

# The signature of river- and wind-borne materials exported from Patagonia to the southern latitudes: a view from REEs and implications for paleoclimatic interpretations

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## Abstract

Riverine and wind-borne materials transferred from Patagonia to the SW Atlantic exhibit a homogeneous rare earth element (REE) signature. They match well with the REE composition of Recent tephra from the Hudson volcano, and hence this implies a dominance of material supplied by this source and other similar Andean volcanoes. Due to the trapping effect of proglacial and reservoir lakes, the larger Patagonian rivers deliver to the ocean a suspended load with a slightly modified Andean signature, that shows a REE composition depleted in heavy REEs. In this paper we redefine Patagonia as a source of sediments, which is in contrast with other sources located in southern South America. Quaternary sediments deposited in the northern and, to a lesser extent, in the southern Scotia Sea, and most of the dust in ice cores of east Antarctica have REE compositions very similar to the loess from Buenos Aires Province and to Patagonian eolian dust. However, we rule out Buenos Aires province as a Holocene major source of sediments. Similarly to Buenos Aires loess (a proximal facies), it is likely that the REE compositions of most sediment cores of the Scotia Sea and Antarctica reflect a distal transport of dust with an admixed composition from two main sources: a major contribution from Patagonia, and a minor proportion from source areas containing sediments with a clear upper crustal signature (e.g., western Argentina) or from Bolivia's Altiplano. Evidence indicates that only during the Last Glacial Maximum, Patagonian materials were the predominant sediment source to the southern latitudes.

*Keywords:* rare earth elements; eolian dust; Patagonia; South Atlantic Ocean; Antarctica

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## 1. Introduction

A considerable proportion of the Quaternary deposits in the South Atlantic Ocean are terrige-

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nous sediments [1]. Although a significant effort has been dedicated to study their origin [1–6], uncertainties remain about their provenance.

The southernmost tip of South America (i.e., south of ca. 40°S) is the closest land mass to the southern latitude environments, which are potentially important in terms of eolian and fluvial terrigenous supply. However, there is insufficient information on the provenance of the material exported from this region. Up to now the importance of Patagonia as a particle supplier to the South Atlantic Ocean and Antarctica was a matter of speculation (e.g., [4–10]), as there is not enough information related to the chemical and mineralogical composition of the high-latitude South American material ready to be transported.

Three main transport agents supply detrital sediments from land to ocean: rivers, glaciers, and winds. A global budget indicates that the riverine supply of lithogenic particles towards the global ocean is about one order of magnitude higher than the eolian supply [11]. However, for the particular case of Patagonia (cliff erosion not being considered), the atmospheric contribution represents a minimum of 90% of the mass of Patagonian sediments delivered to the ocean as compared to the riverine path [12]. This important difference is explained by the trapping effect exerted by numerous proglacial lakes located on the eastern slope of the Andes.

The importance of eolian dust as a supplier of particles to the South Atlantic Ocean has been recently documented [12]. Due to the arid conditions prevailing in the Patagonian plateau, dust deposition is a major process triggered by intense dominant westerlies. Presently, dust fallout data measured at the Patagonian coastline indicate that total dust fluxes have a mean of 35 g m<sup>-2</sup> yr<sup>-1</sup> [12]. Nevertheless, evidence indicates that the dust flux was about 15 times higher during glacial times [13] and points to the importance of this region as a major dust supplier to the surrounding environments during those times.

The rare earth elements (REEs) form a coherent group (La trough Lu) that generally exhibit a similar chemical behavior and so are widely used to address geochemical and oceanographic questions. Their low solubility and relative immobility

in the terrestrial crust make REEs a very useful tool in studying the provenance of sediments because they inherit the REE composition of their source. One of the main objectives of this paper is to assess the role of Patagonia as a past and current supplier of sediment to the South Atlantic and to Antarctica. Hence, by using their REE compositions we seek to establish in this study the main material sources and the chemical signature of riverine and wind-transported particles from the southern tip of South America.

## 2. Study area

Continental Patagonia (between 39° and 52°S) covers an area of about 700 000 km<sup>2</sup>. The climate is controlled by the westerlies dynamics, which blow from the Pacific Ocean, discharging most of their moisture on the Andes and continuing as dry winds to the east.

Only a narrow strip along the Andes (about 15% of the total area) has a rainfall higher than 800 mm year<sup>-1</sup>. It turns out that a reduced area along the Andes, with steep slopes and heavy rainfall, is the active supplier of most of the weathered material that ultimately reaches the ocean.

The geology is dominated by volcanic rocks (basalts, andesites, rhyolites), continental and, to a lesser extent, marine sediments. Outcrops of basement exhibit a wide range of crystalline and sedimentary sequences and are confined to relatively small areas within the Patagonian massif and in the Andean Cordillera. In the Deseado massif, the basement is intruded by early Jurassic monzonitic plutons and represents the easternmost plutonic rocks [14]. In the North Patagonian massif, granitoids form extensive plutonic–volcanic complexes beneath the plateau basalts of the Meseta de Somún Curá. In the southwestern part of the massif, gneisses of possible Carboniferous and Permian age are overlain by the batholith of central Patagonia, with Triassic granodiorite and leucogranites [15].

Jurassic silicic volcanic rocks (Chon Aike province) cover an area of about 1 million km<sup>2</sup> and represent one of the largest rhyolitic provinces in

the world [15,16]. Although these volcanic rocks are predominantly pyroclastic, dominated by ignimbrites of rhyolitic composition [17], they exhibit consistent bimodality between rhyolite and andesite–basaltic andesite [18].

In the Andes, orogenic volcanism is the result of subduction of oceanic lithosphere along and below the western margin of South America. The geomorphological characteristics of Patagonia are mostly delineated by the Cenozoic volcanism. This volcanism is defined by Rapela et al. [19] as the Patagonian Volcanic Province and includes two main volcanic series. The Cordilleran Series to the west (volcanic arc from the Paleocene up to the Present) is located along the Patagonian Andes between 40 and 43°S. Here, the major episodes began with silicic associations and ended with intermediate to basic lava flows [19]. The Plateau Basaltic Series to the east (back-arc) outcrops all along the Patagonian territories with typical basaltic composition [20].

During the Late Pleistocene and Holocene, frequent volcanic eruptions occurred in the Andean region. Quaternary volcanic centers studied by Futa and Stern [21] indicate a dominantly basaltic and basaltic andesite composition for these lavas. Widespread Holocene fallout deposits of tephra in southern Patagonia were attributed to two large explosive eruptions of the Hudson volcano [22]. This volcano has produced at least 12 explosive eruptions during the Holocene, including that of August 1991. The Hudson andesite has a characteristic calc-alkaline pattern [23]. Naranjo et al. [24] suggested that the mixing of mantle-derived basalt with andesite, within an upper crustal magma chamber, triggered the eruption [25]. Furthermore, east of the Andes, Quaternary olivine basalts are widespread, covering an area of about 120 000 km<sup>2</sup> [26,27].

The glaciers of the Southern Andes poured out enormous amounts of rock flour debris during glacial ages. Thus, unconsolidated alluvial deposits of the last cold Pleistocene period were spread over the whole plateau, which is capped by a Holocene fluvial deposit sandy layer (5–10 cm) [28,29].

