrichment; negative Ce and positive Eu anomalies (Fig. 3G). Subgroup III: prominent MREE enrichment ($[La/Tb]_N = 0.35$ in average) at generally high REE abundances (0.38-1.33 $\mu\text{g/L}$) (Fig. 3H). Subgroup IV (westernmost): very low REE concentrations (0.02-0.12 $\mu\text{g/L}$), prominent LREE depletion ($[La/Yb]_N = 0.20-0.93$), and a prominent negative Ce anomaly ($Ce_{anom} = 0.38$); MREE enrichment in the Kultuchnaya and Bezmyannaya rivers (Fig. 3J). Reliable estimation of Eu contents from Ba/Eu concentration ratios is impossible for waters of this

subgroup because of Ba dioxide interference, with the exception of the Kultuchnaya and Bezmyannaya rivers.

6. Discussion

The behavior of REE in stream water depends on many factors, including pH and contents of Fe, Al, Mn and TOC (e.g. Li, Byrne, 1997; Sholkovitz, 1995; Tricca et al., 1999). Although no linear correlation was observed, stream samples with the highest concentrations of dissolved REE show the lowest salinity (TDS) and vice versa (Fig. 4A). No correlation was found between REE concentrations and pH (Fig. 4B), though the highest REE concentrations (up to 2.16 $\mu\text{g/L}$) most often occur at a circumneutral pH of about 7 to 8. This trend misfits the general trend of decrease of REE content in groundwaters and streams in the pH = 4-8 interval as reported by Noack et al. (2014).

Dissolved REE migrate in streams mainly as organic or Fe-rich inorganic colloids (e.g. Ingri et al., 2000; Pokrovsky et al., 2006; Sholkovitz, 1995) and are thus expected to increase proportionally to iron, while greater affinity of LREE (compared to HREE) to the 0-donor surface of colloidal particles should lead to higher La/Yb ratios. In boreal rivers REEs are colloiddally dominated (more than 80 %) elements that exhibit similar size fractionation in all studied settings (Ilina et al., 2016; Vasyukova et al., 2010). Indeed, REE abundances in the Baikal Lake tributaries tend to increase with higher iron concentrations in the water samples (Fig. 4C), but the data points scatter considerably, except for good positive correlations in the large rivers and streams that drain Primorsky and Ulan-Burgassy ridges, and Olkha Plateau. The correlation is more evident between dissolved REE and Al contents (Fig. 4D). When it comes to REE fractionation, however, the greater affinity of the LREE to iron particles is better expressed in the particulate load of the rivers, i.e. particles $> 0.45\mu\text{m}$, and the surface sediments of Lake Baikal (Och et al., 2014).

The degree of REE fractionation ($[\text{La/Yb}]_N$ ratios) does not correlate with the other main stream water parameters, except for correlation with iron contents in the large rivers (Fig. 4E). Note that REE concentrations in the Baikal tributaries vary as a function of season and year. The difference may reach ten times, such as in the Tompuda River (Barguzin Range province), or almost zero, as in the Snezhnaya River from the Khamar-Daban mountains (Fig. 3). However, the REE patterns remain similar irrespective of the total concentrations, which may depend on water abundance at the time of sampling. García et al. (2007) reported that REE concentrations measured in springs and stream waters in mountains of Argentina depended on atmospheric precipitation (rainfall volume and seasonal distribution); they observed an inverse linear correlation between dissolved REE concentration and monthly precipitation, while the shapes of REE patterns did not change much. The same dependence was reported for the Amazon River and its tributaries (Barroux et al., 2006), where differences in REE concentrations may differ for an order of magnitude in different seasons, but REE patterns are similar.

