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High contents of rare earth elements (REEs) in stream waters of a Cu–Pb–Zn mining area

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"Capsule": *The release of REE (lanthanides) into stream waters and their aqueous geochemistry are controlled by Fe-oxides/oxyhydroxides.*

Abstract

Stream waters draining an old mining area present very high rare earth element (REE) contents, reaching 928 μg/l as the maximum total value (ΣREE). The middle rare earth elements (MREEs) are usually enriched with respect to both the light (LREEs) and heavy (HREEs) elements of this group, producing a characteristic "roof-shaped" pattern of the shale Post-Archean Australian Shales-normalized concentrations. At the Fenice Capanne Mine (FCM), the most important base metal mine of the study area, the REE source coincides with the mine tailings, mostly the oldest ones composed of iron-rich materials. The geochemical history of the REEs released into Noni stream from wastes in the FCM area is strictly determined by the pH, which controls the REE speciation and in-stream processes. The formation of Al-rich and mainly Fe-rich flocs effectively scavenges the REEs, which are readily and drastically removed from the solution when the pH approaches neutrality. Leaching experiments performed on flocs and waste materials demonstrate that Fe-oxides/oxyhydroxides play a key role in the release of lanthanide elements into stream waters. The origin of the "roof-shaped" REE distribution pattern as well as the peculiar geochemical behavior of some lanthanide elements in the aqueous system are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: REE elements; Aqueous geochemistry; Lanthanide behavior; Stream waters; Mining waste

1. Introduction

Acidic mine drainage (AMD) has long been recognized as a ubiquitous concern wherever waste materials from mining activity have accumulated. AMD has environmentally significant consequences since it can enhance the leaching of toxic heavy elements from wastes and favor their spread in the environment, particularly affecting the delicate and highly vulnerable aquatic ecosystems. From an ecotoxicological point of view, much attention has traditionally been paid to the danger of elements such as Hg, As, Pb, Cd, etc. whose adverse effects on life are well established. The rare earth (REE) elements (lanthanide series) have largely been considered of minor environmental concern (Bowen, 1979). However, some toxicological studies (Haley, 1991; Hirano and Suzuki, 1996), following the recent employment of hi-tech materials in the electronics and semiconductor industry, have suggested that REEs have significant pathogenic potential.

In the present study, we report on the anomalous contents of lanthanide group elements found in streams draining a mining district in southern Tuscany (central Italy). There, the streams collecting the rain-wash of wastes in abandoned Cu-Pb-Zn-Fe mining areas show absolutely high REE contents in running waters. Furthermore, the "normalized" values of the measured REE contents show a peculiar upward convex, "roof-shaped", distribution pattern, which is not new in the literature but is not yet completely understood. We are particularly concerned with the "in-stream" processes controlling the REE concentrations in surface waters downstream of one of the biggest mines in the area, as well as the behavior and distribution pattern of these elements.

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2. Outlines of REE geochemistry

The REEs lie in the last two rows (at the bottom) of Mendeleev's periodic table, comprising both the lanthanide and actinide series. The REE acronym, however, is mostly employed in geochemistry as a synonym of the lanthanide series. Hereafter, we will adopt this popular meaning of the term.

The 14 stable REEs, from lanthanum to lutetium, are strongly electropositive (electronegativity less than 1.2) and mostly trivalent (3^+) under a wide range of oxygen fugacity. In atoms of rare earth elements, the *4f* orbitals are progressively filled, with increasing atomic numbers. As a consequence, the configuration of the valence electrons of the outermost shell is the same for all the REE species. Another related consequence is the so called "lanthanide contraction" by which the ionic radius progressively decreases from La^{3+} (1.16 Å) to Lu^{3+} (0.97 Å).

From the geochemical point of view, the REEs are not particularly rare (despite their name), since the whole group exceeds 200 ppm in the average crust. For convenience, the REEs are divided into two sub-groups: those from lanthanum to samarium (with lower atomic numbers and masses), referred to as "light rare earth elements" (LREEs), and those from europium to lutetium (higher atomic numbers and masses), referred to as "heavy rare earth elements" (HREEs). Recently, however, the term "middle rare earth elements" (MREEs) has been applied to the group from neodymium to gadolinium (Sholkovitz, 1995).

Because of the high oxidation number coupled with a rather large ionic radii, the REEs are defined as "incompatible elements" by geochemists, since they are hardly hosted in the crystal lattices of common minerals forming igneous rocks. However, the degree of incompatibility varies. The heaviest REEs, for instance, have sufficiently small ionic radii to be accommodated to some degree in common minerals (e.g. substituting Al^{3+}); moreover, europium, which at low oxygen partial pressure can be partially in the divalent state Eu^{2+}, easily replaces Ca^{2+} in the structure of plagioclase feldspar (Henderson, 1984; Krauskopf and Bird, 1995).

Nevertheless, the particular geochemical behavior of REEs has given enormous help to igneous geochemists in understanding many aspects of mantle and crust petrology (Piper, 1974; Henderson, 1984; Lipin and McKay, 1989). The REE distribution in natural materials and their variations, caused by the geochemical behavior, can be illustrated by plotting the relative abundance versus the atomic number. Due to the different abundances of odd and even atomic numbers of the elements within the REE group (as a consequence of nucleosynthesis), a simple plot of their contents produces a saw-tooth pattern with the expected decreasing slope toward the highest atomic numbers. Thus, the REE behavior is better presented if the content values are "normalized" and reported as a relative abundance plot (Masuda, 1962; Coryell et al., 1963). This means that the REE concentrations found in the sample are divided by the concentration of the same REE element contained in a reference material. Most popular reference samples include the CI chondrite Orgueil (Nakamura, 1974), the chondritic meteorite Leedy (Masuda et al., 1973) and the PAAS (Post-Archean Australian Shales) of Taylor and McLennan (1985). There are mainly two advantages of this method. The first is that the abundance variation between REEs of even and odd atomic numbers is eliminated. The second, even more important, advantage is the real possibility of perceiving any fractionation that has occurred among the 14 REEs in the sample. This is because it is reasonably assumed, for instance, that no fractionation among REEs has occurred in chondrites. Hence, the abundance peaks (positive or negative) in the "normalized" REE pattern reflect the geochemical history of the sample.

The aqueous geochemistry of REEs is mainly influenced by their high charge and the ensuing high ionic potential. Since the REEs normally show a very coherent behavior, any shift from the expected distribution pattern can also help to understand the processes involved in the geochemical evolution of an aqueous system.

Various reviews on the aqueous geochemistry of REEs have been published in the last 15 years (Choppin, 1984; David, 1986; Brookins, 1989; Wood, 1990). Indeed the interest in REE aqueous geochemistry arose for various reasons. For instance, a significant aliquot of radioactive nuclides produced by the fission of U in power-generating reactors belongs to the lanthanide series (Brookins, 1984; Rard, 1988). Knowledge of the aqueous geochemistry of the lanthanide REEs can also help in understanding the behavior of the parallel actinide series elements (for which less information is available) in natural solutions.

The dominant oxidation state of REEs in aqueous solutions at 25°C is trivalent (3^+). Under oxidant conditions, however, Ce^{3+} may be oxidized to Ce^{4+}, while under extreme reducing conditions, Eu^{2+}, Sm^{2+} and Yb^{2+} are formed (Henderson, 1984). The oxidation of Ce^{3+} to Ce^{4+} leads to a decrease in ionic radius of about 15%; this enhances the surface reactivity of the element, which is easily scavenged and normally found depleted in oxygenated waters. In particular, ocean waters and phases precipitated in equilibrium with sea water are characterized by a distinctive cerium depletion (Fleet, 1984; Brookins, 1989).

Both theoretical considerations and experimental data (Wood, 1990) indicate that the strongest complexes formed by the trivalent REEs occur with hydroxide, fluoride, sulfate, carbonate and phosphate, while chloride and nitrate complexes are unlikely to be of importance in low-temperature natural waters. The

Table 1
Lanthanide contents (μg/l) in stream waters of the study area and in selected reference rivers

	pH	ΣREE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Luce River[a]	4.40	1.13	0.1920	0.4510		0.2640	0.0590	0.0150	0.0580		0.0430		0.0240		0.0200	
Fraser River[b]	7.15	0.48	0.0971	0.1546	0.0278	0.0879	0.0253	0.0072	0.0533	0.0043		0.0069	0.0142			
Dordogne River[b]		0.20	0.0483	0.0765	0.0105	0.0374	0.0073	0.0013	0.0081	0.0013		0.0012	0.0043	0.0006	0.0037	0.0007
Garonne River[b]		0.20	0.0471	0.0810	0.0052	0.0384	0.0082	0.0016	0.0088	0.0012		0.0016	0.0041	0.0006	0.0036	0.0006
Columbia River[b]	7.85	0.18	0.0301	0.0583	0.0099	0.0230	0.0435	0.0016	0.0065	0.0012		0.0009			0.0045	0.0007
Sacramento River[b]	7.55	0.05	0.0081	0.0114	0.0072	0.0107	0.0025	0.0010	0.0051	0.0005		0.0004			0.0025	0.0003
BC18[c]	3.10	928.83	185.06	389.58	45.75	172.23	34.82	8.65	40.18	5.00	23.66	4.18	10.50	1.21	7.07	0.94
FC15[c]	3.25	258.22	45.15	95.62	12.08	53.07	12.02	2.82	15.28	2.00	10.34	1.72	4.35	0.48	2.93	0.36
FC142*m*[c]	5.65	142.37	26.75	55.66	6.64	28.70	5.60	1.35	7.35	0.95	4.83	0.84	2.12	0.22	1.21	0.15
FC16[c]	3.40	102.09	19.80	41.60	4.56	18.46	4.00	0.95	4.97	0.65	3.42	0.59	1.60	0.18	1.16	0.15

[a] Data from Hoyle et al. (1984).
[b] Data from Keasler and Loveland (1982).
[c] Samples collected in March 1999.

abundance of REEs in natural waters, including hydrothermal solutions, is usually extremely low, typically several orders of magnitude lower than levels found in most rock types. Only very hot acidic hydrothermal fluids exceed the ppb range (see McLennan, 1989).

