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Rare earth geochemistry in sediments of the Upper Manso River Basin, Río Negro, Argentina

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Abstract

The abundance, distribution and fractionation of rare earth elements was studied in solid material transported by the Upper Manso River and in the sediments deposited in Lake Mascardi, Argentina. The pristine condition of the area offers an ideal environment for assessing geochemical processes, and the seasonal cycles to which the basin is subjected permit us to study seasonal variations that are mainly influenced by glacial pulses. The most remarkable characteristics observed in the REE-normalized patterns are a strong HREE enrichment and a positive Eu anomaly. These normalized patterns are atypical as compared to those considered representative of the world's major rivers and are caused by drainage basin geology. Due to the dissected topography and the small size of the basin, intense mixing phenomena are not favoured and the weathering reactions are inhibited by the fast-flowing river. These physicochemical conditions and near-neutral pH values have an important influence on the REE patterns of the sediments, which mainly originated by glacial erosion, that are transported by the river. The feldspars and their secondary products, which are both enriched in Eu, might be the cause of the Eu anomaly.

HREE enrichment, which is mainly associated with high-pH systems or with the presence of accessory phases, shows a clear dependence on source rocks. The calculated $(La/Yb)_N$ ratios oscillate between 0.5 and 0.6, contrasting with the values reported in the literature as average values for suspended load material. Nevertheless, these values are consistent with the dependence of $(La/Yb)_N$ values on the age of drainage area rocks as was observed by Goldstein and Jacobsen [3].

Seasonal variations are not manifested in REE concentrations, and additional elemental determinations showed coherent behaviour during weathering for all elements except Sr and Ba, which exhibited selective elemental mobilization during periods of minimum discharge.

1. Introduction

The study of rare earth elements is one of the main means of evaluating processes in the terrestrial crust: reliable analytical determinations of the lanthanide composition of rocks allows us to propose hypotheses on the chemical evolution of earth [1] and crustal fractionation relative to the bulk earth [2,3].

Due to their low solubility and relative immobility in the upper crust the REE are very useful in studying sedimentary environments, because sediments inherit the REE composition of their source rocks and therefore bear information on the origin of those rocks. Uniformity in the distribution of REE in

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sediments from different sources is generally interpreted as being due to thorough mixing of different lanthanide patterns in the upper crust during weathering, erosion, transportation and deposition. REE mobility is frequently associated with hydrothermal phenomena, but there is also evidence of fractionation and mobilization during weathering, especially in geochemical reactions that involve changes in pH values in soils and river waters [4–6].

In crustal geochemical environments the REE constitute a coherent group of elements in which the trivalent oxidation state predominates. This similarity in chemical behaviour is a consequence of the peculiarities of atomic structure. Important exceptions to the pattern of ionic size occur when some rare earth ions adopt ionic states that differ from the trivalent state. For example, under reducing conditions, Eu is reduced from the trivalent to the divalent state, it increases in ionic radius, and this effect leads to distinctive geochemical behaviour as compared to the other lanthanides, producing enrichment or depletion of this element relative to the other REE. On the other hand, in the presence of free oxygen Ce may lose an electron to become quadrivalent. In both cases, abundances relative to the other trivalent REE are used to assess the redox behaviour in geochemical systems.

The REE have traditionally been divided into two groups, the light rare earths (LREE, the elements from La to Sm) and the heavy rare earths (HREE, from Gd to Lu). This differentiation is related to the inflection in the REE patterns that occurs around Eu