The effect of topography (e.g. Armand et al., 2014) or landscape (e.g. Vasyukova et al., 2010) on REE behavior in the tributaries of the Baikal Lake is poorly constrained for two reasons: i) the landscape conditions of the respective watersheds are relatively similar; ii) all rivers were sampled only in their mouth on the same elevation of the Baikal Lake level (~ 460 m asl.). REE contents, $[\text{La/Yb}]_N$, $[\text{La/Yb}]_N$ or Ce_{anom} do not correlate with the river length, but Ce_{anom} generally increase with elevation of the provinces. In the large rivers (Selenga, Barguzin, V. Angara, Kichera, Turka) and streams of Olkha Plateau, Ulan-Burgassy, Primorsky ranges and lowest eastern part of the Khamar-Daban Range (subprovince I) (800-1500 asl) average Ce_{anom} varies from 0,66 to 0,85 (table 2), being more prominent in the Baikalsky, Barguzin and Khamar-Daban (western part) ranges (1800-2800 m asl) ($\text{Ce}_{\text{anom}} = 0,35\text{-}0,48$). We have no explanation for this phenomenon, which is in disagreement to the good correlation of Ce_{anom} and a distance from outlet in the Garonne and Dordogne river systems (Armand et al., 2014). The explanation by Armand et al., (2014): "...the likely reason for the Ce anomaly amplitude gradual reduction observed mainly relies on the fact that, in low permeability aquifers, water table generally reaches organic soil horizons in bottomland domains, thus allowing incorporation of large quantities of organic colloids in the aquifer bottomland part. This feature is not

seen in the aquifer upland part where the water table always remains far below the upper, organic-rich soil horizons.” (P. 140) does not apply in our case.

The fractionation of REE in the stream waters of the Baikal area depends most strongly on watershed lithology. REE patterns in the dissolved riverine load generally correlate with the main lithological units, and show a well traceable, mixed signal where the provinces are lithologically heterogeneous. This similarity is especially spectacular in the Olkha Plateau, in the Baikalsky and Barguzin ranges, and in the western Khamar-Daban province (Fig. 3).

Gneisses and mafic granulites, which are the predominant lithologies in the Precambrian Sharyzhalgai uplift (Olkha Plateau), show flat normalized REE patterns (Fig. 3A) and moderate LREE depletion. The REE patterns of waters that drain these rocks are similar, but with more prominent LREE depletion; both rocks and stream waters show small Eu anomalies.

The Baikal tributaries that flow across the Primorsky Range originate west of it, and the trace-element composition of water in the province does not show significant correlation with that of the rocks (Fig. 3B). The REE pattern with MREE enrichment in the Goloustnaya water may be due to the presence of phosphorite lenses in the Neoproterozoic Baikal Group sediments (Banfield and Eggleton, 1989; Chaïrat et al., 2007; Hannigan and Sholkovitz, 2001; Jonasson et al., 1985; Leybourne and Johannesson, 2008; Liu and Byrne, 1997). However, it is difficult to compare the REE patterns of stream waters and rocks in this part of the province because the geochemistry of Paleoproterozoic metamorphic clastic sediments remains poorly constrained.

The Baikalsky Range, on the other hand, appears to be a perfect model site to study the watershed lithology effects on the REE compositions of stream waters. All Baikal tributaries flowing from the range (except for four northernmost rivers) are no longer than 20 km and have small and lithologically more or less uniform watersheds. Minor lithological heterogeneities only highlight the influence of the lithology on dissolved load. The area is composed mainly of Paleoproterozoic volcanic rocks, of which most are felsic and rich in alkalis (Donskaya et al., 2008). The rocks show REE patterns with slight LREE enrichment and a prominent negative Eu anomaly, similar to the patterns in stream waters (Fig. 3C). On the other hand, waters in some rivers are enriched in MREE, which may occur due to leaching of apatite (Hannigan and Sholkovitz, 2001). This very part of the Baikalsky Range comprises Neoproterozoic clastics and carbonates of the Baikal Group which enclose lenses and thin beds of phosphorites (Stanevich et al., 2012). Note that a strip of these rocks runs almost all along the western Baikal shore but outside the watershed, except for the southern part of the Primorsky Range where the REE patterns of the Goloustnaya River show the expected MREE enrichment.