Eight main rivers drain this region and their combined drainage areas account for about 30%

of the total Patagonian territory. The remaining 70% corresponds to closed basins and temporary smaller coastal drainage. The localization of each river is shown in Fig. 1. Some important features of Patagonian river basins can be seen in Gaiero et al. [12].

### 3. Sampling and methodology

Suspended particulate matter (SPM), river bed sediments, topsoil and eolian dust samples were obtained in eight different surveys during 1995–1998. The emphasis was placed on sampling the land–ocean interface along Patagonia’s main Argentine road (RN 3). Some field trips, however, included sampling along the Andean eastern slope (RN 40), to sample the headwaters of rivers crossing Patagonia from west to east (Fig. 1).

Using plastic sampling bottles, water samples were taken from bridges integrating three different points across the river width. SPM was pre-concentrated from large water volumes by pressure filtration under 1.5 atm N<sub>2</sub> on 0.45 µm Millipore filters (diameter 142 mm), then removed using an ultrasonic bath, submerging the filter in Milli-Q water and subsequently drying at 50°C for 24 h.

Submerged fine bed sediments were collected in duplicate from opposite riverbanks with plastic scoops during field trips of May and December 1996. With the aim of correcting for the grain size effect [30], sediments from the May 1996 survey were sieved with a 63 µm stainless steel mesh. Grain size was analyzed using standard sieving methods, pre-treating the samples with 10% H<sub>2</sub>O<sub>2</sub> and diluted HCl. The clay fraction (<2 µm) was separated by pipette (Stoke’s law) and analyzed using X-ray diffraction, which was also used to assess silt size mineralogy. The relative abundance of major clay minerals was estimated semi-quantitatively using the peak areas of the X-ray diffractograms [2].

Dust sampling devices were placed at selected spots along Patagonia: Bahía Blanca (ca. 38°S), Puerto Madryn (ca. 43°S), and Comodoro Rivadavia (ca. 45°S) (Fig. 1). The samplers used in each site were 40 cm deep, inverted epoxy-coated fiberglass pyramidal receptacles, with 0.25 cm<sup>2</sup> of

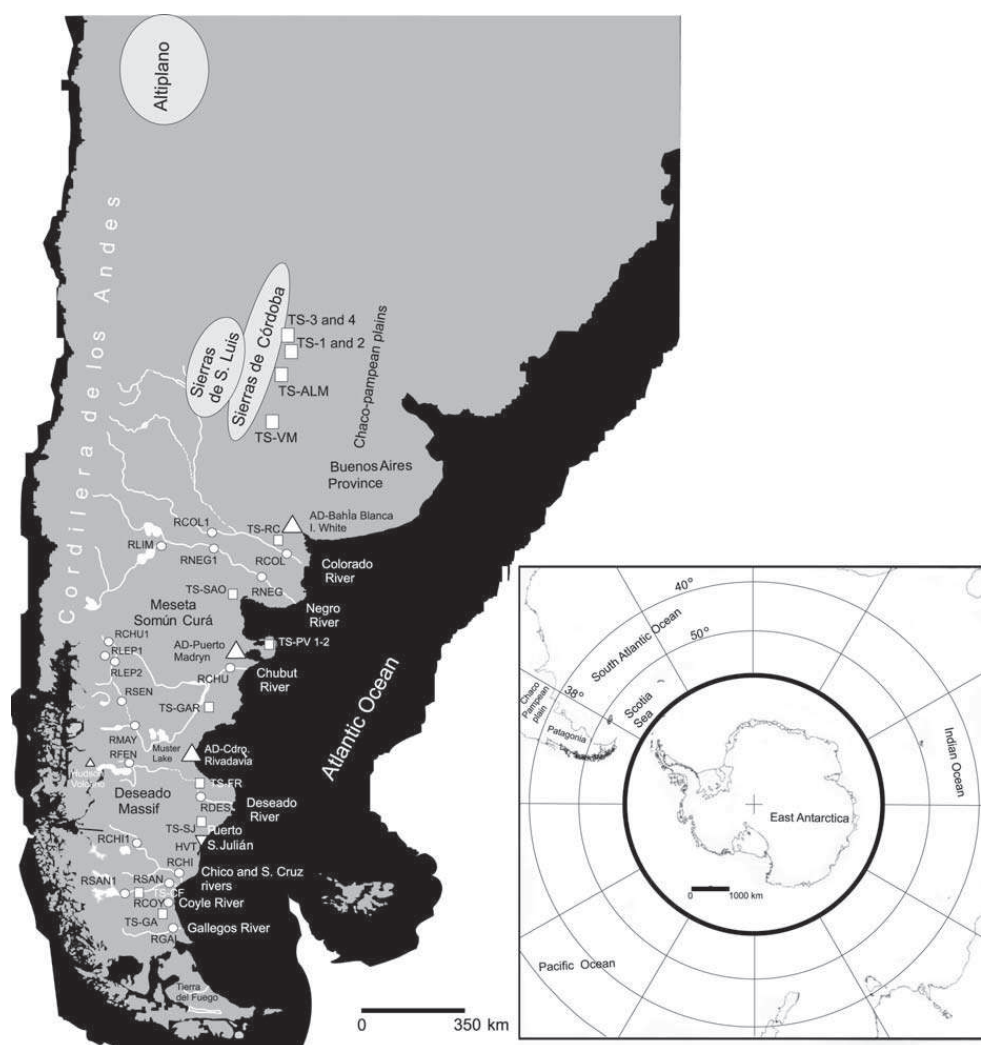


Fig. 1. Map of southern South America and inset showing the surrounding environments of southern latitudes. The Patagonian sector shows the sampling points. Dots indicate suspended particulate matter and bed sediment collected in different rivers. Boxes denote topsoil sampling locations and triangles denote eolian dust sampling stations. See Table 3 for acronyms.

collecting surface, as described by Orange et al. [31]. For more details see Gaiero et al. [12]. In connection with the eolian dust aspect, a set of topsoil samples (upper 5 cm of the soil profile, also sieved with a 63  $\mu\text{m}$  stainless steel mesh) were collected 300–400 km apart along the main north–south Patagonian route (RN 3) (Fig. 1).

Particulate samples (SPM, bed sediments, eolian dust, and topsoils) were digested by means of the alkaline fusion method ( $\text{Li}_2\text{B}_4\text{O}_7$ , 1050°C, with  $\text{HNO}_3$  digestion). REEs were analyzed by inductively coupled plasma mass spectrometry (detection limit = 0.01  $\mu\text{g l}^{-1}$ , and uncertainty based on one relative standard deviation of repli-

cates was 2%). Standard curves of each element were constructed using international standards (BE-N-basalt, GS-N-granite, AN-G-anorthite, FK-N-feldspar) from the CRPG, Nancy, France. This technique was checked using the geostandard OU-4 (Penmaenmawr microdiorite) and the results obtained are reported in Table 1.