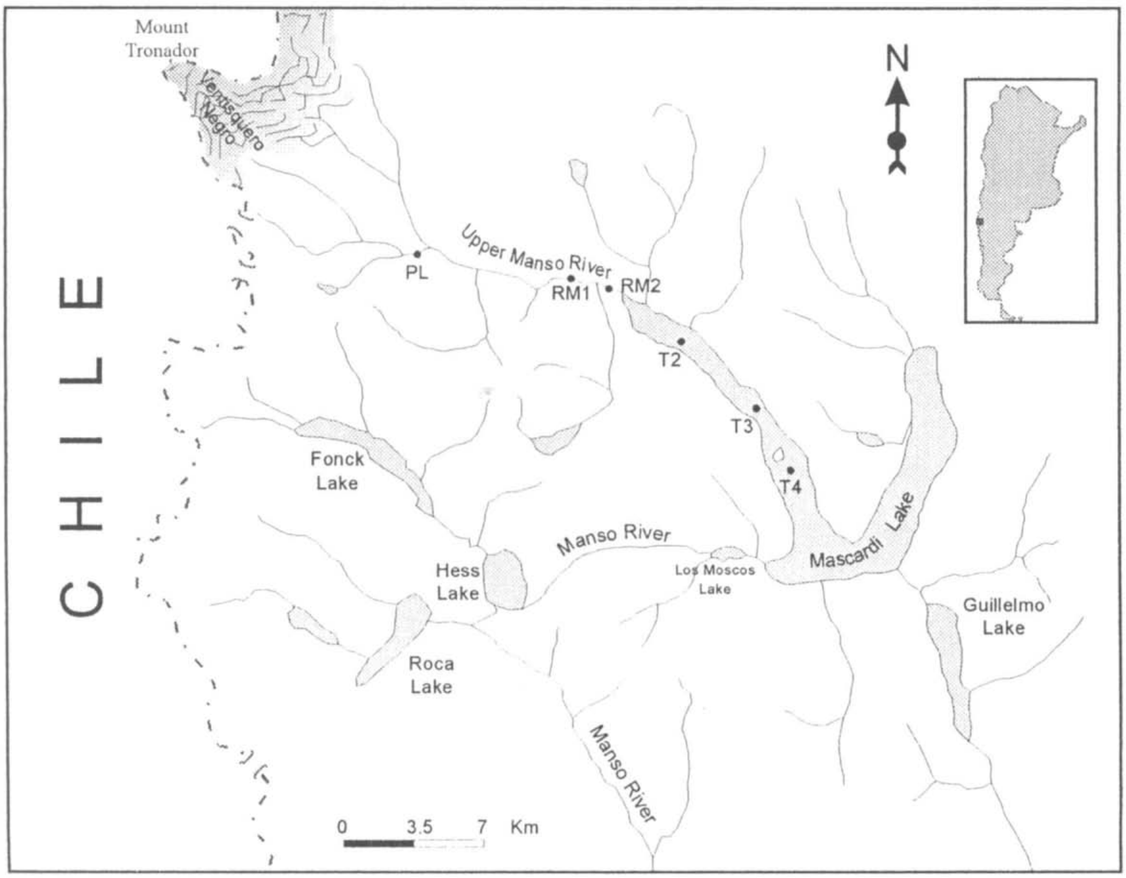

Fig. 1. Sample location map.

due to the difference in ionic radius produced by lanthanide contraction. The LREE/HREE fractionation (i.e., the ratio of the relative abundance of the two groups) is evaluated by means of the La/Yb ratio. This ratio is particularly useful for studying sediment origin and REE mobility in the crust.

Some recent work [7–10] carried out on rivers has examined REE distribution, circulation and fractionation in the world's major rivers, especially in their estuaries, where these elements undergo removal from the dissolved fraction of the river water during estuarine mixing. The chemical composition of suspended particulate matter in some major rivers has been examined by Goldstein and Jacobsen [7]. These authors observed a positive correlation between the La/Yb ratio and the Sm–Nd depleted mantle model age in the rivers they studied, and LREE-enriched patterns relative to the North American Shale Composite (NASC), which has the normalized ratio $(La/Yb)_N = 1.6–2.7$.

In this work we study a small basin with fluvial dynamics that are mainly influenced by the presence of glaciers where weathering and erosion are very rapid. The Upper Manso River Basin provides an ideal environment for studying geochemical processes because it is an unspoiled area that is free of atmospheric and aquatic pollution. Moreover, it has a strong west-to-east precipitation gradient and well-defined seasonal cycles.

Our discussion will be focused on the analysis of REE distribution, circulation and accumulation in this pristine area. Seasonal variability is also explored, by analyzing the minor element concentrations of sediment input into Lake Mascardi.

2. Study area

The Upper Manso River is located in the Argentine Andes at 72° W, 41° S, in the Nahuel Huapi National Park in southwestern Argentina. This river is 23 km long with a drainage area reaching 250 km^2. The river begins at Mount Tronador (3554 m asl) and discharges into Lake Mascardi, subsequently draining through a series of lakes into the Pacific Ocean (Fig. 1). Melt water is derived from three glaciers, the main one being the Ventisquero Negro or Manso Glacier, a regenerated glacier that incorporates an important debris load into the river, especially in the autumn and spring.

The geology of this area has been studied by Larsson [11] and Dalla Salda [12] and mainly involves Paleozoic phillitic, porphyric and granitic rocks, and Tertiary volcanic and sedimentary rocks. In addition, varves, volcanic ashes and glacial and fluvioglacial deposits are widely distributed throughout the basin.

The climate of the area is cold and humid, with a mean annual temperature of 7.3° C near Lake Mascardi that decreases up the valley. Precipitation shows a strong west-to-east gradient, with a mean annual precipitation of 2.7 m at Mount Tronador and 1.4 m at Lake Mascardi. Most of the precipitation falls during May, June and July, as snow or rain. [13]. Water discharge displays a bimodal distribution, with peaks in winter and summer due to maximum precipitation occurring in the winter and maximum temperature occurring in the summer (glacial melt water). During the warm months a large suspended load (glacial flour) is carried by headwaters of the Upper Manso River and discharged into the lake. The river waters are coloured green because of the enormous amount of suspended load. Near-neutral pH values vary between 7.4 for the uppermost reaches and 6.4–6.9 for the lower reaches.

3. Samples and methods

The river bed sediments and suspended load were sampled at three stations along the river (Fig. 1). Sample PL is representative of the conditions dominating in the uppermost reaches; RM1 and RM2 were taken in the lower reaches, close to the outfall system. Two samples of Lake Mascardi suspended load (MASC 1 and MASC 2) were collected at a depth of 0 m near the mouth of the river. The suspended sediments were obtained by water filtration with 0.45 μm Millipore filters.