3. Study area and sampling

The study area in southern Tuscany lies within the central part of the so-called Metalliferous Hills. This is a chain of hills hosting several ores that were intensively exploited from the Etruscan Era through the Middle Ages until the early 1980s (Tanelli and Lattanzi, 1986). The geology of the area is quite complex from both the stratigraphic and tectonic points of view. Rocks formed between the Paleozoic and the late Tertiary crop out and were folded through several strain events during different orogenic cycles. The ore deposits mined in the study area were mostly pyrite-rich Cu–Zn–Pb sulfides bearing ore-veins. These ores are genetically linked to the hydrothermal fluid circulation active in this area during the late Tertiary, in coincidence with the waning of tectonics related to the rise of the Apennine chain. The sulfide-bearing ore-bodies usually lie along normal faults. They mostly consist of variable amounts of pyrite and magnetite, which accompany sphalerite, galena and chalcopyrite (the metal-bearing mineral phases) and, as gangue minerals, carbonates (calcite + ankerite), Ca-Fe-silicates (pyroxene + garnet + epidote) and quartz (Burtet-Fabris and Omenetto, 1971).

In several mining sites of the area, the ore mineral extraction was coupled with milling and smelting processes; thus huge piles of wastes are locally exposed to rain-wash. Because of the abundance of iron disulfide in the waste materials, this situation favors AMD and the flow of very low pH waters into streams (Davies, 1983; Jambor and Blowes, 1994; Morin and Hutt, 1997).

About 3 km south of the town of Massa Marittima (Fig. 1) is located the most important base metal mining site of the Metalliferous Hills, the Fenice Capanne Mine (FCM), with which we are particularly concerned in this paper. The Fenice Capanne mining area extends over a 4.5 km-wide band which follows two N-S trending lodes, from Capanne Vecchie to Pesta del Carpignone, near Accesa Lake. A number of very old to recent mining works and related wastes are scattered throughout the entire zone. The waters of the streams draining this territory often show strongly anomalous contents of several heavy elements.

The analytical results of a preliminary hydrogeochemical survey, we performed in spring 1999 in this area, showed extremely high REE contents in surface waters sampled downstream of the mining works (Table 1). To investigate this unusual geochemical feature, we planned a special sampling campaign carried

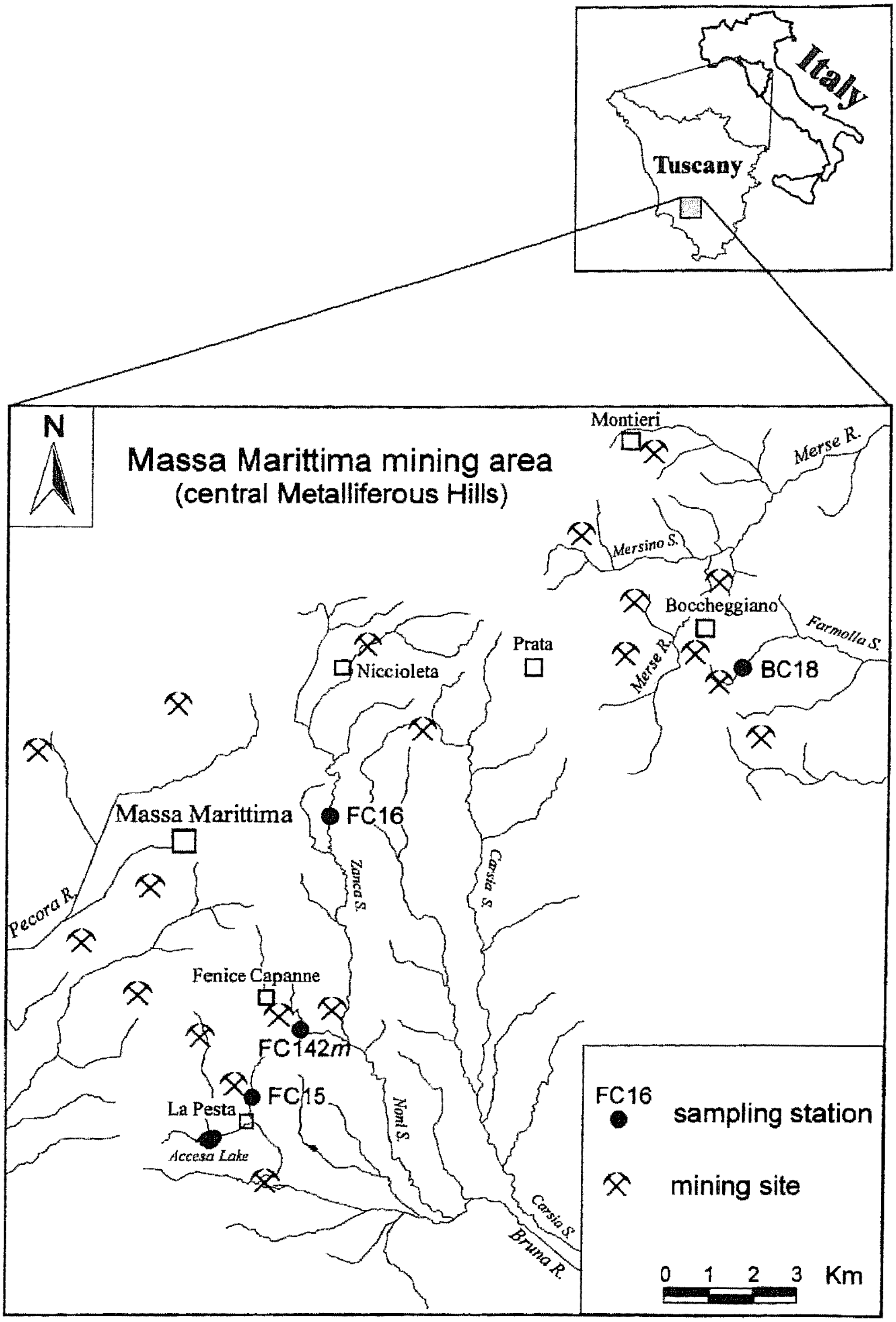

Fig. 1. Map of the Massa Marittima mining area (central Metalliferous Hills).

out in autumn 1999 and spring 2000. Although high REE contents were recognized in several stream waters of the area, we chose to concentrate our efforts on Noni stream, which crosses and drains the waste piles of the FCM, as previously stated the biggest base metal (Cu–Pb–Zn) producer in the Metalliferous Hills.

The FCM was active until 1985 and in its long history produced an imposing stock of wastes, which extends over more than 20 ha. The mining wastes show particular features of spatial distribution. Waste materials lying on the northern and southwestern side of the mining site are the most recent ones and coincide with a vast tailings impoundment where the wastes of milling and flotation processes have accumulated. On the southeastern side, instead, lie gravel-sized reddish materials representing older mine dumps which, in turn, are capped by gray-green colored, cut-off grade materials.

Noni stream (Fig. 2) begins about 1.5 km north of the FCM and crosses the tailings impoundment, receiving the rain-wash and seepage of the wastes. At the southeastern end of the mining site, some waters seep through the older reddish wastes and flow into the stream. Noni stream merges with Bruna River about 6 km downstream of the FCM.

To study the REE distribution in flowing water downstream of the FCM, we established 11 sampling stations along Noni stream. They were distributed (Fig. 2) along a 5 km tract, although most were grouped in the first 1000 m downstream of the FCM wastes.

After a 1-day sampling campaign (TCWD), the stream waters were re-sampled at intervals of a few days following a rainstorm to investigate the expected evolution of water geochemistry due to the progression of both drainage and in-stream phenomena. The water samples were collected at five selected stations during four different sampling cycles performed 2, 6, 10 and 17 days after the rainstorm; they were labeled TCW1–TCW4. Finally, a TCW5 water sampling was also performed 30 days after the main rainstorm, even though some further precipitation occurred at this time; this sampling was specifically for ultra-filtration experiments on flowing stream waters at critical stations. Water samples were filtered on the spot with 0.45 μm cellulose acetate membranes (Scleicher and Schuell) and collected in 1000 cc nalgene bottles.