## 4. Results and discussion

### 4.1. Mineralogy

Table 2 shows the bulk and clay mineralogical

Table 1

Results for international geostandard OU-4 (Penmaenmawr microdiorite) and comparison with certified values

	Laboratory analysis	Certified value
Zr	180	195.1 ± 1.7
Th	7.6	8.42 ± 0.12
La	22.9	24.96 ± 0.35
Ce	61	55.7 ± 0.8
Pr	6.4	6.85 ± 0.11
Nd	26.4	27.9 ± 0.4
Sm	6.52	6.94 ± 1.3
Eu	1.53	1.64 ± 0.02
Gd	6.36	7.39 ± 0.12
Tb	1.17	1.25 ± 0.02
Dy	7.4	7.81 ± 0.11
Ho	1.53	1.63 ± 0.03
Er	4.22	4.83 ± 0.09
Tm	0.68	0.72 ± 0.01
Yb	4.2	4.7 ± 0.06
Lu	0.68	0.72 ± 0.01

Concentrations are in ppm.

composition of the three different sediment fractions corresponding to each Patagonian river and topsoil sample. Unfortunately, the eolian dust samples were not large enough to carry out mineralogical analyses. The mineralogical composition of Recent Patagonian sediments is very homogeneous and consists basically of clay minerals, quartz and plagioclase. The relative abundance of minerals in bed sediments, topsoils, and SPM shows that the percentage of clay minerals is highest in the suspended load (mean = 57%), while a high proportion of quartz is found in the bottom sediment samples (mean = 41%). Topsoil mineralogy is more heterogeneous than bed sediment samples with a relatively higher percentage of clay minerals. The clay mineralogy of the sample set is homogeneous with typical dominance of smectite (~75%) and subordinate kaolinite; illite and chlorite accounting for only 7–12%. With respect to eolian dust mineralogy Ramsperger et al. [32], studying sites surrounding Bahía Blanca city (ca. 38°S), found that clay minerals in the eolian dust samples were also dominated by smectite and illite with small amounts of kaolinite. Similarly to bed sediments, topsoils, and SPM, eolian dust has feldspars and quartz as principal constituents of the bulk mineralogy [32].

## 4.2. Sources of Recent Patagonian sediments deduced from REE compositions

### 4.2.1. REE compositions of rock sources

Fig. 2 shows the mean composition of REEs normalized to the upper crust (REE<sub>UCC</sub>) [33] for the most abundant igneous rock outcroppings in Patagonia. This figure indicates that the mean REE<sub>UCC</sub> for the older and more evolved silicic

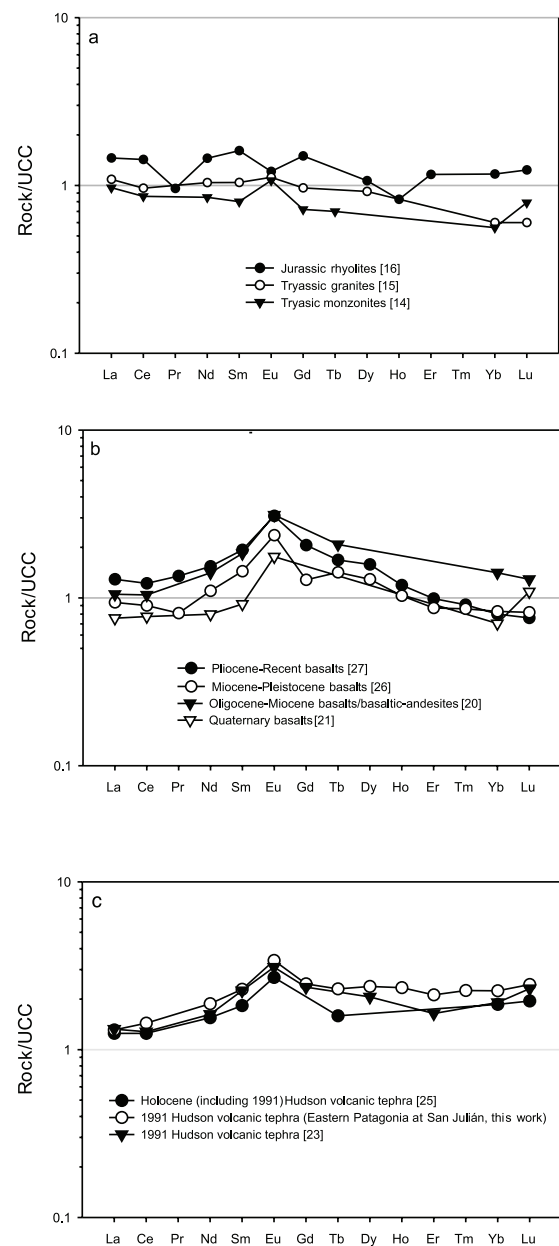


Fig. 2. Mean REE patterns of the most abundant igneous rocks outcropping in Patagonia.