Special attention was directed towards the REE behavior during transport in stream waters of the Big Cheremshan River in the Baikalsky Range, which remained beyond our attention during the mass sampling of tributaries in 2007. The reason was, that the river split into three arms in the lower reaches and seemed to have a low discharge, but the water was clear. However, sampling in 2012 showed enrichment in REE and other elements higher than in other rivers of the Baikalsky Range, and the water looked whitish. A hunter who lived near the B. Cheremshan mouth told us that the river had changed colour in 2011. Later, in 2013, we discovered and sampled a cold acid spring in the middle reaches, which contributed about 20% to the river water and was responsible for its unusual color and chemistry (Sklyarov et al., 2015).

The Milky Spring (called so for its turbid whitish water) has unusual Mg-Ca-SO₄ major-element chemistry, low pH (3.7 at 2013 year), and Al, Mn, Ni, Co, Zn, Y, and REE enrichments (Table 3). This particular chemistry may result from reaction of groundwater with a buried Pb-Zn-sulfide deposit, like the one explored 20 km far from the spring but outside the watershed (Sklyarov et al., 2015).

Additionally, we sampled the river water at different distances from the spring (Ch-1, Ch-2, Ch-3, Ch-5) and cold spring at lower reaches of the river (Ch-9), but only filtered water samples were analyzed. Sampling in 2014 revealed notable changes in the river water salinity and other physico-chemical parameters (see Table 2, with data of both 2013 and 2014, and Fig. 5, with only the REE patterns of 2014 when both filtered and unfiltered water samples were used for analyses). The B. Cheremshan water upstream of the spring shows well-pronounced MREE enrichment and very small Ce and Eu anomalies (Ch1 in Fig. 5). The REE concentration in the Milky Spring (ICh-6) water is two

orders of magnitude higher than in the B. Cheremshan (132 against 1.2 $\mu\text{g/L}$, respectively), but the REE patterns in the spring and river waters are similar. Most of the REE must be dissolved, i.e. $< 45 \mu\text{m}$, judging by similarity of their concentrations in filtered and unfiltered water samples (Ch2 in Fig. 5), but they adsorb onto suspended particles 200 m downstream, where the spring and river waters mix up (Fig. 5). Already 800 m downstream of the spring, the concentration of dissolved REE decreases markedly and approaches that for stream water prior to the spring inlet and in the mouth. However, the contents of REE in particulate matter remain high (see Table 2). Note also that the effect of the acid spring on the stream-water REE patterns shows up as only a minor Ce depletion relative to other streams within the Baikalsky Range (Fig. 3C).

The behavior of Eu in different segments of the B. Cheremshan River provides another proof for the lithology control of water composition. The negative Eu anomaly is lacking in head waters draining volcanic rocks with REE patterns free from this anomaly (Donskaya et al., 2008). However, it becomes prominent in the lower reaches after the inflow of several small streams (Ch-9 is one of them) where the watershed is composed of Mesoarchean granites with a negative Eu anomaly (Donskaya et al., 2009). The same trends are well pronounced in the REE patterns of water samples from a tributary of the Big Cheremshan.

Stream-water REE patterns in the Barguzin Range province obviously bear the imprints of the Angara-Vitim batholith composed of granite, syenite, monzonite, and less abundant gabbro (Litvinovsky et al., 2011; Tsygankov et al., 2010). However, minor HREE depletion and a positive Eu anomaly make them rather similar to the Chivyrkui granite, the dominant lithology in this part of the Barguzin Range (Fig. 3D).

The Angara-Vitim granitoids are also present in the Ulan-Burgassy province, which comprises metamorphic rocks of the Olkhon terrane of yet unknown geochemistry. The REE patterns of stream waters from the Barguzin and Ulan-Burgassy provinces differ, for two possible reasons: either they are controlled by watershed lithology but some additional lithological inputs remain unknown for the lack of data, or there are other controls as well. This part of the Baikal area has the flattest topography and, as a consequence, the streams are slower and deposit fine alluvium in their lower reaches. The REE patterns of all stream waters in the Ulan-Burgassy province are similar to those of the Turka and other large tributaries of the great Baikal catchment. Thus, low-energy fluid dynamics may mitigate the REE distribution in streams relative to the drained rocks.