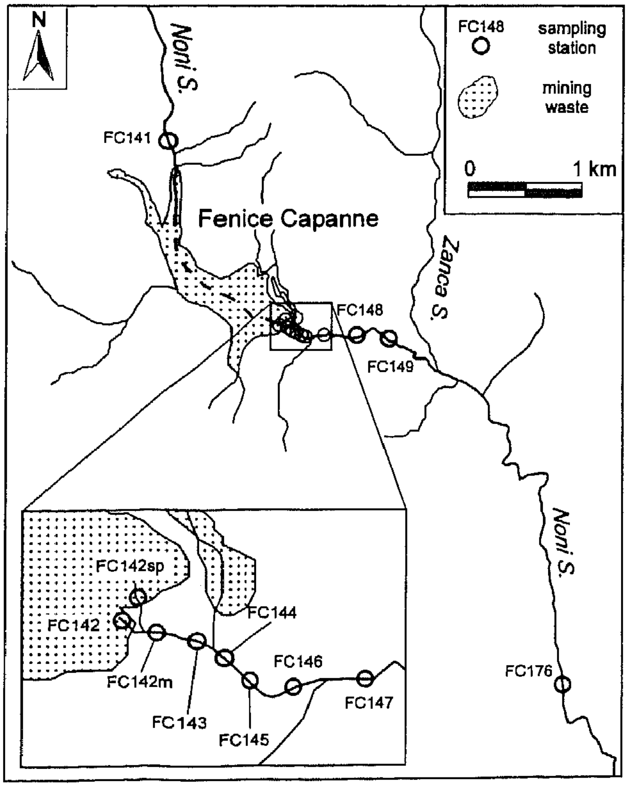

Fig. 2. Map of the Fenice Capanne Mine area with the location of the sampling stations along Noni stream.

As acidic waters move downstream, they become progressively neutralized by possible dilution with clean water flowing into the stream[1] and mostly by the reaction with carbonate rocks of the streambed. As neutralization occurs and pH rises, dissolved ions begin to precipitate. A floating amorphous white floc forms at first, in the upper tract of the stream, when the pH rises above 4.5. The main detected mineral phases in the floc are Al-oxyhydroxide and gypsum.

Further downstream, at higher pH (≅6), divalent iron is massively oxidized to ferric iron and a carpet of orange floc forms; it is mostly composed of poorly crystalline, hydrous ferric oxyhydroxide (HFO) and possibly ferrihydrite.

Both flocs (white and orange) become particularly evident some time after a rainstorm when, and where, the water flow slackens. We collected samples of these flocs for REE content determination, using 100 cc polyethylene syringes with a 30 cm tygon tube at the end to facilitate sample collecting.

Representative samples of the waste materials in the mining site were also taken to determine both the total REE content and the response to leaching experiments.

4. Analytical methods

Stream water samples were routinely filtered at 0.45 μm, collected in 100 cc nalgene bottles and acidified on the spot adding 0.5 cc of trace grade concentrated HNO_3 (Mallinckrodt Baker). It is well known, however, that even 0.2 μm filtered water can contain a mixture of true dissolved species and colloidal particles. Since the colloids can strongly affect the speciation of the elements in stream waters, we also collected some water samples (with no acid added) downstream of the FCM for ultra-filtration to assess the amount of REE elements in the truly dissolved form (Salbu et al., 1985). The ultra-filtration of stream waters was carried out, to the nominal cut-off of 3 kD, by the cross-flow (or tangential) method employing a MidGee system and polysulfone hollow fiber membranes.

The flocs collected along Noni stream were dried at 60°C in an oven. Then 0.15 g were attacked with 3 ml of HCl and 1 ml of HNO_3 and digested in Teflon bombs with a microwave lab-station (Milestone's Ethos 900) to determinate the REE contents. About 0.5 g of the orange (iron-rich) floc were also treated with 20 ml of a

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[1] In its upper tract, a single tributary of Noni stream (Fig. 2) brings some waters with pH 7.8 into the stream during the rainy season.

solution of 0.04 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 25% acetic acid for 6 h at 95°C (Tessier et al., 1979; Kim and Fergusson, 1991) to determine the REEs associated with the amorphous, easily reducible, iron precipitates.

The samples (about 3 kg) of waste materials in the FCM dumps were sieved at 2 mm and then passed through a sample splitter. A 100 g aliquot of the homogeneous sample was powdered in a mechanical agate mortar. About 0.2 g of the fine powder were then attacked with 3 ml of HCl and 1 ml of HNO_3 according to the preparation procedure previously described. We also performed leaching experiments on the samples using 0.43 M acetic acid and 0.1 M nitric acid with a sample/solution ratio of 1 g/40 ml.

Concentrations of REEs and Al were measured by ICP–MS with a Perkin–Elmer Sciex Elan 6100 spectrometer. Since it is difficult to find certified water samples for REE, we performed the analyses against Perkin–Elmer REE standard solutions following the method of additions. Water samples with extremely low REE values were concentrated by partial evaporation to improve the intensity of the signal.

Iron, manganese and calcium contents were determined by AAS with a Perkin-Elmer 5000 spectrophotometer while sulfate ion concentrations in the stream water were measured with a Hatch DR-4000 UV–Visible spectrophotometer following Hatch's 3450 method. The reference materials were the SRM 1643d (Trace Elements in Water) and SRM 2709 (San Joaquin Soil) standards from NIST.

Temperature, pH, Eh and conductivity of the stream water were measured during the field work at the sample collection sites. Temperature, pH and Eh were measured with a Delta-Ohm HD/8705 pH-mV-T meter. Conductivity was measured with a Delta-Ohm HD/8706 conductivity meter.

5. Results and discussion

Water samples collected in streams of the Metalliferous Hills showed unusually high contents of REEs, among the highest published values for surface waters. Table 1 shows the REE contents found in four streams flowing in the study area together with those of six selected rivers reported for comparison. The total REE contents in our water samples are rather variable, but always substantial, reaching the very high maximum value of 928 μg/l.

Fig. 3 illustrates the normalized (PAAS) patterns of the REE contents reported in Table 1. As can be seen from the graph, the REE contents of surface waters in the study area exceed those in reference river waters by at least three orders of magnitude. Furthermore, the stream water in the study area systematically shows a clear convex-up ("roof-shaped") REE distribution pattern. This means that REEs with intermediate atomic numbers and masses (MREEs), from Nd to Gd, are enriched with respect to the LREEs and HREEs elements. A rather similar roof-shaped REE distribution pattern was also found for Luce River (Fig. 3) draining a peaty soil area in southwestern Scotland; its waters are marked by low (4.4–4.5) pH values (Hoyle et al., 1984). Indeed high REE contents often appear to be linked to natural waters with rather low pH (Sholkovitz, 1995; Johannesson et al., 1996; Gimeno et al., 1996; Leybourne et al., 2000).

However, the ultimate source of the REE distribution patterns observed in natural fresh waters is a much debated question. The opposing hypotheses are the signature of outcropping rocks and the effects of "instream" processes. Keasler and Loveland (1982) studied the REE concentrations in some Pacific northwest rivers and found that the abundance of dissolved lanthanide elements were generally similar to the relative abundance in sedimentary rocks. Likewise Hall et al. (1995) found the REE distribution pattern in lake water in

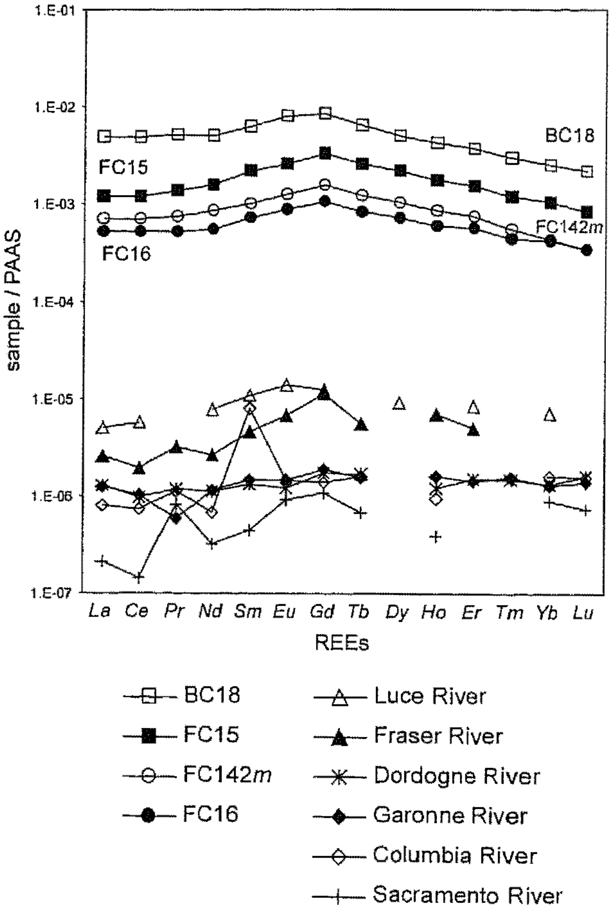

Fig. 3. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for stream waters of the study area and selected reference river waters.