Table 2  
Semi-quantitative mineral composition of Recent Patagonian materials

Reference	Mineral abundance				Ratio			Clay mineral composition <sup>a</sup>				
	Clay minerals	Quartz	Plagio-clase	Calcite	Clay/Qz	Clay/Pg	Pg/Qz	Smectite	Kaolinite	Illite	Chlorite	
	%	%	%	%				%	%	%	%	
Suspended particulate matter												
RCOL	Colorado R. (R. Colorado-Apr. 1998)	20	34	25	18	0.59	0.80	0.74	75	5	13	7
RNEG	Negro R. (Gral. Conesa-Dec. 1997) <sup>b</sup>	10	50	36	0	0.20	0.28	0.72	na	na	na	na
RCHU	Chubut R. (Trelew-Apr. 1998)	70	22	8	0	3.18	8.8	0.36	95	5	0	0
RCHU	Chubut R. (Trelew-during flood, Apr. 1998)	67	17	12	2	3.94	6.0	0.71	88	9	5	0
RDES	Deseado R. (Jaramillo-Dec. 1997)	82	10	4	4	8.20	21	0.40	89	5	2	4
RCHI	Chico R. (Río Chico-Apr. 1998)	66	24	10	0	2.75	6.6	0.42	74	3	18	5
RSAN	Santa Cruz R. (Cte. Piedrabuena-Apr. 1998)	38	41	21	0	0.93	1.8	0.51	57	30	0	13
RCOY	Coyle R. (Río Coyle-Dec. 1997)	62	30	8	0	2.07	7.8	0.27	84	3	10	3
Bed sediment < 63 µm size fraction												
RCOL	Colorado R. (Río Colorado)	19	31	40	7	0.61	0.48	1.29	74	6	9	11
RNEG	Negro R. (Gral. Conesa)	26	48	25	2	0.54	1.0	0.52	75	7	11	7
RCHU	Chubut R. (Trelew)	31	45	24	2	0.69	1.3	0.53	90	6	4	0
RDES	Deseado R. (Jaramillo)	62	25	9	6	2.48	6.9	0.36	86	11	3	0
RCHI	Chico R. (Río Chico)	42	43	15	0	0.98	2.8	0.35	74	9	10	7
RSAN	Santa Cruz R. (Cte. Piedrabuena)	11	65	22	0	0.17	0.50	0.34	60	13	14	13
RCOY	Coyle R. (Río Coyle)	35	44	21	1	0.80	1.7	0.48	70	7	9	14
RGAL	Gallego R. (Güer Aike)	25	43	25	1	0.58	1.0	0.58	67	12	8	13
Bed sediment total fraction												
RCOL	Colorado R. (Río Colorado)	16	28	43	0	0.57	0.37	1.54	63	8	11	18
RNEG	R. Negro (Gral. Conesa)	26	38	33	3	0.68	0.79	0.87	66	13	10	11
RMAY	Mayo R. (Río Mayo)	18	37	23	6	0.49	0.78	0.62	87	3	4	6
RSEN	Senguer R. (RN 40)		60	35	0	0.00	0.00	0.58	63	10	11	16
RCHU1	Chubut R. (El Maiten)	29	37	19	3	0.78	1.53	0.51	80	10	3	7
RCHU	Chubut R. (Trelew)	24	46	30	0	0.52	0.80	0.65	81	14	5	0
RFEN	Fénix R. (P. Moreno)	25	18	38	3	1.39	0.66	2.11	87	3	4	6
RDES	Deseado R. (Jaramillo)	69	19	8	4	3.63	8.63	0.42	73	17	10	0
RCHI1	Chico R. (Tamel Aike)	37	47	16	4	0.79	2.31	0.34	76	6	6	12
RCHI	Chico R. (Río Chico)	32	49	19	0	0.65	1.68	0.39	73	13	7	7
RSAN1	Santa Cruz R. (C. Fuhr)	17	61	8	0	0.28	2.13	0.13	70	7	15	8
RSAN	Santa Cruz R. (Cte. Piedrabuena)	8	64	24	0	0.13	0.33	0.38	56	12	13	14
RCOY	Coyle R. (Río Coyle)	43	40	17	0	1.08	2.53	0.43	74	7	15	4
RCOL	Colorado R. (Río Colorado)	16	28	43	0	0.57	0.37	1.54	63	8	11	18
RGAL	Gallego R. (Güer Aike)	14	44	26	0	0.32	0.54	0.59	45	15	16	24
Topsoils < 63 µm size fraction												
Patagonia												
TS-RC	Río Colorado	52	10	12	24	5.2	4.3	1.2	70	8	14	8
TS-SAO	San Antonio Oeste	59	11	30	0	5.4	2.0	2.7	75	5	nd	13
TS-PV1	Península de Valdéz	55	16	17	6	3.4	3.2	1.1	80	6	7	7
TS-PV2	Península de Valdéz	34	12	54	0	2.8	0.6	4.5	75	nd	nd	25
TS-GAR	Garrayalde (RN 3)	43	26	28	0	1.7	1.5	1.1	na	na	na	na
TS-FR	Fitz Roy (RN 3)	33	11	7	46	3.0	4.7	0.6	100	0	0	0
TS-SJ	San Julián	54	18	19	9	3.0	2.8	1.1	85	3	12	0
TS-GA	Güer Aike	38	27	12	21	1.4	3.2	0.4	na	na	na	na
TS-CAL	El Calafate	33	40	26	0	0.8	1.3	0.7	61	9	18	12
TS-CF	Charles Fuhr	33	38	19	0	0.9	1.7	0.5	72	4	18	6
Central Argentina												
TS-ALM	Almafuerte (Córdoba Province)	32	37	31	0	0.86	1.0	0.84	41	nd	50	5
TS-VM	Vic. Mackena (Córdoba Province)	39	39	17	0	1.0	2.3	0.55	58	0	42	0
TS1	Falda del Carmen (Córdoba Province)	na	na	na	na	na	na	na	35	8	57	0
TS3	Surrounding Córdoba City	na	na	na	na	na	na	na	21	15	64	0

nd = not detected, na = not analyzed.

<sup>a</sup> Clay mineral composition is the relative abundance of clay fractions.

<sup>b</sup> The amount of sample was small and semi-quantitative analysis may have important bias.

rocks forming the Patagonian upper crust have a flat pattern with a minor light REE (LREE) enrichment ( $Yb/La_{UCC} = 0.56-0.90$ ). On the other hand, Fig. 2b shows that the widespread Tertiary

and Quaternary volcanic rocks of essentially basic to intermediate composition (basalts and andesites) depict an enrichment of middle REE, with a prominent europium anomaly (mean  $Eu^* = 1.5$ )

and a very wide range of  $\text{Yb/La}_{\text{UCC}}$  values (0.30–5.1).

The pyroclastic materials erupted from the Hudson volcano during the Holocene (including the last eruption of 1991) have a distinct shape when their REE composition is compared to the upper crust (Fig. 2c). They show a clear heavy REE (HREE) enrichment (mean  $\text{Yb/La}_{\text{UCC}} = 1.6$ ) and an important europium anomaly (mean  $\text{Eu}^* = 1.5$ ). Basically, the difference between the  $\text{HREE}_{\text{UCC}}$  composition of the oldest and the youngest basalt and andesite (Fig. 2b,c) would be explained by the abundance in the youngest tephros of minerals containing high field strength (e.g., Hf and Zr) and incompatible elements. Samples with similar silica contents derived from other volcanoes from the southern Andes [22–24] or from Tertiary volcanic materials have low concentrations of high field strength and incompatible elements.

#### 4.2.2. Riverine sediments

Table 3 lists the REE compositions of Patagonian river-borne, topsoils, and eolian dust samples. Fig. 3 indicates that the different grain size fractions corresponding to Patagonian riverine sediments have a very homogeneous REE<sub>UCC</sub> composition, revealing that all of them are depleted in LREEs and enriched in HREEs relative to the upper crust. HREEs are preferentially removed during weathering of source rocks, while LREEs are preferentially adsorbed onto particle surfaces in adsorption/equilibrium reactions in rivers [34]. Hence, most of the sediments transported by the major world rivers (e.g., Amazon, Congo, Indus, Chianjiang, Huanghe, Mississippi) have similar and uniform patterns with enrichment of LREEs and depletion of HREEs relative to North American Shale, but also to UCC, with low  $\text{Ce}^*$  and  $\text{Eu}^*$  anomalies [35–38]. Contrarily, the REE compositions of the sediments transported by Patagonian rivers differ from major world rivers showing a pattern more similar to rivers draining young island arcs (e.g., Shinano and Papanga rivers) [35] or tholeiitic flood basalts or young volcanic arc rocks (e.g., Paraná and Uruguay rivers) [39]. Comparing the REE compositions of Patagonian riverine sediments (Fig. 3)

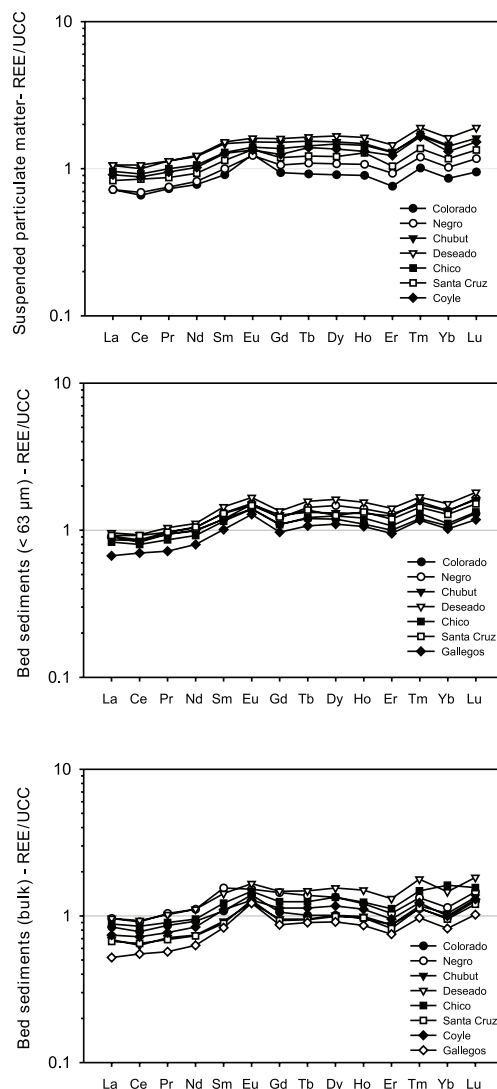


Fig. 3. Comparison of REE abundance patterns of materials transported by Patagonian rivers to the ocean.

with their probable rock sources (Fig. 2), it is apparent that their patterns are analogous to undifferentiated rocks and particularly to Recent volcanic tephros.