The stream-water REE patterns are the most diverse in the Khamar-Daban province with its four subprovinces (Fig. 1). REE patterns in samples from the easternmost subprovince I are similar to those in the Ulan-Burgassy area, and their correlation with poorly known lithology is problematic as well. The lithology of the subprovince also includes the Angara-Vitim granitoids, with their REE patterns different from the stream-water ones, as well as the stress-metamorphic rocks of the Selenga metamorphic core complex (MCC), which have not been studied in terms of geochemistry.

Three rivers of subprovince II flow from different sides of a bare mountain and have uncommon sulfate-rich water chemistry and REE patterns with prominent LREE depletion. The geochemistry of the rocks in this watershed is likewise poorly constrained, although sulfide Au-Ag mineralization, responsible for the sulfate-rich stream-water with peculiar REE patterns, may be expected within the inferred detachment zone of the Selenga MCC by analogy with other such zones (e.g. Yang et al., 2014). The local geology also includes Neoproterozoic metamorphic mafic and intermediate rocks with REE patterns similar to those of stream waters sampled farther in the west.

Stream waters in the subprovince III farther westward have well pronounced MREE enrichment, presumably due to interaction with apatite (Hannigan and Sholkovitz, 2001). This part of the Khamar-Daban Range is mainly composed of metamorphosed clastic and carbonate rocks with meta-phosphorite interbeds. Meanwhile, the Slyudyanka River of the westernmost subprovince IV drains a thick bed of apatite-bearing rocks in its lower reaches (Vasil'ev et al., 1881), but its water paradoxically lacks MREE enrichment. Therefore, stream waters appear not to interact much with rocks on the surface but rather to correlate geochemically with feeding groundwaters. This hypothesis applies to rapid mountain streams which lack fine alluvium in the lower reaches. MREE enrichment is

restricted to the Kultuchnaya River samples, while the REE composition of stream waters generally correlates with that of metamorphosed sandstones and amphibolites.

7. Conclusions

The tributaries of Lake Baikal demonstrate a large diversity in total abundances (0.05-2.16 µg/L) and fractionation ($[La/Yb]_N = 0.20-5.58$) of REE. Total REE contents differ seasonally and yearly, while the REE patterns remain more or less stable.

The REE patterns of stream waters are mainly controlled by watershed lithology and form six groups according to six lithological provinces: the Olkha Plateau and the Primorsky, Baikalsky, Barguzin, Ulan-Burgassy, and Khamar-Daban ranges. The Khamar-Daban province is lithologically heterogeneous and comprises four subprovinces with different stream-water REE patterns, respectively.

Waters in short and rapid streams, which lack fine alluvium even in the lower reaches, interact only weakly with rocks on the surface, and the lithological control of their REE composition is rather due to rock-water interaction in the feeding subsurface aquifers.

REE fractionation shows up only as Ce depletion in almost all stream-water samples ($Ce_{anom} = 0.12-0.97$), except for those of large tributaries (Selenga, Turka, Barguzin, Upper Angara, and Kichera). The reason of the exception is that the greater length, relatively slow current, and the presence of fine-grained streambed alluvium make the water composition more uniform and the REE patterns more similar to one another and less strongly dependent on local variations in watershed lithology.

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Figure captions

Fig. 1. Location map of sampled streams (numbers 1 through 60 around Lake Baikal (A) and watershed lithology (B). See Table 1 for river names corresponding to the numbers.

Fig. 2. REE in large tributaries of Lake Baikal (a) and some large rivers of the World (b). Data on REE contents for Amazon River after Barroux et al. (2006) and World rivers after Gaillardet et al., (2014), Tepe and Bau (2015) and references therein.

Fig. 3. REE in stream waters compared to the rocks of the respective watersheds.

Data on REE in solid rocks after Donskaya et al., 2005; Turkina et al., 2009 (a); Savel'eva, Bazarova, 2012 (b); Donskaya et al., 2008, 2009 (c); Litvinovsky et al., 2011; Tsygankov et al., 2007, 2010; (d); Litvinovsky et al., 2011 (e); Kovach et al., 2013; Litvinovsky et al., 2011; Shkol'nik et al., 2011, 2016 (f-j).

Fig. 4. REE concentrations as a function of salinity (a), pH (b), and contents of Fe (c) and Al (d); and $[La/Y]_N$ ratio as a function of contents of Fe (e) and Al (f).