Newfoundland to be very similar to that in the associated sediments, both mirroring the local geology. Conversely, Goldstein and Jacobsen (1988), Elderfield et al. (1990) and Sholkovitz (1995) maintained that the REE pattern in surface water depends mainly on aquatic chemistry rather than on bedrock geology.

Recently Leybourne et al. (2000) argued that this apparent inconsistency can be overcome and at least partially explained by the different scale used by the authors in approaching the phenomenon. For instance, Elderfield et al. (1990) collected their samples from large rivers and it is reasonable to imagine that very large watersheds tend to average the input of different bedrocks. In general, however, it can be assumed that both mechanisms inextricably coexist and control the REE distribution in fresh surface waters.

5.1. The origin of high REE contents and their distribution patterns in surface waters of the FCM area

A strong enrichment of MREEs, with respect to both LREEs and HREEs, and a consequent roof-shaped pattern of normalized values has been recorded frequently in natural waters (Hoyle et al., 1984; Elderfield et al., 1990; Smedley, 1991; Gosselin et al., 1992; Sholkovitz, 1995; Johannesson et al., 1996; Gimeno et al., 1996; Leybourne et al., 2000), mineral phases (Palmer and Elderfield, 1986; Wright et al., 1987; Grandjean-Lécuyer et al., 1993; Hecht et al., 1999) and metamorphic and sedimentary rock leachates (Schaltegger et al., 1994; Zhou et al., 1995).

Nevertheless, the ultimate origin of the roof-shaped pattern in terrestrial natural waters is still not well understood. In fact, Johannesson et al. (1996) listed four different mechanisms as likely reasons for the MREE enrichment. Likewise, Leybourne et al. (2000), at the end of a thorough discussion of the possible source of the MREE enrichment in surface and ground waters at the Bathurst Mining Camp, concluded that MREEs are either more easily leached from the source rocks or are more soluble under the local Eh and pH conditions.

Table 2 reports the REE contents found in water samples collected along Noni stream, together with the values of some relevant parameters, such as pH and Eh, and the concentrations of the main ion species in the aqueous system. As seen in Fig. 2, all the sampling stations are located downstream of the huge pile of wastes in the mining area, except the sample labeled FC141, which refers to Noni stream water collected immediately upstream of the FCM.

An abrupt change of aqueous geochemistry occurs downstream of the FCM, as is clearly seen in the values reported in Table 2. The concentration of various chemical species, such as REEs but also Fe and sulfate ions, is greatly enhanced in sample FC142 in comparison

Table 2
Field parameters, REE and major ion concentrations in Noni stream waters collected during the TCWD 1-day sampling campaign

Sample	pH	Eh (mV)	EC (μS/cm)	$SO_4^{=}$ (mg/l)	Ca (mg/l)	Fe (mg/l)	ΣREE (μg/l)	La (μg/l)	Ce (μg/l)	Pr (μg/l)	Nd (μg/l)	Sm (μg/l)	Eu (μg/l)	Gd (μg/l)	Tb (μg/l)	Dy (μg/l)	Ho (μg/l)	Er (μg/l)	Tm (μg/l)	Yb (μg/l)	Lu (μg/l)
FC141	8.00	210	452	21	66	0.37	0.13	0.0212	0.0194	0.0397	0.0203	0.0101	0.0029	0.0069	0.0010	0.0051	0.0005	0.0002	0.0041	0.0021	0.0007
FC142	5.83	195	1826	1273	331	13.60	75.53	17.200	32.420	3.420	12.700	2.150	0.549	3.095	0.386	1.881	0.350	0.818	0.093	0.408	0.063
FC142*sp*	4.93	272	2110	1753	375	34.50	238.62	49.668	116.790	8.920	28.540	7.890	1.993	9.938	1.371	6.937	1.258	2.976	0.342	1.767	0.228
FC142*m*	5.22	237	1990	1618	360	28.40	174.61	28.818	85.845	7.178	26.710	5.961	1.494	7.713	1.020	5.072	0.923	2.194	0.246	1.271	0.165
FC143	5.75	215	2020	1344	364	26.50	139.55	26.322	56.423	6.520	26.205	5.404	1.380	7.061	0.925	4.781	0.865	2.097	0.230	1.188	0.153
FC144	5.75	156	2020	1613	364	24.00	141.57	26.929	57.374	6.607	26.580	5.421	1.381	7.103	0.923	4.772	0.866	2.076	0.227	1.166	0.149
FC145	5.89	152	1945	1498	361	20.70	125.19	24.351	51.019	5.836	23.409	4.626	1.181	6.089	0.803	4.091	0.741	1.765	0.191	0.961	0.122
FC146	6.11	149	1838	1502	355	8.70	113.06	21.333	63.172	4.577	9.561	3.261	0.822	4.539	0.566	2.785	0.506	1.183	0.120	0.564	0.074
FC147	6.70	146	1411	1030	269	0.29	11.28	4.129	4.617	0.374	1.213	0.148	0.043	0.324	0.038	0.199	0.042	0.099	0.009	0.039	0.005
FC148	6.99	235	1642	1159	321	0.05	8.15	3.587	2.875	0.258	0.816	0.102	0.031	0.202	0.023	0.129	0.027	0.066	0.006	0.026	0.003
FC149	7.13	245	1603	1146	317	0.05	5.25	2.411	1.771	0.156	0.516	0.064	0.019	0.127	0.017	0.082	0.019	0.043	0.006	0.018	0.003
FC176	7.68	182	1448	891	131	0.05	0.34	0.0957	0.1028	0.0171	0.0617	0.0171	0.0089	0.0155	0.0019	0.0089	0.0022	0.0054	0.0011	0.0040	0.0012

with FC141. These chemical variations are also coupled with a significant lowering of the pH.[2]

The normalized patterns of the REE values reported in Table 2 are shown in Fig. 4, which shows a clear MREE enrichment in the group of stream water samples with the higher REE concentrations (FC142–FC146). However, the roof-shaped graph appears rather regular only for four of the seven patterns shown at the top of the figure. Indeed samples FC142*sp*, FC142*m* and FC146 show an unevenness of slope on the LREE side due to a positive peak of cerium and a negative peak of neodymium. We will discuss the meaning of these particular features later. From this situation, it appears intrinsically obvious that both the high concentrations of REEs in Noni stream and the related upward convex shape of the normalized values strictly depend on the acidic washing out of the FCM wastes.

Indeed the infiltrating rain waters interact with the mineral phases in the waste piles, which have different compositions and solubility. The oxidation reactions involving some metal sulfides but mostly iron disulfides (pyrite and marcasite) induce rather low pH values of these waters, which in turn favor the dissolution of particularly sensitive phases such as carbonates. Calcite is relatively abundant in ores of this area and was found as a late mineral in skarn paragenesis, both as vug-filling and substituting Ca-pyroxene and garnet of the main assemblage.

Hydrothermal crustal fluids, such as those likely involved in the formation of the ores of the FCM area, are known in some cases to deposit carbonate minerals with a roof-shaped pattern of normalized REE values (Lüders et al., 1993; Hecht et al., 1999). For instance, Hecht et al. (1999) studied the talc deposit of Göpfersgrün in Bavaria (Germany) and found that vug-filling calcite has relatively high REE contents as well as a roof-shaped pattern of the normalized values. According to Lüders et al. (1993), this feature can be ascribed to a deficiency of LREE remobilization from deep source rocks coupled with a depletion of HREEs. They would be leached with difficulty from the less soluble phases by the chemical element mobilization processes linked to the ascent of the parent hydrothermal fluids.

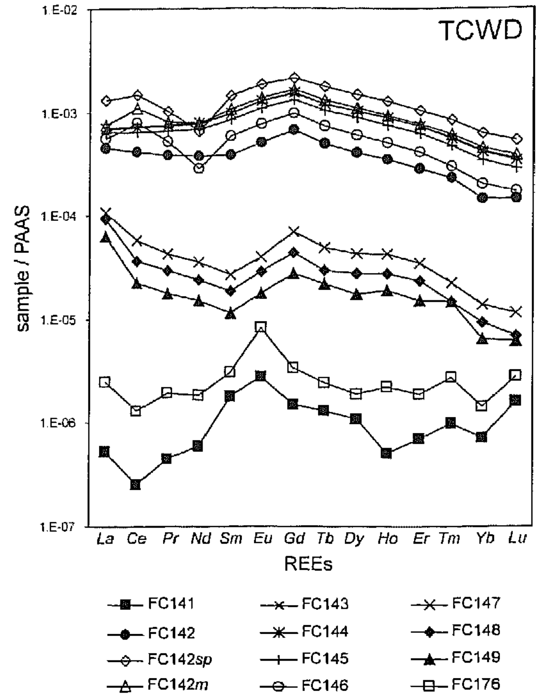

Fig. 4. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for waters of Noni stream (collected during the TCWD 1-day sampling campaign).