#### 4.2.3. Eolian dust

Fig. 4 shows the REE compositions of dust sampled at the Patagonian coast. Their patterns are strikingly similar to those shown for riverine sediments. However, and in contrast with the bulk of sediments transported by rivers, the sources of eolian dust are strongly dependent on the atmosphere dynamics and, hence, they could be linked

Table 3  
REE concentrations in riverine, eolian and topsoil sediments from Patagonia

Reference	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	Yb/La	Eu*
Suspended particulate matter																		
RCOL Colorado R. (R. Colorado-Dec. 1996)	23.7	46.5	5.69	22.2	4.51	1.19	4.16	0.60	3.46	0.78	1.83	0.31	1.99	0.30	158	8.05	1.14	1.27
RCOL Colorado R. (R. Colorado-Apr. 1998)	19.3	38.2	4.72	18.2	3.69	1.05	3.01	0.51	2.92	0.66	1.69	0.30	1.79	0.27	130	7.13	1.26	1.45
RCHU Chubut R. (Trelew-Dec. 1996)	29.5	60.2	7.47	29.0	6.19	1.34	5.60	0.88	5.06	1.14	2.84	0.48	3.09	0.49	198	9.24	1.43	1.04
RCHU Chubut R. (Trelew-Apr. 1998)	33.7	68.3	8.63	34.0	7.14	1.40	5.84	0.97	5.59	1.22	3.14	0.52	3.14	0.48	203	11.0	1.27	0.99
RCHU Chubut R. (Trelew-during flood, Apr. 1998)	35.8	73.2	8.71	32.5	6.81	1.27	5.63	0.93	5.29	1.13	2.98	0.52	3.01	0.47	202	10.2	1.15	0.94
RFEN Fénix R. (P. Moreno-Dec. 1996)	24.6	52.0	6.42	25.9	5.77	1.44	5.13	0.78	4.70	1.07	2.61	0.45	2.74	0.45	177	7.00	1.52	1.22
RDES Deseado R. (Jaramillo-Sep. 1996)	29.1	60.9	7.19	28.2	5.96	1.29	5.52	0.86	5.27	1.19	2.86	0.48	3.18	0.51	186	9.36	1.49	1.03
RDES Deseado R. (Jaramillo-Dec. 1996)	36.5	78.5	9.40	37.9	8.36	1.84	7.43	1.17	7.00	1.55	3.92	0.65	4.19	0.68	214	10.2	1.57	1.07
RDES Deseado R. (Jaramillo-Dec. 1997)	29.9	63.4	7.52	29.7	6.21	1.21	5.24	0.93	5.27	1.18	3.24	0.58	3.31	0.53	197	9.62	1.51	0.97
RCHI1 Chico R. (Tamel Aike-Dec. 1996)	29.2	59.8	7.22	28.0	6.06	1.31	5.70	0.88	5.33	1.23	3.11	0.52	3.35	0.52	156	10.8	1.56	1.02
RCHI1 Chico R. (Río Chico-Dec. 1996)	28.8	59.7	7.19	28.3	6.07	1.32	5.79	0.89	5.53	1.24	3.13	0.50	3.38	0.53	167	11.4	1.60	1.02
RCHI1 Chico R. (Río Chico-Apr. 1998)	28.9	58.0	6.97	26.7	5.56	1.20	4.61	0.83	4.76	1.07	2.82	0.52	2.94	0.47	147	10.8	1.39	1.09
RSAN S. Cruz R. (C. Fuhr-Dec. 1996)	27.4	60.2	6.81	26.6	5.69	1.37	5.22	0.77	4.63	1.04	2.55	0.42	2.79	0.43	154	9.69	1.39	1.16
RSAN S. Cruz R. (Cte. Piedrabuena-Apr. 1998)	22.5	48.0	5.55	21.8	4.57	1.06	3.82	0.70	3.87	1.01	2.23	0.40	2.34	0.37	151	8.94	1.42	1.17
RNEG Negro R. (Gral. Conesa-Dec. 1996)	20.8	43.1	5.23	20.8	4.41	1.07	4.08	0.61	3.74	0.83	2.05	0.33	2.24	0.35	138	6.56	1.38	1.22
RNEG Negro R. (Gral. Conesa-Dec. 1997)	22.2	44.9	5.45	21.8	4.60	1.14	3.98	0.69	3.81	0.88	2.21	0.39	2.24	0.35	152	6.84	1.47	1.16
RCOY Coyle R. (Río Coyle-Dec. 1997)	27.4	56.3	6.72	26.6	5.71	1.21	4.77	0.83	4.77	1.05	2.82	0.49	2.89	0.46	155	9.23	1.44	1.07
Bed sediment < 63 µm size fraction																		
RCOL1 Colorado R. (La japonesita)	33.4	66.5	8.15	31.6	6.44	1.37	4.79	0.79	4.39	0.90	2.37	0.36	2.41	0.40	417	11.2	0.98	1.13
RCOL Colorado R. (Río Colorado)	27.0	53.4	6.65	25.7	5.37	1.26	4.18	0.72	4.17	0.88	2.29	0.36	2.35	0.39	301	9.36	1.18	1.23
RLIM Limay R. (Nahuel Huapi outlet)	23.5	49.4	6.16	24.4	5.78	1.21	4.52	0.86	5.14	1.09	2.83	0.44	3.00	0.49	268	7.61	1.74	1.09
RNEG1 Negro R. (Chelforò)	31.9	62.9	7.72	30.1	6.30	1.38	4.89	0.85	4.99	1.05	2.81	0.44	2.97	0.48	379	8.85	1.27	1.14
RNEG Negro R. (Gral. Conesa)	27.3	55.2	6.88	27.1	5.91	1.37	4.60	0.86	5.14	1.12	2.97	0.45	2.96	0.49	261	8.8	1.48	1.20
RCHU1 Chubut R. (El Maiten)	26.9	58.0	6.97	27.1	5.57	1.33	4.91	0.83	4.77	1.06	2.88	0.47	2.95	0.48	246	9.80	1.50	1.16
RCHU Chubut R. (Trelew)	25.7	54.6	6.68	26.1	5.35	1.35	4.81	0.79	4.59	1.04	2.88	0.47	3.00	0.48	382	7.81	1.59	1.22
RFEN Fenix R. (P. Moreno)	20.0	42.1	5.27	21.4	4.74	1.28	3.73	0.67	3.96	0.84	2.19	0.34	2.22	0.37	207	5.16	1.51	1.40
RDES Deseado R. (Jaramillo)	29.0	59.7	7.35	28.8	6.47	1.50	5.14	0.94	5.67	1.24	3.25	0.50	3.32	0.54	232	8.8	1.57	1.20
RCHI1 Chico R. (Tamel Aike)	34.0	67.5	8.11	31.2	6.65	1.48	5.23	0.96	5.60	1.23	3.35	0.54	3.59	0.62	698	11.0	1.45	1.15