Shaded area in (b) for groundwaters after Noack et al. (2014).

Fig. 5. Geology of B. Cheremshan watershed (A) and REE patterns of Milky Spring and B. Cheremshan River waters (B).

f = filtered, n/f = non-filtered. Open circle marks location of Milky Spring; black circles are sampling sites in B. Cheremshan River. Ch-1, Ch-2, Ch-5 are from B. Cheremshan River; ICh-6 is from Milky Spring, and Ch-9 is from cold spring.

Table 1. Synthesis of data from tributaries of Lake Baikal. Numbers in the first column correspond to numbers in Fig. 1A.

Near Baikal mountains	River	№ Sample	L river (km)	Bedrock lithology
Large Baikal tributaries	Selenga		1024	mixture
	Barguzin		480	
	V. Angara		438	
	Kichera		126	
	Turka		272	
Olkha Plateau	Angasolka	1	13	Early Precambrian gneisses, mafic granulite, enderbite and granites of the margin of the Siberian craton
	B.Krutaia Guba	2	17	
	Shabartuy	3	14	
	Marituy	4	5	
	B.Polovinnaya	5	44	
	B.Shumikha	6	13	
	Baranchiki	7	8	
Primorsky Range	Kotinka	8	6	Early Precambrian rocks (see above) and Jurassic conglomerate
	Goloustnaya	9	122	Late Precambrian terrigenous and carbonate rocks of the Baikal series
	Buguldeika	10	78	Late Precambrian terrigenous and carbonate rocks of the Baikal series, Lower Proterozoic metasedimentary rocks and rapakivi granite of the margin of the Siberian craton
	Anga	11	99	
	Sarma	12	66	
Baikalsky Range	Zama	13	15	Paleoproterozoic metasedimentary rocks of the Sarma series (upper reaches), Early Paleozoic high grade metamorphic rocks (gneiss, mafic granulite, marbles) of the Olkhon terrane
	Rity	14	18	Paleoproterozoic metasedimentary rocks of the Sarma series
	Zavorotnay	15	10	Mainly felsic, mafic and less often intermediate volcanic rocks, volcanoclastic sandstones and gravelite of the Paleoproterozoic North Baikal volcano-plutonic belt. Neoproterozoic terrigenous and carbonate rocks of the Baikal series. Archean gneissic granites (lower reaches of B. Cheremshan and Khibelen rivers)
	Ledinaya	16	5	
	Elokhin	17	8	
	M.Chерemshan	18	5	
	B. Cheremshan	19	10	
	Khibelen	20	7	
	Molokon	21	17	
	Kurkula	22	30	Mainly felsic, mafic and less often intermediate volcanic rocks, volcanoclastic sandstones and gravelite of the Paleoproterozoic North Baikal volcano-plutonic belt, Paleoproterozoic metasedimentary rocks and granite (upper reaches). Neoproterozoic metamorphic complexes, Quaternary moraine deposits (lower reaches)
	Rel	23	50	
	Slyudinka	24	45	
	Tyia	25	120	
Barguzin Range	Frolikha	26	18	Late Paleozoic granitoids, less alkaline gabbro of the Angara-Vitim batholith
	Shirilda	27	22	
	Tompuda	28	108	
	Shegnanda	29	67	
	Urbikan	30	22	
	Kabanya	31	72	
	Bolshaya	32	70	
	Davsha	33	29	
	Tarkulik	34	44	
	Sosnovka	35	29	
	Cheremshanka	36	35	
	B.Chivyrkuy	37	39	