However, whatever the real reasons for MREE enrichment in some hydrothermal calcite, we were obliged to consider the calcite in the FCM waste piles as a main candidate phase for the observed discharge of REEs into the stream water. To test this hypothesis, we collected two different calcite samples from the waste materials. We were particularly careful to obtain representative specimens of vug-filling calcite from two sample sets of several hand-picked skarn pieces. The analytical results for REEs contained in these calcite samples are reported in Table 3, while the normalized patterns of the concentrations are shown in Fig. 5. The pattern (quite similar for the two samples) has an asymmetrical shape that indicates a strong enrichment of HREEs and rules out the possibility that calcite dissolution per se explains the REE chemistry observed in our stream water samples.

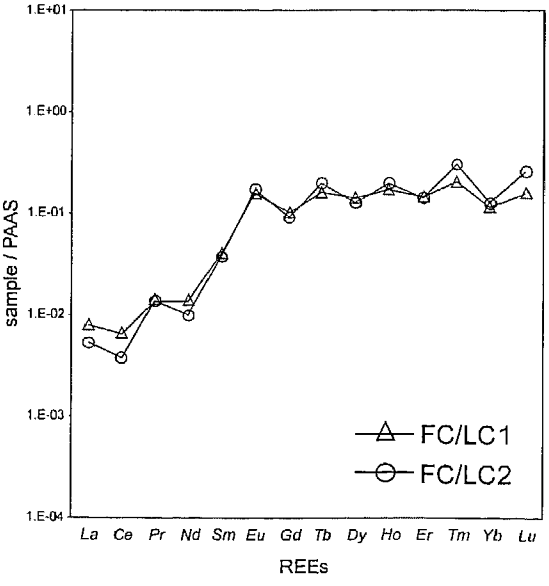

Fig. 5. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for averaged samples of late hydrothermal calcite.

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[2] Even lower pH values have been measured at the FC142 and FC142*sp* sampling stations, depending on the abundance of precipitation and the timing of sampling operations. The lowest recorded values are pH = 4.85 and pH = 3.80, respectively.

Table 3
REE contents (mg/kg) in late hydrothermal calcite

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
FC/LC1	307.97	515.81	118.94	471.21	227.00	172.91	479.98	125.93	671.58	171.44	421.80	84.65	329.94	68.85
FC/LC2	204.78	305.23	121.83	338.58	209.59	187.92	431.12	155.46	604.98	198.84	411.71	124.05	360.21	114.27

To settle the question, we performed several leaching experiments on representative samples of the various materials at the mining site. Samples of seven materials were collected from the FCM wastes and attacked with 0.43 M acetic acid to simulate the leaching ability of acidic waters on the REEs. The sample labeled FC/OW1, from the southeastern side of the mining site and representing the reddish gravel-sized material of the oldest dumps, was also subjected to leaching tests with both 0.1 M nitric acid and a $HCl+HNO_3$ mixture ("aqua regia"). Table 4 reports the analytical results of the leaching experiments while Fig. 6 illustrates the pattern of the normalized values of the REE concentrations.

The experiments performed on the waste materials were very instructive about the concerns being faced. Indeed all the waste materials released important aliquots of REEs after acidic leaching, albeit to a variable degree. Furthermore, MREE enrichment appears to be a generalized trend, as shown by the upward convex shape of the distribution patterns which, except for the enhanced peak of europium in some samples, show the characteristic roof-like form. In particular, the materials from the oldest mining wastes appear to be the main contributors to the stock of REEs periodically released by acidic washing and deposited in Noni stream. However, the question remains about the identity of the important REE-bearing phases in the waste materials. We will not avoid discussion of this thorny subject but will defer it to a later section.

5.2. *Contents and geochemical behavior of REEs in the waters of Noni stream*

Fig. 4 summarizes the evolution of both the contents and distribution patterns of REEs along Noni stream up to 5 km from the FCM, where the lanthanide concentrations (FC176) become comparable with those of flowing water upstream of the mining site (FC141). In general, the REE concentrations decrease with the distance from the FCM, while the distribution patterns also exhibit significant changes in shape. Nevertheless, the reduction of REE concentrations is not regular and shows a sharp discontinuity between samples FC146 and FC147 when the pH value is near neutrality.

However, in discussing the phenomenological meaning of this graph, it seems convenient to begin with the cluster of REE distribution patterns situated at the top of the figure.

The highest REE content is in the FC142*sp* sample, which represents the important seep flowing from the southeastern side of the mining site into Noni stream. In addition to a clear enrichment of MREEs, the pattern of this water sample (like that of the subsequent sample FC142*m*) also shows a sharp positive peak for cerium and a slight indication of a negative peak for neodymium. However, both features appear to be quickly reabsorbed, since the next water sample downstream (FC143) presents a rather regular slope, indicating a sudden drop in the cerium content. This probably reflects the oxidation of Ce^{3+} to Ce^{4+} and its removal from solution on account of its high surface reactivity with respect to the adjacent trivalent REEs (Byrne and Kim, 1990).

Since terrestrial waters frequently show more or less pronounced negative cerium anomalies (Elderfield et al., 1990; Smedley, 1991; Miekeley et al., 1992; Leybourne et al., 2000; Johannesson et al., 2000), our data strongly support the conclusions of Leybourne et al. (2000) concerning a rather rapid development of these anomalies in surface waters.

A further positive peak for cerium and a pronounced negative peak for neodymium appear in the pattern of sample FC146, which disproves (at least apparently) our previous statements. We will demonstrate, however, that the cerium peak is not real, but hides the complex dynamics of the in-stream processes. This water sample and the preceding one (FC145) coincide with a sort of boundary (established by the pH values), beyond which (FC147) the dissolved iron is drastically depleted (Table 2) and its precipitation heavily affects the aqueous geochemistry of the REEs. The dramatic changes in the REE geochemistry of stream waters when the pH shifts from slightly acidic ($pH \cong 6$) to neutral ($pH \cong 7$) is mirrored in Table 5 (which reports the data from the ultrafiltration[3] experiments at two critical sampling stations).

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[3] The ultra-filtration experiments (using a 3 kD filter) showed that nearly all the REEs are largely in the dissolved form until the pH is slightly acidic ($pH < 6$). Indeed both free metal and REE complexes, with various ligands, can theoretically be present in the aqueous solution, and several authors have attempted speciation modeling calculations of REEs in natural waters (Wood, 1990; Lee and Byrne, 1992; Millero, 1992). Nevertheless, a great many studies have been performed on waters with relatively high pH (e.g. seawater), while relatively few studies have dealt with acidic waters (Johannesson and Lyons, 1995). According to these authors, in low pH and high sulfate waters (which might be our case), REE-sulfate complexes form an important component of the REE speciation and may increase the dissolved concentrations of REEs with respect to low sulfate waters. The same authors suggested that, according to their calculations, REE-sulfate complexes dominate in such a situation over the free metal form. However, Leybourne et al. (2000) found that at acidic pH values ($pH < 6$), free REEs are the dominant species, particularly the LREEs.

Table 4
REE concentrations (μg/kg) and Fe contents (%) in leachates of the FCM waste materials

Sample	Sample description	Leached by[a]	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Fe (%)
FC/OW1	Gravel-sized reddish material from the oldest dumps	AcA	1388.72	3086.57	445.54	2388.29	498.86	115.44	470.56	47.98	301.94	41.36	125.11	11.43	78.76	7.80	0.010
	Gravel-sized reddish material from the oldest dumps	Na	3844.33	8460.68	1060.26	5286.16	1073.36	237.86	1026.00	102.13	614.05	82.07	242.94	21.67	145.83	14.09	0.126
	Gravel-sized reddish material from the oldest dumps	AR	17028.39	34206.66	3822.88	14172.29	2501.27	641.82	2342.23	280.33	1292.59	218.21	515.76	56.62	319.95	38.33	16.44
FC/OW2	Gravel-sized reddish material from the oldest dumps	AcA	895.25	2530.52	360.35	1939.77	406.47	94.16	384.92	37.42	191.58	33.71	85.24	9.28	56.28	6.32	0.009
FC/FB1	Yellow-brown sandy material from the tailings impoundment	AcA	103.41	187.06	28.06	114.05	27.12	7.99	24.53	3.35	16.80	3.13	8.22	1.04	5.79	0.71	0.004
	Yellow-brown sandy material from the tailings impoundment	AR	2948.20	5923.93	707.32	2744.97	502.06	139.36	470.82	62.79	291.52	56.01	137.65	18.80	94.73	14.89	1.51
FC/FB2	Whitish sandy material from the tailings impoundment	AcA	24.20	49.54	6.01	26.01	5.13	6.97	6.05	0.57	4.18	0.65	1.80	0.29	1.75	0.50	0.001
	Whitish sandy material from the tailings impoundment	AR	1890.86	3766.87	441.95	1692.38	305.51	94.87	267.29	33.13	134.29	24.74	59.51	8.58	41.89	6.05	0.18
FC/FB3	Grey-brown sandy material from the tailings impoundment	AcA	2621.48	4587.19	583.38	2241.85	436.01	117.90	496.37	68.76	388.69	74.97	198.73	23.78	137.56	17.83	0.055
	Grey-brown sandy material from the tailings impoundment	AR	9696.36	19341.63	2287.52	8832.89	1752.30	452.86	1888.09	254.72	1334.17	242.65	631.13	79.04	445.14	54.77	3.22
FC/FB4	Yellow-brown silty material from the tailings impoundment	AcA	150.57	355.83	46.67	192.92	39.05	9.98	35.10	3.68	19.37	2.89	7.74	0.58	4.87	0.37	0.007
	Yellow-brown silty material from the tailings impoundment	AR	3503.94	7271.88	869.08	3338.35	581.74	156.43	528.91	63.13	299.51	50.84	138.39	17.36	86.35	11.20	2.83
FC/FB5	Yellow silty material from the tailings impoundment	AcA	76.52	181.12	21.84	89.18	19.19	10.22	18.97	2.00	13.00	2.02	5.99	0.44	4.48	0.24	0.004
	Yellow silty material from the tailings impoundment	AR	4016.76	8123.10	913.71	3525.99	644.22	225.41	594.47	70.57	321.57	57.88	151.60	18.96	108.21	13.70	2.52

[a] AcA, acetic acid 0.43 M; Na, nitric acid 0.1 M; AR, 3 HCl + 1 HNO_3.