RCHI1 Chico R. (Río Chico)	24.9	51.3	6.14	24.0	5.16	1.25	4.14	0.73	4.36	0.97	2.45	0.39	2.44	0.40	211	6.94	1.34	1.24
RSAN1 Santa Cruz R. (C. Fuhr)	31.3	65.6	7.66	29.6	6.07	1.32	4.82	0.83	4.98	1.09	2.85	0.47	3.12	0.52	596	9.68	1.36	1.12
RSAN Santa Cruz R. (Cte. Piedrabuena)	27.6	59.2	6.90	27.2	5.83	1.32	4.67	0.82	4.42	1.07	2.74	0.43	2.81	0.45	306	8.49	1.39	1.17
RGAL Gallego R. (Güer Aike)	20.1	44.6	5.12	20.7	4.56	1.15	3.67	0.64	3.86	0.85	2.19	0.35	2.24	0.35	161	5.54	1.52	1.29
Bed sediment total fraction																		
RCOL Colorado R. (Río Colorado)	25.3	49.9	6.12	23.9	4.84	1.25	4.03	0.61	3.55	0.77	1.99	0.34	2.14	0.38	325	9.13	1.15	1.30
RNEG R. Negro (Gral. Conesa)	28.8	58.4	7.37	28.9	6.96	1.37	5.47	0.83	4.68	0.97	2.40	0.40	2.51	0.44	302	10.2	1.19	1.02
RMAY Mayo R. (Río Mayo)	20.0	41.1	5.15	20.4	4.54	1.30	3.92	0.63	3.88	0.83	2.18	0.37	2.38	0.41	198	5.92	1.62	1.42
RSEN Senguer R. (RN 40)	25.1	48.1	5.84	20.6	3.99	1.12	3.47	0.52	3.17	0.69	1.78	0.32	2.00	0.35	186	7.87	1.09	1.38
RCHU1 Chubut R. (El Maiten)	30.4	59.7	7.29	28.0	5.48	1.18	4.74	0.70	3.94	0.83	2.14	0.37	2.33	0.43	397	9.02	1.04	1.06
RCHU Chubut R. (Trelew)	20.8	40.6	5.05	19.2	4.15	1.11	3.60	0.57	3.54	0.80	2.01	0.35	2.28	0.40	258	6.26	1.49	1.32
RFEN Fenix R. (P. Moreno)	19.3	41.2	5.00	20.2	4.43	1.27	3.76	0.61	3.64	0.79	1.97	0.34	2.13	0.36	187	5.02	1.50	1.43
RDES Deseado R. (Jaramillo)	28.7	59.3	7.26	28.9	6.39	1.49	5.59	0.89	5.43	1.20	3.01	0.53	3.22	0.55	193	8.99	1.53	1.15
RCHI1 Chico R. (Tamel Aike)	29.5	57.7	6.87	26.0	5.40	1.31	4.54	0.70	4.19	0.92	2.29	0.40	2.60	0.44	298	7.90	1.20	1.22
RCHI1 Chico R. (Río Chico)	26.5	54.1	6.38	24.7	5.50	1.32	4.75	0.75	4.68	1.00	2.58	0.44	3.56	0.47	218	8.17	1.83	1.19
RSAN1 Santa Cruz R. (C. Fuhr)	24.2	50.3	5.74	22.2	4.68	1.25	3.90	0.63	3.80	0.79	1.99	0.34	2.19	0.36	177	6.63	1.23	1.34
RSAN Santa Cruz R. (Cte. Piedrabuena)	20.0	41.4	4.93	18.9	3.99	1.15	3.55	0.57	3.46	0.78	1.88	0.34	2.10	0.36	215	5.98	1.43	1.40
RCOY Coyle R. (Río Coyle)	22.2	45.9	5.50	21.8	4.95	1.15	4.28	0.68	4.11	0.89	2.18	0.37	2.21	0.39	165	6.50	1.36	1.15
RGAL Gallego R. (Güer Aike)	15.7	35.4	4.02	16.4	3.74	1.10	3.30	0.54	3.19	0.69	1.72	0.29	1.80	0.31	99	4.96	1.56	1.44
Eolian dust																		
AD-BB Bahía Blanca-Aug. 1997 to Mar. 1998	19.5	40.3	4.82	18.8	3.91	1.00	3.39	0.57	3.35	0.76	1.84	0.32	1.98	0.32	174	7.36	1.38	1.28
AD-BB Bahía Blanca-Mar. to Oct. 1998	19.7	38.8	4.81	19.1	4.02	1.09	3.40	0.57	3.39	0.76	1.94	0.33	2.02	0.34	186	6.76	1.40	1.38
AD-BB Bahía Blanca-Sep. to Nov. 1998	22.0	44.8	5.43	21.1	4.49	1.15	3.85	0.64	3.96	0.88	2.21	0.38	2.35	0.38	206	8.20	1.46	1.30
AD-BB Bahía Blanca-Dec. 1998 to Feb. 1999	24.6	50.4	6.34	25.1	5.56	1.34	4.80	0.80	4.68	1.04	2.62	0.46	2.72	0.45	188	8.73	1.51	1.22
AD-BB Bahía Blanca-Sep. 1999	20.8	41.4	5.12	20.2	4.27	1.05	3.81	0.63	3.59	0.78	1.98	0.36	2.12	0.34	153	6.55	1.33	1.18
AD-IW Ing. White-Sep. 1997 to Jul. 1998	18.3	36.7	4.04	17.9	3.65	0.93	3.10	0.54	3.20	0.71	1.77	0.32	1.90	0.31	179	8.36	1.42	1.30
AD-IW Ing. White-Jul. to Dec. 1998	21.5	42.9	5.44	21.7	4.74	1.11	4.09	0.69	4.18	0.89	2.25	0.41	2.39	0.40	197	8.20	1.52	1.18
AD-PM Puerto Madryn-May to Nov. 1998	23.0	45.5	5.53	21.7	4.60	1.07	3.82	0.62	3.66	0.83	2.04	0.36	2.23	0.38	224	8.13	1.32	1.20
AD-PM Puerto Madryn-Jan. to Feb. 1999	19.3	39.8	4.98	20.1	4.42	1.12	3.82	0.66	3.87	0.87	2.17	0.36	2.33	0.38	170	6.15	1.65	1.28
AD-PM Puerto Madryn-Feb. to Mar. 1999	20.4	42.4	5.19	20.2	4.40	1.05	3.81	0.66	3.91	0.87	2.16	0.38	2.27	0.39	217	6.39	1.52	1.21
AD-PM Puerto Madryn-May 1999	19.9	39.3	4.83	18.9	4.16	1.03	3.60	0.59	3.43	0.74	1.92	0.33	2.09	0.33	252	5.30	1.43	1.25
AD-PM Puerto Madryn-Jun. to Jul. 1999	17.6	35.0	4.35	16.9	3.67	0.97	3.37	0.58	3.27	0.72	1.84	0.34	2.04	0.33	209	5.07	1.58	1.30
AD-PM Puerto Madryn-Sep. to Oct. 1999	19.7	39.5	4.81	19.0	4.10	1.02	3.69	0.61	3.52	0.76	2.01	0.35	2.16	0.34	242	5.70	1.49	1.23
AD-CR Com. Rivadavia-Apr. to Jul. 1999	18.4	38.1	4.61	18.3	4.06	1.07	3											



Table 3 (Continued).