Ulan Burgassy Range	Maksimikha	38	24	Late Paleozoic granitoids, less alkaline gabbro of the Angara-Vitim batholith. Early Paleozoic gneisses, amphibolites, and marbles of the Olkhon terrane (lower reaches)
	Nalimovka	39	23	
	Kika	40	82	
	B.Sukhaya	41	33	
Khamar- Daban Range	Zagza	42	13	Early Cretaceous Selenga metamorphic core complex with Late Paleozoic granitoids of the Angara-Vitim batholith and Early Paleozoic gabbro in its central part
	B.Rechka	43	43	
	B.Kultuchnaya	44	32	
	Manturikha	45	54	
	Mysovka	46	28	
	B.Ivanovka	47	19	
	Mishikha	48	40	Detachment zone of the Early Cretaceous Selenga metamorphic core complex
	Pereemnay	49	42	
	Anosovka	50	22	
	Vydrinaya	51	33	Terrigenous and carbonate sediments metamorphosed in the Early Paleozoic, containing apatite-rich rocks
	Snezhnaya	52	173	
	Khara-Murin	53	86	
	Osinovka	54	15	
	Solzan	55	34	
	Utulik	56	86	Mostly carbonate rocks, containing apatite-rich layers, metaterrigenous rocks, metamorphosed (up to granulite facies) in Early Paleozoic, Early Paleozoic granites
	Bezemyannaya	57	18	
	Slyudyanka	58	21	
	Pokhabikha	59	20	
	Kultuchnaya	60	24	

Table 2. Average REE concentrations, corresponding PAAS-normalized Ce and Eu anomalies, and [La/Yb]_N, [La/Tb]_N ratios in waters of different watersheds.

Geomorphological structure	n		Σ REE μg/L	Ce _{anom.}	Eu _{anom.}	[La/Tb] _N	[La/Yb] _N
Major tributary	5	mean	0.51	0.79	1.21	0.96	1.51
		min-max	0.28-0.75	0.68-0.88	1.05-1.40	0.52-1.27	0.73-2.47
Olkha Plateau	7	mean	0.85	0.66	1.20	0.64	0.71
		min-max	0.58-1.23	0.62-0.74	1.12-1.24	0.46-0.85	0.45-0.95
Primorsky Range	6	mean	0.29	0.61	1.01	0.71	0.95
		min-max	0.13-0.54	0.40-0.83	0.50-1.24	0.52-1.11	0.57-1.84
Baikalsky Range	15	mean	0.65	0.35	0.57	0.88	1.42
		min-max	0.08-2.16	0.12-0.70	0.32-0.97	0.54-1.67	0.68-2.39
Barguzin Range	13	mean	0.26	0.49	1.32	1.82	3.39
		min-max	0.05-0.80	0.19-0.92	1.18-1.45	0.86-2.59	1.02-5.58
Ulan Burgassy Range	6	mean	0.24	0.85	1.00	0.83	0.91
		min-max	0.08-0.42	0.73-0.95	0.84-1.17	0.65-1.21	0.71-1.56
Khamar Daban Range	(I)	mean	0.17	0.67	1.13	0.84	1.02
		min-max	0.08-0.26	0.38-1.01	0.95-1.32	0.63-0.97	0.72-1.37
	(II)	mean	0.11	0.48	1.51	0.35	0.44
		min-max	0.06-0.21	0.33-0.84	1.17-1.69	0.30-0.41	0.36-0.67
	(III)	mean	0.68	0.36	1.01	0.63	1.17
		min-max	0.08-1.33	0.17-0.52	0.83-1.19	0.49-0.79	0.91-1.37
	(IV)	mean	0.06	0.38		0.70	0.51
		min-max	0.02-0.12	0.21-0.61		0.51-1.20	0.20-0.93

n – number of samples

Table 3

Field parameter pH, total dissolved solid (TDS) values for 0.45 μm filtered water samples, REE (ng/L) and Al, Fe, Mn ($\mu\text{g/L}$) concentrations for 0.45 μm filtered (f) and unfiltered (unf) water samples, corresponding PAAS-normalized Ce and Eu anomalies, and $[\text{La/Yb}]_{\text{N}}$ and $[\text{La/Tb}]_{\text{N}}$ ratios