Table 5
REE concentrations (μg/l) in filtered waters (TCW5) of Noni stream

Sample	Nominal cut	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
FC145	0.45 μm	5.94	20.089	38.091	3.993	15.112	2.687	0.678	3.827	0.456	2.247	0.408	0.966	0.096	0.441	0.061
	3 KD		19.173	36.969	3.989	14.864	2.634	0.674	3.799	0.454	2.239	0.407	0.956	0.093	0.437	0.059
FC149	0.45 μm	6.70	10.720	14.437	1.214	3.957	0.491	0.135	1.023	0.106	0.493	0.096	0.208	0.017	0.079	0.011
	3 KD		5.062	4.294	0.266	0.700	0.054	0.016	0.149	0.013	0.058	0.010	0.022	0.002	0.007	0.001

In Fig. 7, the REE and Fe contents in stream waters appear to be very closely related. This clearly indicates the strong scavenging property of colloidal iron flocs towards REEs.

The rather regular slope of the plots is broken, however, by sample FC146 (we have explained previously the case of samples FC142*sp* and FC142*m*). The anomaly of this sample is particularly evident for the cerium content, although some shifting can also be perceived (more or less clearly) for other REEs. To explain the odd anomaly constituted by sample FC146, we must first consider that it was filtered at 0.45 μm. Thus colloidal, REE-bearing fine particles were likely taken up along with the dissolved phase. This hypothesis is also suggested by the evidence of the mentioned solute removal and the presence of iron precipitates coating the streambed. However, any explanation of these observations by co-precipitated REE elements together with iron colloids is refuted by the data of Tables 2 and 6. In fact, if the cerium enrichment observed in sample FC146 was due to the entrapment of particles of REE-rich Fe precipitates, we also would have found a proportionally much higher Fe content.

An hypothesis involving Al-rich or Ca-sulfate phases is certainly possible, or even probable, on the basis of the presence upstream of the whitish flocs previously

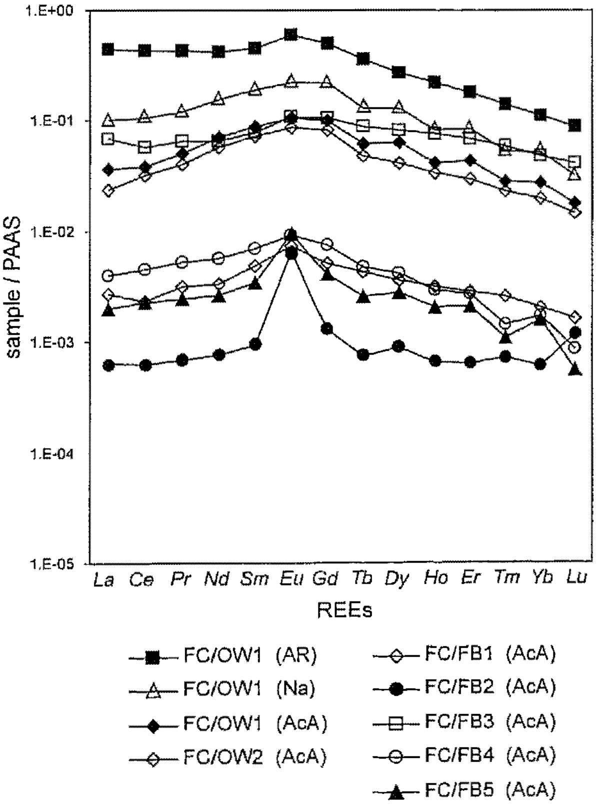

Fig. 6. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for the leachates of waste materials of the Fenice Capanne Mine.

Table 6
REE, Fe, Mn and Al concentrations in leachates of flocs in Noni stream

Sample	Leached by[a]	La (μg/kg)	Ce (μg/kg)	Pr (μg/kg)	Nd (μg/kg)	Sm (μg/kg)	Eu (μg/kg)	Gd (μg/kg)	Tb (μg/kg)	Dy (μg/kg)	Ho (μg/kg)	Er (μg/kg)	Tm (μg/kg)	Yb (μg/kg)	Lu (μg/kg)	Fe (%)	Mn (mg/kg)	Al (%)
WHF1	AR	903	2622	381	1660	466	138	457	77	496	87	269	44	318	38	3.4	202	28.3
WHF2	AR	1193	3822	584	2622	742	195	720	121	780	145	418	65	509	64	4.6	195	16.5
OF1	hh	9198	26 579	3589	15 134	3492	867	3615	831	2816	507	1309	164	984	121			
	AR	15 113	38 617	5068	20 657	4596	1058	4704	903	3575	635	1624	203	1216	155	16.8	581	8.2
OF2	hh	15 020	43 340	4568	19 328	3666	911	4240	537	2779	493	1218	127	678	84			
	AR	17 515	45 202	5625	22 202	4436	1065	5049	649	3222	577	1406	153	819	102	25.9	501	5.8

[a] AR, 3 HCl + 1 HNO_3; hh, hydroxylamine hydrochloride 0.04M.

described. Nevertheless, alternative options, such as formation of a scavenging organic colloid or REE polymeric hydroxyl, cannot be disregarded.

The sharp depletion of neodymium in sample FC146 is likely related to a preferential fractionation of the element into the early forming iron colloids. The gap in REE contents dividing sample FC146 from the following three samples (Fig. 4) and the different shape of their normalized patterns undoubtedly are the result of the near complete precipitation of the dissolved iron and the related REE scavenging. This statement is strengthened by the results of the chemical analyses of the collected flocs reported in Table 6. It is interesting to note the great difference in absolute REE contents between the early precipitated Al-rich flocs and the Fe-rich ones. Indeed the REEs contained in the whitish Al-rich flocs present in the uppermost tract of the stream are quite subordinate. This means that iron colloids have by far the major role in scavenging REEs from aqueous solution.

As seen in Fig. 8, the sharp quantitative diversity of REE contents in the two floc types is also coupled with a different distribution pattern of the normalized values; in fact, the Al-rich flocs also show a significant enrichment of HREEs. However, the most important feature expressed in Fig. 8 is the roof-shaped REE pattern of the Fe-rich flocs. The survival of this pattern in the in-stream processes strongly suggests that iron oxides/