Reference		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Zr	Th	Yb/La	Eu*
Patagonia																			
TS-RC	Río Colorado	27.0	55.9	6.99	26.8	5.79	1.23	4.58	0.75	4.39	0.92	2.54	0.40	2.48	0.42	286	9.99	1.25	1.12
TS-SAO	San Antonio Oeste	21.9	45.8	5.79	22.8	5.28	1.22	4.29	0.73	4.32	0.92	2.45	0.40	2.46	0.40	240	7.50	1.54	1.20
TS-PV	Península de Valdéz 1	22.3	46.9	5.84	22.7	5.11	1.21	4.18	0.71	4.29	0.93	2.53	0.41	2.58	0.42	320	7.41	1.58	1.23
TS-PV	Península de Valdéz 2	21.8	44.9	5.48	20.9	4.61	1.16	3.75	0.64	3.84	0.83	2.26	0.37	2.33	0.40	375	7.95	1.46	1.31
TS-GAR	Garrayalde (RN 3)	23.4	49.4	6.10	24.0	5.43	1.42	4.39	0.76	4.55	0.98	2.69	0.46	2.80	0.48	453	6.51	1.52	1.21
TS-FR	Fitz Roy (RN 3)	20.2	41.8	5.22	20.4	4.45	1.04	3.64	0.63	3.75	0.80	2.22	0.36	2.25	0.39	379	6.06	1.63	1.37
TS-SJ	San Julián	24.4	51.6	6.32	24.7	5.60	1.35	4.61	0.78	4.71	1.00	2.68	0.43	2.65	0.44	278	7.32	1.21	1.32
TS-GA	Güer Aike	18.3	39.5	4.79	18.9	4.12	1.02	3.30	0.56	3.36	0.72	1.91	0.31	1.93	0.32	303	4.68	1.49	1.24
TS-CAL	El Calafate	25.2	53.5	6.12	23.4	5.07	1.30	4.20	0.70	4.21	0.87	2.33	0.37	2.23	0.37	248	7.07	1.44	1.30
TS-CF	Charles Fuhr	27.3	57.4	6.97	26.5	5.71	1.26	4.52	0.79	4.77	1.05	2.92	0.49	3.21	0.56	1141	9.62	1.61	1.17
Central Argentina																			
TS-SR	Santa Rosa (La Pampa Province)	43.2	85.0	10.9	41.0	8.60	1.43	6.40	1.03	5.78	1.20	3.20	0.52	3.23	0.55	890	18.0	1.48	1.25
TS-ALM	Almafuerte (Córdoba Province)	28.4	58.0	7.20	27.1	5.78	1.15	4.44	0.76	4.47	0.95	2.56	0.41	2.58	0.42	381	11.4	1.24	1.07
TS-VM	Vic. Mackena (Córdoba Province)	20.7	42.4	5.31	20.2	4.39	1.05	3.50	0.60	3.64	0.79	2.15	0.35	2.24	0.37	248	8.34	1.02	0.91
TS1	Falda del Carmen (Córdoba Province)	30.5	59.8	7.20	27.3	5.43	1.15	4.37	0.75	4.23	0.95	2.35	0.40	2.53	0.39	254	10.9	1.13	1.11
TS2	La Lagunilla (Córdoba Province)	32.7	65.7	7.77	30.0	5.87	1.24	4.89	0.83	5.09	1.11	2.92	0.49	3.15	0.50	335	11.6	1.31	1.09
TS3	Surrounding Córdoba City	35.5	70.9	8.42	31.8	6.22	1.32	5.07	0.85	5.13	1.15	2.95	0.48	2.98	0.49	355	12.5	1.15	1.10
TS4	Surrounding Córdoba City	47.5	94.8	11.2	42.4	8.23	1.48	6.43	1.06	6.10	1.33	3.43	0.58	3.59	0.58	479	16.2	1.03	0.96
HVA	Hudson volcanic ash-1991 (P. San Julián)	43.1	92.9	11.0	46.6	9.51	2.61	8.62	1.42	8.04	1.70	5.15	0.75	4.61	0.69	332	6.33	1.46	1.35

Concentrations of La–Th are in  $\mu\text{g g}^{-1}$ . Yb/La and Eu\* are normalized to UCC.

to local or remote areas. For example, Ramsperger et al. [32] recognized that for the areas surrounding Bahía Blanca, the collected dust is a mixture of local and far-travelled material. Typical lithogenic element ratios (e.g., Fe and Mn) from Patagonian topsoils and eolian dust samples show a similar slope to the one found for the Earth's crust [33] and were interpreted as indicative of a natural weathered material source [12]. Considering the scarcity of industrial activity in the region, other clues indicate that far-travelled pollutants (heavy metals) occurring in Patagonian dust are scavenged by wind-transported soils and thus, their seasonal concentrations are much higher than expected from normal crust weathering [12]. Although eolian dust samples suggest a seasonal increase in REE concentrations, they depict noticeably homogeneous REE patterns, indicating a common source (Fig. 4).

#### 4.3. Geochemical control of REE compositions in riverine and eolian sediments

##### 4.3.1. Riverine sediments

The most important load carried by rivers contributing lithogenic particles to the ocean is the suspended load. Changes in the suspended load composition occur during sediment transport and are in part due to sorting: residual heavy minerals settle near the source, leaving the sus-

ended matter depleted in HREE, Zr, Hf, etc. [40]. Two main features characterize the REE compositions of Patagonian riverine sediments entering the South Atlantic Ocean: a gradual decrease of normalized Eu values with decreasing grain size (Fig. 3) and a lower Yb/La<sub>UCC</sub> ratio in the suspended load of the larger rivers (Fig. 5a,b) (i.e., Negro, Santa Cruz, and Colorado).

A positive Eu\* anomaly in sediments is generally controlled by plagioclase contributed by source rocks. Fig. 6 indicates the existence of a general trend of negative correlation between Eu\* anomaly and clay/plagioclase ratios. Notably, the lowest Eu\* values are found in the suspended load, which in turn accounts for higher clay/plagioclase ratios. Moreover, the suspended sediment samples with the highest clay/plagioclase ratios (e.g., Deseado and Chubut rivers, Table 2) and with smectite as major clay mineral (89–95%, Table 3) depict a negative Eu\* anomaly (see inset in Fig. 6). A marked negative Eu\* anomaly seems to be a common feature in smectites [41,42].