The shallow bedload was sampled with a plastic spoon and initially stored in polyethylene bags. The samples were air dried at room temperature and then at 110° C in a drying chamber. They were subsequently sieved and the minor 63 μm fraction was

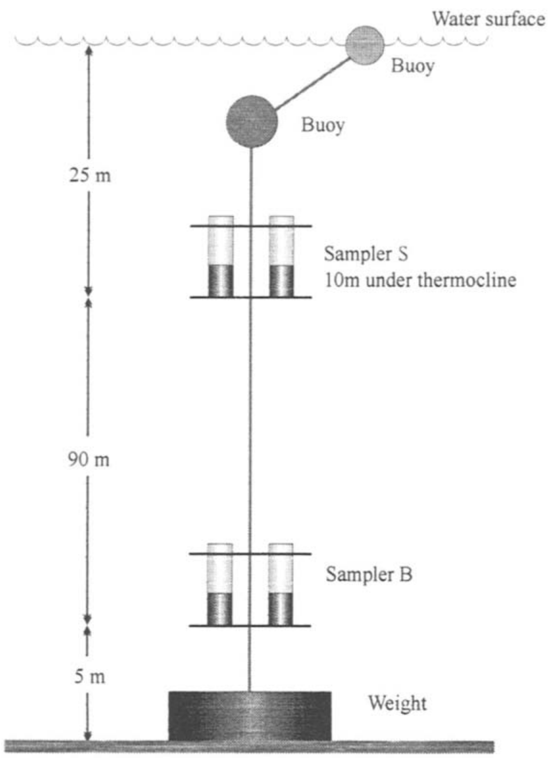

Fig. 2. Sediment traps (design ETH, Zürich).

selected for analysis. In order to compare these sediments with those deposited at the bottom of the lake, two samples extracted from 10 and 20 cm below the top of a Lake Mascardi core were analyzed and incorporated in the discussion.

A systematic monthly sampling routine was established to determine the sedimentation rates and seasonal variations in the sediments contributed by the river. To this end sediment traps were set at three locations in Lake Mascardi (T2, T3 and T4) by personnel from Progeba (Bariloche) and the *Instituto Antártico Argentino* (Fig. 1). The samplers consist of a set of four collectors (two at the surface and two at the bottom, Fig. 2) anchored to the lake bottom. The sediments obtained were dried and weighed before they were analyzed.

All sample concentrations were determined by instrumental neutron activation analysis (INAA) in the RA-6 Bariloche research reactor. The measurements were performed with a 67 cm^3 ORTEC HPGe intrinsic-N coaxial detector which has a resolution of 2.0 keV FWHM at 1.33 MeV and an efficiency of 12.3% relative to a 7.6×7.6 cm NaI(Tl) crystal at 1.33 MeV and 25 cm distance. Data collection was carried out in 4096 channels with a Nuclear Data ND76 multichannel analyzer. Gamma-ray spectra were analyzed for peak position and intensity either with the Nuclear Data analyzing package [14] on a DEC 11/780 computer or with the GAMANAL analyzing routine (within the GANAAS package distributed by the IAEA [15]) on a 486 PC.

The samples, which range in mass from 90 to 200 mg, were shaped into discs of 1 cm in diameter that ranged in thickness from about 0.10 to 0.20 cm and were placed in plastic vials. The filters with the suspended material, together with an unused filter, were assembled individually in sealed plastic bags. The samples were irradiated for 7–9 h in the reactor core (thermal flux $\sim 9.0 \times 10^{12}$ cm^{-2} s^{-1}, epithermal flux $\sim 3.5 \times 10^{11}$ cm^{-2} s^{-1}). The samples were irradiated inside an aluminium can together with two sets of two monitors for each set ($\sim$ 1 mg Co and $\sim$ 1 mg 0.112% Au–Al). One of these sets was positioned at the bottom of the can and the other set was located at the top (i.e., about 6 cm between each set) to correct for non-uniformity in both the thermal and the epithermal flux. After irradiation the filters with the suspended material were folded and tightly packed into a final disc shape of 1–2 cm in diameter. Two measurements were performed for each sample, the first after 5–9 days of decay and the second after 10–20 days of decay. The thermal and epithermal neutron fluxes were determined with the Co and Au–Al monitors. With the fluxes determined in this manner for each run, and fundamental constants and nuclear parameters from current tables [16–19], the different concentrations were obtained for the samples studied. In all these runs, the samples were measured in the original irradiated polyethylene vial, but corrections were made for the small traces present in the vials themselves. On the basis of the average of several determinations made at various opportunities over the years these small traces are well known in our laboratory. The clean filter was used to make a blank correction for the suspended load samples. All the concentration values reported refer to dry weight samples.

4. Results and discussion

4.1. Suspended load

In Table 1 we present the REE concentration in the river and lake suspended load. Data normalization was achieved using REE concentrations taken from the literature [20].