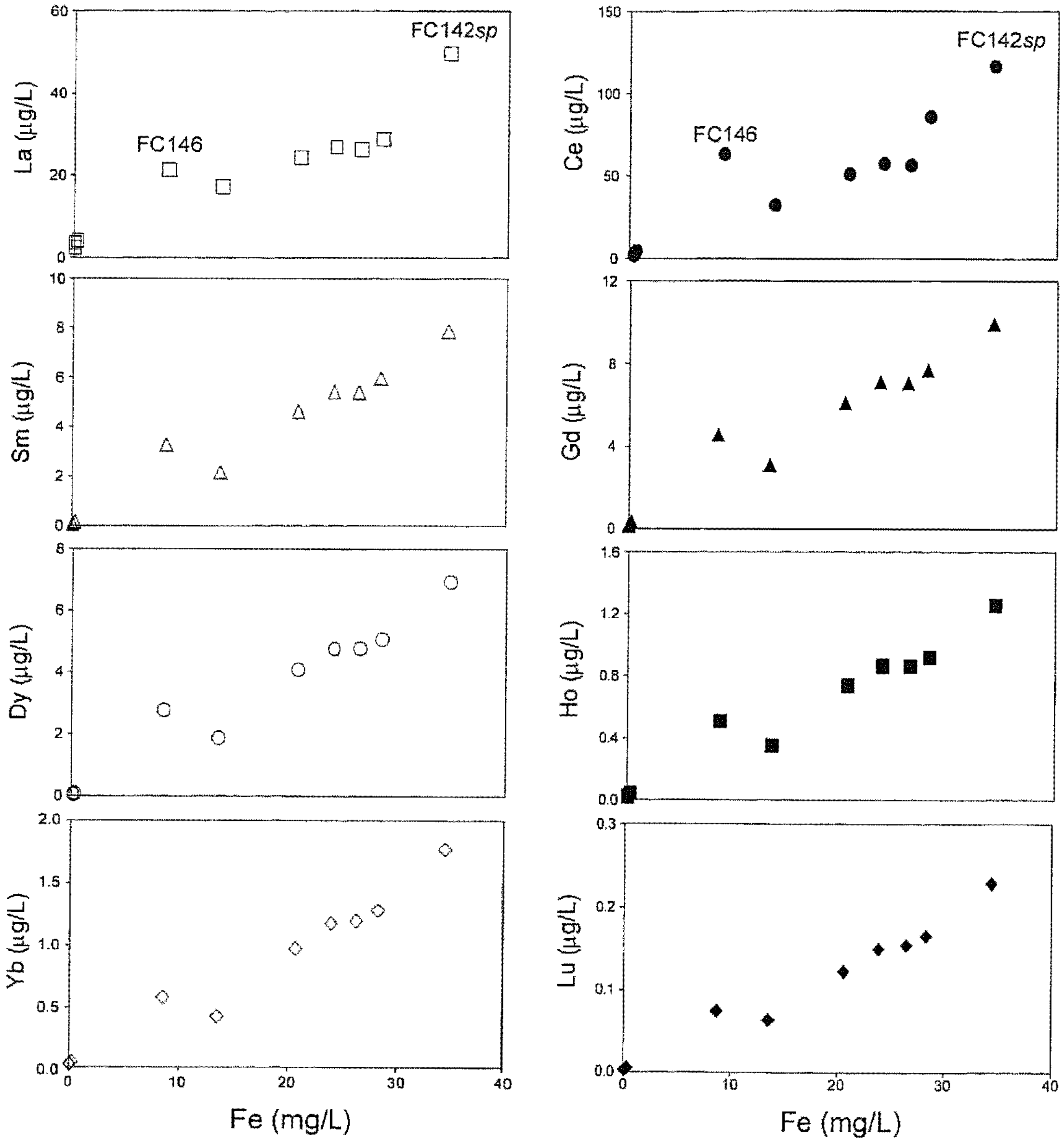

Fig. 7. Binary plots of Fe versus REE concentrations in water samples of Noni stream (collected during the TCWD 1-day sampling campaign). It is remarkable the close relationship between Fe and rare earth element (REE) concentrations. Conversely the relationships between Mn/REEs and Al/REEs resulted rather random.

oxyhydroxides are the chief REE-bearing phase at the source and are the ultimate controlling factor responsible for the roof-shaped REE pattern of the stream water. In our opinion, it is not by chance that the reddish gravel-sized material of the oldest FCM wastes (which appears to be the main REE contributor) has such a high Fe content (Table 4). Thus, all the results clearly support the hints, or the (more or less) explicit suggestions, of various authors (Elderfield, 1990; Gosselin et al., 1992; Johannesson and Lyons, 1995; Johannesson et al., 1996; Johannesson and Zhou, 1999; Leybourne et al., 2000) about the close relationship between iron oxides and the MREE enrichment sometimes observed in natural waters.

Although the last water sample (FC176), collected some kilometers downstream of the FCM, has slightly higher REE values than the unpolluted sample (FC141), it greatly resembles it in pattern shape (Fig. 4). Both samples present a negative peak of cerium while, curiously, the peak constantly centered on gadolinium in all previous samples is sharply shifted onto europium in both FC176 and FC141. For sample FC176, this coincides with a drastic lowering of the dissolved calcium contents (Table 2). It is likely related to the precipitation of specific calcium phases, such as carbonates, preferentially hosting gadolinium rather than europium. Indeed de Baar et al. (1985) noted a slightly different behavior of gadolinium with respect to the neighboring europium in seawater and suggested that the difference might be due to the special electronic configuration of Gd, particularly the different number of electrons in the inner *4f* shell. This point of view, however, was later questioned by Taylor and McLennan (1988) and Brookins (1989).

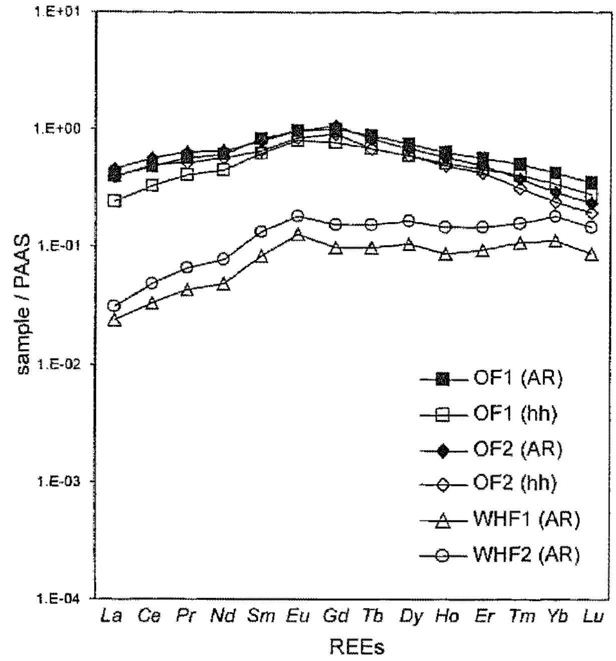

Fig. 8. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for Noni stream flocs attacked with both hydroxylamine hydrochloride (hh) and a 3 HCl+1 HNO_3 mixture (AR).

Table 7
REE concentrations (μg/l) in water samples of Noni stream collected at intervals of a few days after a rainstorm (see text)

Sampling cycle	Sampling station	Date	pH	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
TCW1	FC142	13/07/2000	5.48	17.782	35.755	3.912	15.813	2.709	0.542	4.026	0.485	2.554	0.443	1.037	0.090	0.508	0.048
	FC142*sp*	13/07/2000	3.96	81.326	201.300	24.259	106.770	24.075	6.127	32.643	4.362	23.217	4.069	10.077	1.148	6.368	0.781
	FC142*m*	13/07/2000	5.08	28.083	61.002	7.012	29.391	5.912	1.422	8.301	1.103	5.545	1.015	2.398	0.289	1.361	0.199
	FC145	13/07/2000	5.43	23.497	46.947	5.226	21.724	4.059	0.906	6.065	0.741	3.871	0.677	1.599	0.145	0.773	0.081
	FC147	13/07/2000	5.74	19.704	35.290	3.773	15.123	2.428	0.525	4.159	0.480	2.451	0.436	1.003	0.081	0.390	0.034
TCW2	FC142	17/07/2000	5.14	34.448	73.098	8.446	34.652	6.706	1.480	23.694	2.979	15.615	2.694	6.668	0.711	3.906	0.492
	FC142*sp*	17/07/2000	3.92	83.543	203.101	24.610	109.337	25.353	6.205	84.751	11.302	60.526	10.727	26.534	2.997	16.724	2.122
	FC142*m*	17/07/2000	4.83	45.047	100.306	11.844	50.396	10.714	2.528	39.282	5.187	26.970	4.786	11.774	1.412	7.197	1.026
	FC145	17/07/2000	5.12	40.883	86.803	10.168	42.779	8.871	2.030	30.983	3.944	21.052	3.612	8.984	0.977	5.353	0.663
	FC147	17/07/2000	5.77	31.363	61.765	7.071	29.513	5.682	1.256	20.693	2.583	13.347	2.328	5.610	0.568	2.952	0.369
TCW3	FC142	21/07/2000	4.85	33.607	70.195	8.249	40.526	8.163	2.046	9.443	1.019	6.469	0.905	2.774	0.252	1.731	0.172
	FC142*sp*	21/07/2000	3.80	67.635	162.861	19.866	103.857	24.101	6.312	29.323	3.252	21.245	3.023	9.394	0.867	6.040	0.604
	FC142*m*	21/07/2000	4.72	36.608	79.672	9.395	47.141	9.968	2.530	11.873	1.265	8.226	1.172	3.571	0.318	2.204	0.221
	FC145	21/07/2000	4.94	34.643	72.562	8.612	43.137	9.078	2.341	10.999	1.158	7.468	1.063	3.191	0.295	1.967	0.200
	FC147	21/07/2000	5.76	28.993	57.540	6.666	32.971	6.743	1.694	8.254	0.847	5.512	0.776	2.296	0.201	1.286	0.131
TCW4	FC142	28/07/2000	4.98	30.883	65.067	7.512	36.765	7.348	1.830	8.616	0.916	5.939	0.824	2.497	0.233	1.553	0.157
	FC142*sp*	28/07/2000	3.88	66.088	160.777	19.460	103.252	23.916	6.220	28.920	3.159	21.107	3.002	9.255	0.853	5.908	0.611
	FC142*m*	28/07/2000	4.81	35.818	76.740	9.059	45.453	9.530	2.460	11.545	1.240	7.975	1.139	3.413	0.311	2.127	0.215
	FC145	28/07/2000	4.99	35.332	73.971	8.660	43.678	9.205	2.329	11.102	1.182	7.670	1.081	3.251	0.301	2.004	0.203
	FC147	28/07/2000	5.59	30.582	60.833	7.201	35.292	7.186	1.869	8.811	0.932	5.894	0.842	2.522	0.219	1.456	0.141

Finally, Table 7 and Fig. 9 present the data from the repeated stream water collection performed at intervals of various days along Noni stream after a violent rainstorm. Fig. 9 clearly shows that the patterns of normalized REE concentrations in the water change shape somewhat with time. These changes (particularly evident in TCW2) reflect the dynamics of progressive extraction of REE elements (from waste materials), which appear to behave rather dissimilarly (Fig. 10). The lack in TCW1 of the previously observed positive cerium peak might be related to this, at least in part.