Samples	Ch-1	ICCh-6	Ch-2	Ch-9	Ch-5	Ch-1	Ch-1	ICCh-6	ICCh-6	Ch-2	Ch-2	Ch-9	Ch-9	Ch-5	Ch-5
	Filtered water samples, July 2013					Water samples, July 2014									
						f.	unf.	f.	unf.	f.	unf.	f.	unf.	f.	unf.
pH	6.7	3.6	5.3	7.2	7.5		7.2		5.0		7.6		7.6		7.3
TDS[mg/L]	45	390	122	133	132	52		229		109		122		104	
Al	27	30192	4079	3	74	29	166	4835	19711	20	3250	3	1	49	952
Mn	62.9	1406	292	0.1	94.8	21.8	22.5	494	522	104	115	0.1	0.1	42.6	44.7
Fe	88.9	16.0	25.5	1.5	1.6	5.0	30.3	1.2	392.8	2.5	150.5	3.0	1.6	0.2	23.4
La	253.1	16998	3417	8.0	81.4	58.6	162.3	4732	4393	1013	1377	5.8	11.1	47.6	566.9
Ce	338.0	39746	7751	4.8	113.9	64.9	269.2	10581	11601	1842	3398	2.9	8.5	60.7	1241.6
Pr	59.8	6452	1320	1.7	17.4	10.9	43.2	1700	1871	273	561	1.2	2.3	9.6	203.5
Nd	264.1	29747	5872	7.9	72.0	47.0	190.3	7761	8655	1179	2611	5.1	9.7	40.6	945.2
Sm	59.9	7852	1656	1.4	16.1	9.6	51.1	2093	2376	245	720	0.8	2.0	8.1	256.4
Eu	17.1	2094	402	0.3	2.5	2.2	14.1	524	758	57	189	0.1	0.2	1.0	64.7
Gd	66.1	9699	1874	2.3	20.6	10.1	69.5	3283	3714	359	957	1.6	2.4	10.9	315.5
Tb	11.1	1513	310	0.4	2.8	1.6	9.5	500	558	53	151	0.3	0.4	1.5	50.0
Dy	51.0	7652	1679	1.7	13.3	9.2	50.7	2334	2602	271	790	1.4	2.1	8.8	271.3
Ho	10.9	1556	334	0.4	2.9	1.8	9.3	423	478	50	142	0.2	0.5	1.5	48.6
Er	29.8	4329	916	1.5	7.5	5.2	25.6	1149	1297	129	385	0.7	1.6	4.4	133.5
Tm	4.3	605	127	0.2	1.1	0.6	3.6	159	182	17	53	0.1	0.2	0.6	18.5
Yb	28.2	3528	780	1.4	5.6	3.8	22.7	1036	1187	99	358	0.5	1.2	3.2	118.3
Lu	4.4	539	115	0.2	1.0	0.8	3.6	168	194	16	58	0.1	0.2	0.6	20.2
Ce _{anom}	0.63	0.85	0.81	0.30	0.70	0.59	0.74	0.84	0.89	0.80	0.86	0.25	0.39	0.65	0.82
Eu _{anom}	1.26	1.10	1.05	0.72	0.61	1.04	1.07	0.89	1.13	0.87	1.04	0.46	0.46	0.46	1.04
$[\text{La/Yb}]_{\text{N}}$	0.66	0.36	0.32	0.42	1.07	1.12	0.53	0.34	0.27	0.75	0.28	0.79	0.66	1.08	0.35
$[\text{La/Tb}]_{\text{N}}$	0.46	0.23	0.22	0.44	0.59	0.72	0.35	0.19	0.16	0.39	0.18	0.47	0.55	0.64	0.23
ΣREE	1198	132309	26554	32	358	226	924	36445	39867	5603	11749	21	42	199	4254

ACCEPTED MANUSCRIPT

Highlights:

REE dissolved in waters from sixty five sampled tributaries of Lake Baikal show diversity in abundances ($\sum \text{REE} = 0.02 - 2.16 \mu\text{g/L}$) and distribution patterns ($[\text{La/Yb}]_{\text{N}} = 0.20-5.58$; $[\text{La/Tb}]_{\text{N}} = 0.30-2.59$).

The REE patterns in stream waters apparently depend on watershed lithology.

Six lithological provinces with different stream-water REE patterns have been distinguished.

REE patterns in stream waters shows up as negative Ce anomalies ($\text{Ce}_{\text{anom}} = 0.12-0.97$), in contrast to the large tributaries (Selenga, Turka, Barguzin, Upper Angara, and Kichera).