Based on the essentially erosional character and small size of the basin it is possible to foresee a REE distribution controlled by the mineralogy of the sediment transported. The glacier dynamics and the dissected topography favour a large amount of sediment load circulation, especially in the spring when this phenomenon becomes particularly important due to glacier melting. These sediments are mainly composed of feldspars, clays, heavy minerals and volcanic material. The clay minerals accumulating at the mouth of the River Manso in Lake Mascardi were reported by Depetris [21] to be smectites, chlorites and illites.

The Upper Manso River and Lake Mascardi normalized REE patterns show a strong depletion in LREE and a noticeable positive Eu anomaly (Fig. 3a and b), in contrast to the average values suggested as representative of suspended river load [7]. In Fig. 4

Table 1
Rare earth element concentrations (ppm) in Upper Manso River and Mascardi Lake sediments

Sample	La	Ce	Nd·	Sm	Eu	Tb	Tm	Yb	Lu	$(La/Yb)_N$ (★)	Eu Anom. (§)	Ce Anom.
Suspended load												
Upper Manso River												
PL	21.3	43.8	22.1	5.43	1.31	0.77	-	3.31	0.69	0.62	1.02	0.89
RM1	27.5	51.7	24.1	6.65	1.75	1.01	-	4.15	0.84	0.64	1.20	0.87
RM2	23.5	47.9	23.2	5.85	1.70	0.87	-	3.96	0.80	0.57	1.25	0.92
Mascardi Lake												
MASC. 1	31.7	69.4	25.6	5.98	1.54	0.87	-	4.60	0.83	0.67	1.17	1.03
MASC. 2	22.6	54.0	21.0	5.23	1.47	0.85	-	3.37	0.71	0.65	1.23	1.09
River bed sediments												
Upper Manso River												
PL	21.9	44.9	26.5	6.18	1.57	1.06	0.56	3.16	0.71	0.67	1.18	0.86
PL (Replicate) #	21.5	42.3	28.9	5.29	1.59	0.84	-	3.24	0.73	0..64	1.23	0.77
RM	20.8	44.8	29.5	5.99	1.62	1.06	0.57-	3.82	0.71	0.53	1.24	0.84
RM(Replicate) #	23.0	45.9	31.4	5.50	1.65	0.77	-	2.77	0.76	0.80	1.26	0.78
Botton Lake sediments												
MDI 1	23.1	48.4	34	6.72	1.53	1.24	0.66	4.18	0.69	0.54	1.03	0.80
MDI 2	25.8	52.1	33.1	7.40	1.63	1.23	0.74	4.65	0.80	0.53	1.03	0.81
Rocks												
Basalt 1	18.7	45.1	29.7	5.61	2.01	1.05	-	3.35	0.75	0.54	1.51	0.90
Basalt 2	22.6	53.1	32.5	6.04	2.12	1.02	-	3.48	0.85	0.63	1.52	0.91
VN (glacial flour)	27.6	66.0	40.6	6.86	2.30	1.06	-	4.49	0.89	0.59	1.52	0.92
Sediment traps												
Surface												
7/93	25.1	56.7	29.5	6.27	1.70	0.95	0.58	4.65	0.83	0.52	1.20	0.96
8/93	20.2	47.4	19.0	4.95	1.44	0.74	0.54	3.46	0.71	0.57	1.17	1.06
10/93	19.3	43.0	16.6	4.80	1.46	0.66	0.50	3.35	0.68	0.56	1.22	1.04
12/93	23.9	56.7	31.1	5.90	1.64	0.97	0.61	4.61	0.82	0.50	1.20	0.96
Bottom												
5/93	22.0	45.7	24.2	5.55	1.57	0.92	0.54	4.16	0.82	0.51	1.49	0.90
7/93	23.6	48.6	26.3	5.88	1.51	0.91	0.59	4.34	0.89	0.53	1.11	0.88
7/93 (Replicate) #	24.5	48.8	34.5	5.98	1.56	0.88	--	3.27	0.82	0.73	1.13	0.78
8/93	22.7	51.4	17.3	5.57	1.65	0.85	0.58	3.51	0.99	0.63	1.23	1.08
10/93	19.2	38.5	18.8	5.05	1.42	0.74	0.56	3.52	0.75	0.53	1.15	0.90
12/93	23.0	52.1	19.5	5.84	1.89	0.98	0.55	3.76	0.79	0.59	1.39	1.05
12/93(Replicate) #	26.2	59.4	31.1	5..88	1.90	0.96	--	4.59	0.82	0.55	1.39	0.72
Standards												
IAEA-Soil-7	29.8	61.7	30.0	5.14	1.04	0.668	-	2.71	0.59			
IAEA-SL1	50.5	106	48.1	8.34	2.13	1.20	-	5.34	0.72			

(★) values normalized with NASC (North American Shale Composite) [2].
(§) values calculed with an average Gd content of 6.5 ppm.
(#) Replicated analyses