On the whole, the impression is that we are looking each time at a single frame of a rather complicated movie. However, in view of the rate and variability of

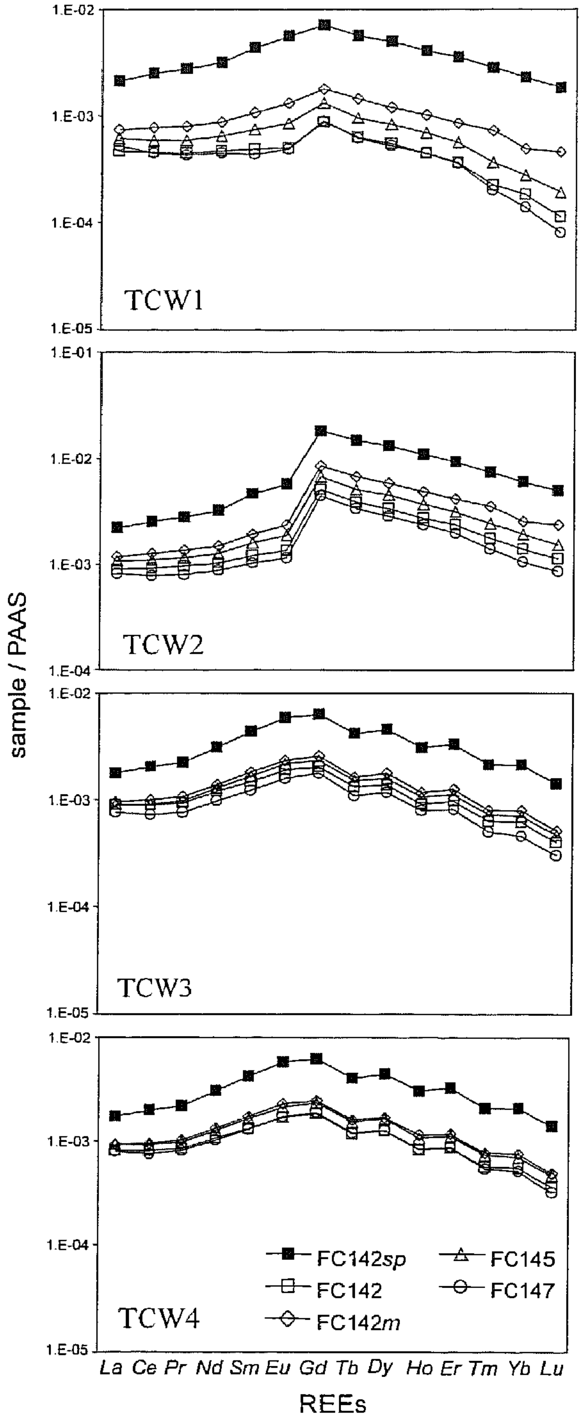

Fig. 9. Rare earth element (REE) diagram normalized to Post-Archean Australian Shales (PAAS) for Noni stream waters collected during the periodic re-sampling campaigns.

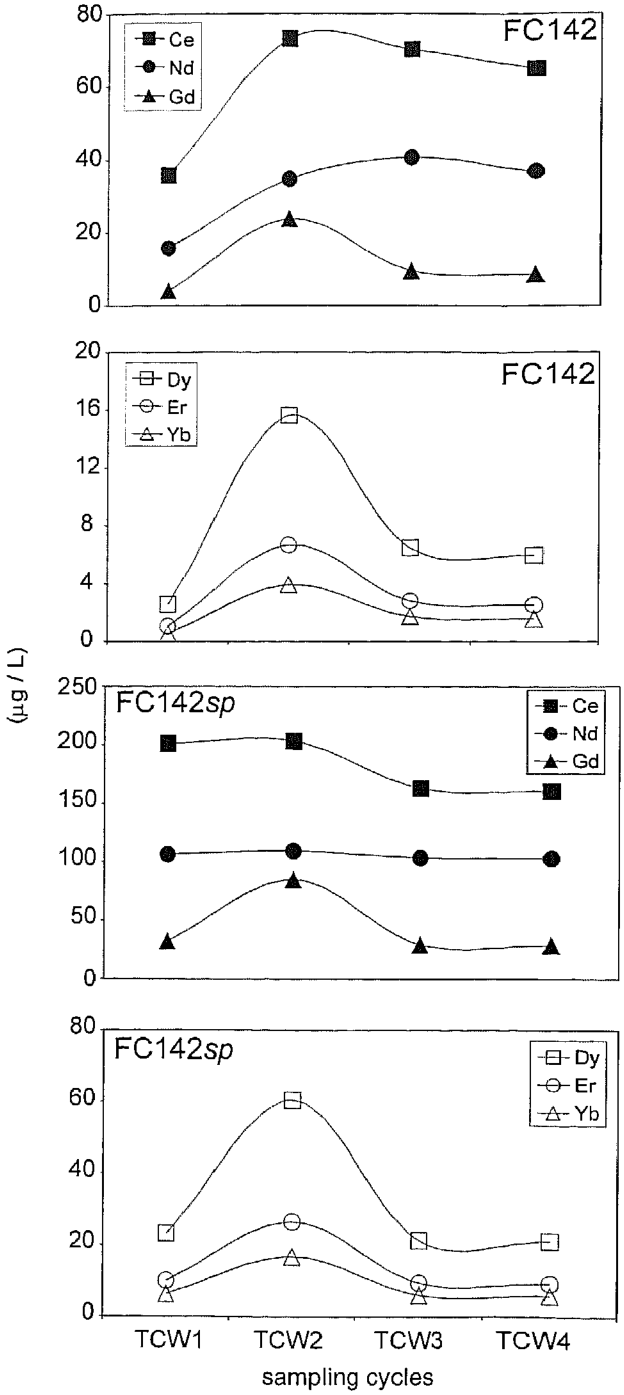

Fig. 10. Variation in time of the natural rare earth element (REE) leaching, as recorded in Noni stream waters by repeated sampling cycles downstream of the Fenice Capanne Mine (FCM) wastes (see text).

water flow through the waste piles, coupled with the many possible solution/precipitation reactions and their kinetics (easy to imagine in such a complex geochemical system), the observed differences among the diagrams are not surprising. We will avoid commenting further on these graphs (which despite the evident discrepancies substantially confirm our previous observations) and will defer a full discussion of this interesting topic to future works.

6. Concluding remarks

Acidic waters of streams draining old mining sites in the Metalliferous Hills (southern Tuscany) show abnormally high concentrations of rare earth elements (lanthanide series). The PAAS-normalized values of REEs provide a peculiar "roof-shaped" distribution pattern, indicating that MREEs are enriched with respect to both LREEs and HREEs. The REE signature of these waters clearly derives from the rain-wash of tailings. This is also true for Noni stream, which drains the wastes of the Fenice Capanne Mine where the oldest iron-rich dumps release bulk REEs.

The in-stream geochemical history of REEs, whose evolution along Noni stream was investigated, offers some interesting insights into the behavior of this group of elements in aqueous solution:

- Cerium undergoes rather rapid oxidation processes (Ce^{3+} to Ce^{4+}) in the stream water. Thus, the positive cerium peak, present in waste leachates, is promptly reabsorbed in the initial tract downstream of the FCM.
- The pH is once again a crucial parameter and clearly affects the geochemistry of REEs in stream water.
- Gypsum-bearing Al-rich flocs precipitate as the pH exceeds 4.5. These flocs fractionate a relatively small aliquot of REEs ($\cong$10% with respect to later precipitated Fe-oxyhydroxides) and are HREE enriched.
- There is a very good positive correlation between the measured concentrations of Fe and REEs in the stream waters (as shown by the Fe versus REE plots).
- As pH approaches neutrality, Fe-oxyhydroxides precipitate and effectively scavenge REEs, which are drastically removed from aqueous solution. In particular, neodymium seems to be scavenged earlier or faster than other rare earth elements.
- Water samples collected progressively further from the FCM wastes show both a clear evolution of the shape of the patterns of normalized REE concentrations and a decrease of the absolute values.
- The progressive change in the shape of the REE patterns involves a shift of the MREE peak value from gadolinium to europium. This likely reflects competition by the two elements for the lattice sites of newly forming Ca-bearing phases (i.e. carbonates).
- About 5 km downstream of the FCM, the REE patterns (despite the slightly higher absolute values) again become quite similar to the upstream FMC values.

Finally, the leaching experiments conducted on waste materials and Fe-rich flocs showed that Fe-oxides/oxyhydroxides play a crucial role in both the input and removal of REEs in stream waters. These mineral phases should be considered a chief factor that can strongly influence the geochemistry of REEs in terrestrial waters.

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