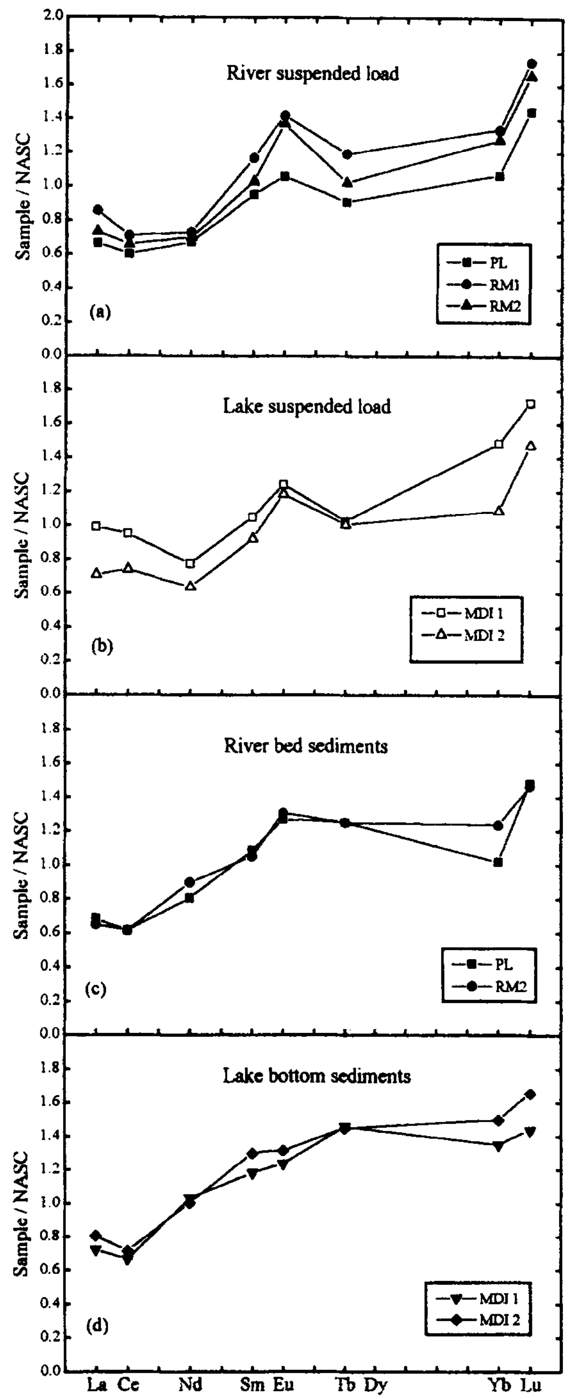

Fig. 3. NASC-normalized REE abundance in the Upper Manso River and Lake Mascardi sediments.

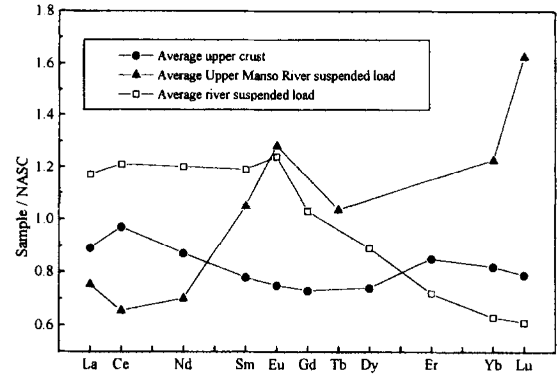

Fig. 4. NASC-normalized REE abundance of average upper crust [2], average river suspended load [7], and average Upper Manso River suspended load.

we show average normalized REE patterns for the average upper crust and suspended river load and for the average Upper Manso River suspended material. Important differences in these patterns are observed. Goldstein and Jacobsen [7] suggest that the major river suspended load average reflects more accurately the modern surface composition of the continents than the NASC, and that the difference between these materials and the average upper crust content is due to changes in the nature of the continental crustal surface exposed to erosion. Differences between the patterns of major rivers and this small catchment can be attributed to the efficient physical mixing of sediments occurring in large basins.

As regards the La/Yb ratio the Upper Manso data are situated between chondrite (1.48) and the NASC (10.3). This accords with the relationship observed by Goldstein and Jacobsen [7] between $(La/Yb)_{susp}$ and the Sm–Nd depleted mantle model age for these materials: suspended materials derived from young rocks tend to have La/Yb ratios that are lower than suspended materials derived from older rocks. Typical values reported in the literature for $(La/Yb)_N$ in suspended river load range between 1.6 and 2.7 [7], whereas our data show values of between 0.5 and 0.6. Heavy minerals can produce enrichment in HREE and their presence can be evaluated from the Hf and Zr concentrations. These minerals are preferentially transported on the river bed, and therefore suspended load sampled near the water surface might not be affected by them. The Hf content is useful for determining the presence of zircon. The average Hf content of the major rivers is typically between 4.0 and 8.4 ppm [7]. The sediment concentrations for the Upper Manso River lie between 3.5 and 5 ppm (see Table 2). We therefore conclude that the HREE enrichment is not produced by the presence of heavy minerals. In most cases, HREE-enriched normalized patterns are associated with systems with high pH values [6,22,23], but in this case the recorded pH values are close to 7 in all seasons.

The fast-flowing nature of the river inhibits hydrographic and biogeochemical processes that would

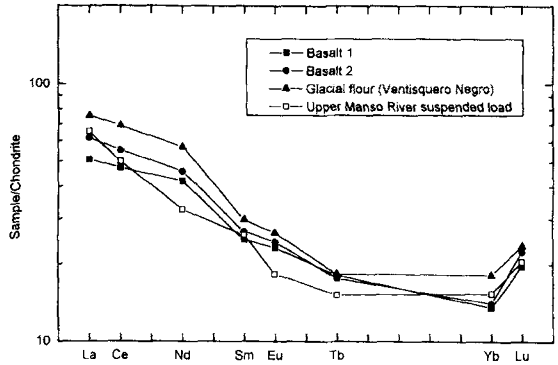

Fig. 5. Chondrite-normalized REE abundance in source rocks.

Table 2
Major and trace-element concentrations in Upper Manso River and Mascardi Lake sediments

Sample	Fe(*)	K(*)	Na(*)	Sc	Ba	Co	Cr	Cs	Rb	Th	Hf	Sr	Ta	Zn	Zr
Suspended load															
Upper Manso River															
PL	4.99	1.62	1.97	18.46	385	16.35	17.23	2.73	63.20	5.56	3.81	199	0.378	114	-
RM1	6.68	1.21	1.49	24.32	298	22.4	24.77	5.11	69.86	7.14	4.88	210	0.365	302	252
RM2	5.64	1.36	2.20	20.22	469	19.13	27.39	3.01	63.34	6.32	4.30	157	0.370	114	-
Mascardi Lake															
MASC. 1	5.92	1.22	1.53	22.54	545	23.38	38.14	4.28	67.30	7.41	4.94	-	0.458	363	193
MASC. 2	4.94	1.21	1.56	18.35	383	18.43	37.08	4.20	71.89	6.42	3.69	169	0.298	379	304
River bed sediments															
Upper Manso River															
PL	5.98	-	3.07	21.34	470	19.35	38.4	2.37	56	7.01	4.60	-	0.510	113	330
PL (Replicate) #	6.58	0.81	2.74	23.20	41.9	20.26	50.1	1.65	51	5.97	5.40	5.48	0.311	92.2	357
RM	5.72	-	2.95	20.88	430	19.08	30.6	2.54	58	6.82	4.46	-	0.528	94.6	334
RM (Replicate) #	5.80	0.81	2.74	21.78	371	18.52	39.0	2.60	64	6.20	5.22	309	0.438	95.0	350
Botton lake sediments															
MDI 1	6.67	-	2.19	22.80	449	25.3	29.1	4.98	71.2	7.52	4.55	-	0.516	126	-
MDI 2	6.67	-	2.11	23.40	518	25.1	35.2	5.29	54	8.38	4.85	-	0.574	151	380
Rocks															
Basalt 1	6.84	-	2.73	26.43	210	25.56	40.8	1.62	35.0	4.94	4.01	-	-	95.6	599
Basalt 2	7.28	-	3.12	27.58	402	26.08	35.7	2.53	35.5	5.73	4.02	282	0.385	118	462
VN (glacial flour)	7.08	-	3.22	23.39	427	20.95	39.5	2.89	53.0	6.92	5.16	331	0.486	114	399
Sediment traps															
Surface															
7/93	6.84	1.28	2.05	22	474	23.84	31.79	4.24	62.15	7.37	4.64	268	0.409	210	298
8/93	12.16	0.93	1.58	18.26	425	23.08	35.83	4.01	59.83	5.6	3.58	<200	0.316	355	166-
10/93	6.18	1.20	1.91	17.67	376	20.00	33.30	2.66	52.81	5.43	3.49	190	0.295	119	158
12/93	5.79	1.65	2.56	20.11	414	20.70	23.37	3.10	62.47	6.84	4.64	412	0.380	146	229
Bottom															
5/93	6.32	1.15	2.30	22.4	491	23.51	35.59	3.33	46.93	5.97	4.41	187	0.316	143	294
7/93	5.97	1.38	2.59	21.73	422	21.96	31.05	2.98	63.44	6.24	4.21	277	0.375	117	297
7/93 (Replicate) #	6.45	-	2.66	23.2	394	23.37	37.02	3.35	53.8	6.66	4.95	367	0.388	125	-
8/93	9.60	1.00	1.90	21.2	482	25.95	39.43	3.95	53.23	6.11	4.27	85.5	0.336	224	152
10/93	7.55	0.82	1.66	17.73	398	24.17	35.80	3.24	57.41	5.34	3.36	165	0.337	161	137
12/93	6.92	-	-	21.22	485	24.66	29.49	3.24	54.31	6.47	4.44	341	0.395	135	258
12/93 (Replicate) #	7.32	1.25	2.58	27.08	574	27.61	27.52	3.69	52.6	7.05	4.85	3.60	0.399	130	264
Average upper continental crust (**)	**3.50**	**3.58**	**3.07**	**7.96**	**550**	**17.1**	**80.6**	**3.7**	**98.6**	**2.5**	**5.5**	**350**	**2.2**	**81.9**	**210**

(*) In wt %
(**) Taken from [2]
(#) Replicated analyses

modify REE patterns along the course of the river. The REE patterns of the suspended load of the Upper Manso River must therefore be controlled by the source rocks. By analyzing the REE patterns of the source rocks we found a noticeable coincidence between suspended load REE patterns and those for the Mount Tronador basaltic rocks (Fig. 5). The rock beneath the glacier is mainly granitic but the REE composition of the sediments transported by the river is influenced by rock eroded by the upper reaches of the glacier. This glacier is regenerated in the valley (Ventisquero Negro, or Manso Glacier) and produces important amounts of glacial flour. The normalized REE composition of this material was included in Fig. 5, where we observe a clear similarity between this REE pattern and that determined for the basalts.

Several correlation studies show that, *in general*, there is no correlation between clay mineralogy and REE content [24,25]. Caggianelli et al. [26], analyzing a set of samples from a borehole in the southern Apennines of Italy found a positive correlation between illite and REE content, whereas smectites showed the opposite behaviour. From clay mineralogy analysis in the Manso Basin we observe that smectite is widely distributed along the river and that illite is especially present near the mouth. A slight difference between sample PL and samples RM1 and RM2 is observed in the NASC-normalized REE patterns for the suspended load of the Upper Manso River (Fig. 3a): Sample PL has lower REE concentrations than the others, probably due to the presence of illite in the lower watershed, which could be producing an increase in the total REE content of RM1 and RM2.

The anomalous behaviour of Eu is important in evaluating geochemical processes. The essential discussion about this subject has been about whether the observed anomaly is produced in the liquid phase or by weathering reactions. Crustal material shows a uniform lanthanide pattern with a regular depletion in Eu produced by retention of this element in the deep crust where reducing conditions are more intense. The positive Eu anomaly observed in the normalized Upper Manso River patterns might be caused by feldspars contributed by basaltic rocks. Feldspar is enriched in Eu because of the substitution of Eu^{2+} for Sr^{2+} in the Ca^{2+} lattice sites [20], and it is actively present throughout the basin, as has been verified by X-ray diffraction analysis of the suspended load.

As expected, because of the absence of changes in the physicochemical conditions of the two systems there are no important differences between the Upper Manso River and Lake Mascardi REE patterns.

4.2. *River bed sediments*

The REE concentrations determined for river bed sediments are similar to those obtained from suspended load sediments (Fig. 3c), with the sole exception of a flattening in the patterns produced by minerals such as quartz that act as dilutants due to their very low REE contents.

In most natural materials the characteristics of the Eu anomaly are determined by reactions at high pressure and temperature during crystallization [1,27]. However, McRae et al. [28], by studying a positive Eu anomaly produced by diagenetic remobilization in the Pleistocene muds of the Amazon deep-sea fan, proposed that during diagenesis Eu can be reduced and move upward in solution. The reducing conditions of the Lake Mascardi bottom are not so severe as in the Amazon fan, but differing redox condition do appear to affect slightly REE behaviour in lacustrine sediments, introducing modifications to the Eu anomaly (Fig. 3d), whose value, approaching 1, shows a change with respect to the other sediments of the basin (see Table 1).

Ce anomalies also become more negative, indicating the presence of fractionation relative to the neighbouring elements. This fractionation is only possible by changes in the redox conditions, but more data are necessary to confirm this (in particular data on REE concentrations in pore water).

As we have pointed out above, typical patterns for sedimentary rocks are characterized by light-lanthanide enrichment and a pronounced depletion in Eu relative to chondrite. The atypical normalized pattern observed in the Upper Manso bedload, with a pronounced enrichment in HREE, is due to the rock types in the drainage basin. In these sediments, heavy minerals, which have high HREE contents, could exert a greater influence than the suspended load, because the river bed is the natural environment for heavy mineral separation and concentration. However, there is no difference in Hf and Zr concentrations between the suspended load and the bedload.

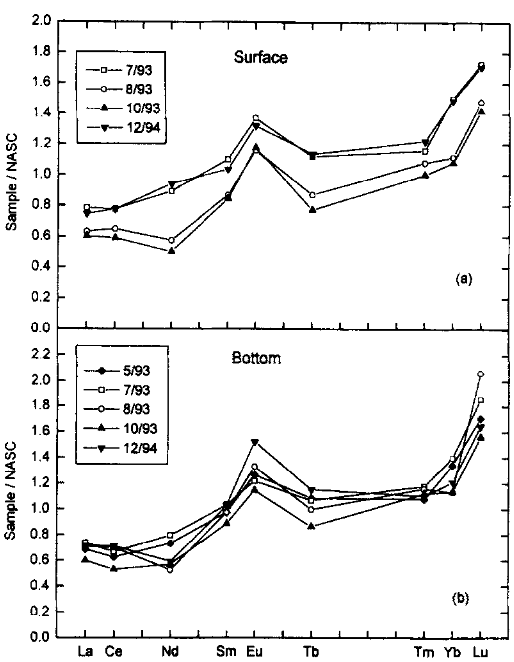

Fig. 6. NASC-normalized REE abundance in sediments collected with sediment traps in Lake Mascardi.

We use Hf as an indicator because of the limitations of INAA in determining Zr. To verify the influence of heavy minerals in the HREE enrichment we consider variations in La/Yb vs. Hf. The scatter of these data suggests the absence of selective separation of minerals, and the fact that the $(La/Yb)_N$ values are similar to those determined for the source rocks allows us to conclude that HREE enrichment is not produced by heavy mineral occurrence.

4.3. Sediment traps

The analysis of REE distribution in sediment obtained from traps serves the purpose of verifying seasonal changes in sediment input into the lake. We analyzed samples from station T2 in May 1993 (autumn), July and August 1993 (winter), October 1993 (spring) and December 1993 (summer). These were designated with an 'S' (surface) and a 'B' (bottom) to distinguish their origin. The REE concentrations of the sediments collected are presented in Table 1 and the NASC-normalized REE patterns are plotted in Fig. 6a and b).

Seasonal variations do not show up in normalized REE concentrations, despite the very strong seasonal cycles to which the basin is subjected. In the autumn and summer the river transports large volumes of glacier load in its main stream and during the winter the low temperatures partially freeze the bed of the glacier, decreasing the glacial sediment input. Precipitation in autumn and winter dilutes water coming from the glacier and contributes to incorporation of sediment from the entire drainage basin. The effects of seasonal changes on the glacier are clearly manifested in data on sediment weight, which show the same bimodality as the discharge data.

The normalized REE patterns show the same characteristics as the suspended load and are insensitive to fluctuations in glacier behaviour and sediment provenance.

Additional determinations of other elements were performed to evaluate weathering effects in the watershed (see Table 2). Feldspars exert a great influence on REE circulation, especially in Eu enrichment in the sediment circulating in the basin. Sr and Ba are also included in the feldspars, and by analyzing the Sr/Ba ratio it is possible to study differential weathering by examining the mobility of Sr relative to Ba [29]. We observe that July and December show the higher Sr/Ba ratios, coinciding with the maximum discharge into the lake. These periods are characterized by high energy in the system, which inhibits the differential weathering of Sr and Ba. This fact is reflected in values close to 1 for the Sr/Ba ratio. The lower Sr/Ba ratios correspond to the autumn and spring, when there are indications of differential weathering but without a regular dependence.

Most of the elements determined (Table 2) exhibit great uniformity in their concentrations in the different materials, and differences due to grain size are not clearly manifested. Cs shows values that are similar to those in [2], and despite the widespread distribution of micas (the host minerals) in the basin and their preference for the minor fractions, this element shows dependence on neither grain size nor seasonal variations. Rb, K, Na, Ta and Cr exhibit values that are lower than those of the average continental upper crust. The low K and Na concentrations may be caused by the absence of sediments of marine origin in the catchment. Finally, Sc, Th, Co and Zn exhibit contents that are higher than those for the crust. All these elements demonstrate coherent behaviour with no differential weathering and low fractionation with respect to the source rocks.

5. Conclusions

The atypical normalized rare earth element patterns observed in the Upper Manso River materials are strongly influenced by drainage basin geology. This accords with the conclusions reported by Goldstein and Jacobsen [7] regarding small catchment areas. In addition, the LREE/HREE fractionation originates in the source rocks and the low values of the La/Yb ratio may be due to Tertiary volcanic rocks exposed to erosion and weathering. The values reported for the Upper Manso materials agree with those reported in the literature for modern rocks.

Systems with HREE enrichment are generally associated with high pH values or with the presence of heavy minerals. In this case, however, both these associations are rejected because the river has near-neutral pH and the Hf and Zr concentrations show values that are considered to be standard concentrations for crustal material. The absence of an increase in these elements in the bedload sediments suggests that the influence of heavy minerals is not important in the basin.

The circulation of feldspars and their secondary products contributed by volcanic source rocks is responsible for the positive Eu anomaly that is clearly manifested in the suspended load; the minor Eu anomaly in the lacustrine sediments occurs where a slight change in the redox conditions affects this anomaly, creating a value close to 1.

The strong seasonal changes to which the basin is subjected are not manifested in the normalized REE patterns. The lacustrine sediment trap samples show uniformity in their general composition and coherent behaviour for most of the elements during weathering. Only the feldspars present evidence of selective differential weathering, with major mobility of Ba relative to Sr during autumn and spring and a clear lack of selective element mobilization during periods of maximum discharge.

Grain size is not a determining factor in the REE concentrations. Analytical determinations on material of different grain size have not revealed large differences, with the exception of a slight flattening in the normalized REE patterns in river bed sediment.

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