The Andean mountains are the only water source for Patagonian rivers and thus, it is the only source of weathered material transported to the ocean. Although large sediment yields are generated in the Andes, a significant proportion of the particulate load carried by the largest rivers is retained in proglacial lakes (i.e., Limay River – a tributary of the Negro – and Santa Cruz River)

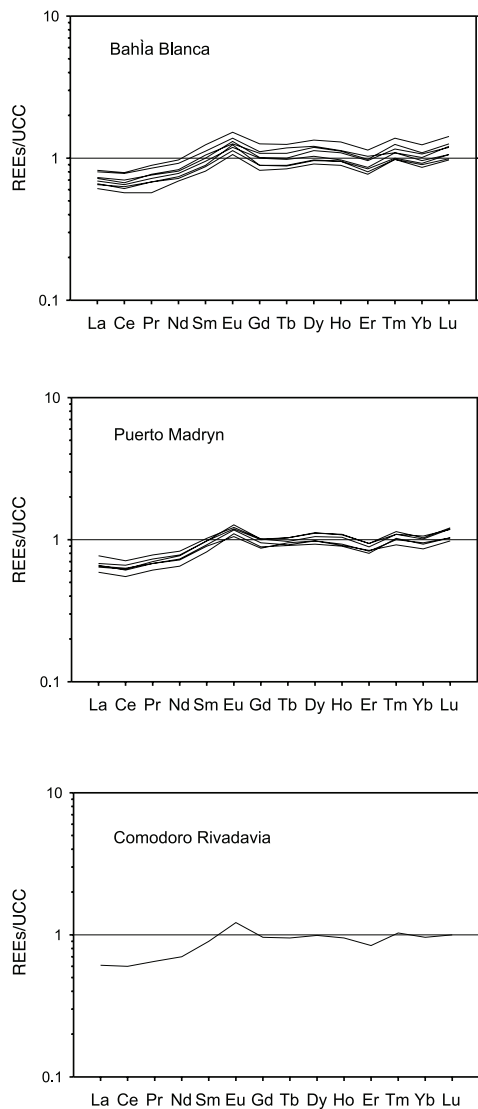


Fig. 4. REE patterns of eolian dust samples taken at three different localities along the Patagonian coast.

or reservoirs (i.e., in the Negro, Colorado, and Chubut rivers), promoting low sediment yields for the region [12]. Evidently, the trapping effect of lakes and reservoirs could have an important role modifying the final REE compositions of riverine material reaching the ocean. This is illustrated in Fig. 5, where the REE<sub>UCC</sub> composition of the suspended load of Patagonian rivers can be compared to that of the Manso River. The Upper Manso River is located in the Andean sector of Patagonia and transports glacial debris [43,44]. The normalized REE compositions of the suspended load transported by the Patagonian rivers

that do not have proglacial and reservoir lakes in their drainage basins exhibit a noticeable coincidence with the Upper Manso River, suggesting a limited mineralogical fractionation (Fig. 5a). On the contrary, the lower Yb/La<sub>UCC</sub> observed in the suspended load of larger rivers can be linked to mineral retention in proglacial or reservoir lakes. Thus for example, zircons are known to play an important role in REE compositions as they have a considerable HREE content and may modify the REE patterns of bulk bed sediments [45]. This is illustrated in Fig. 7a, where riverine bed sediments with higher Zr also have higher Yb concentrations. This is likely explained by the presence of zircons in the sand and silt fraction.

The slope of the relationship, however, is steeper for the suspended load and reflects the

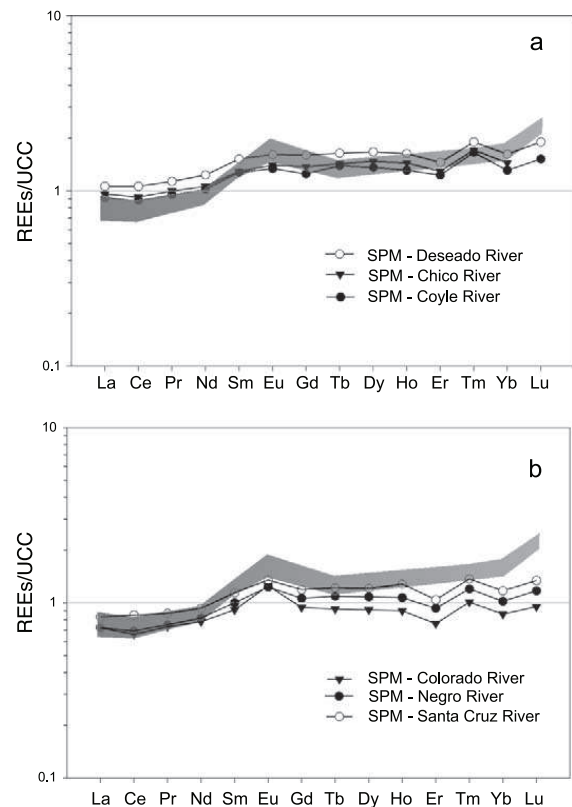


Fig. 5. REE compositions of SPM of Patagonian rivers draining two different types of basin: (a) without proglacial or reservoir lakes and (b) with proglacial (Santa Cruz and Negro) and reservoir lakes (Negro and Colorado). The shadowed areas correspond to REE patterns of SPM from the Manso River, located in the higher Andean sector of Patagonia (without proglacial and reservoir lakes).

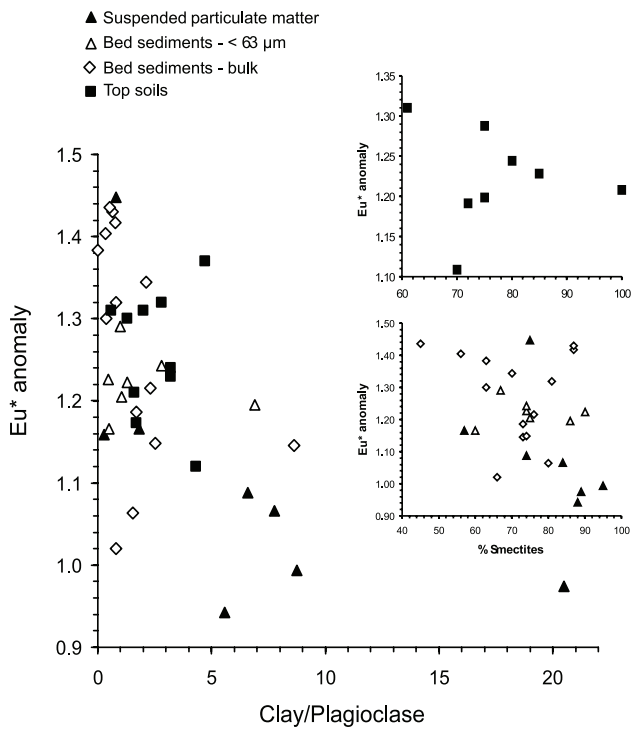


Fig. 6. Relationship between  $Eu^*$  anomaly and clay/plagioclase for Patagonian riverine and topsoil materials. Insets shows the relationship between  $Eu^*$  anomaly and percentage of smectite for the same materials.

constancy of Zr content in the upper crust. Moreover, the inset in Fig. 7a indicates that the suspended sediments transported by the largest rivers present the lowest Zr/Yb ratios because Zr is a hydrolysate and its concentration remains in the 120–200 ppm range. It also illustrates a significant covariance with Yb, thus showing that both elements are subjected to a similar control, although different from the one ruling their concentrations in bed sediments.

#### 4.3.2. Eolian dust

Patagonian topsoils were identified as important contributors to the eolian dust delivered to the ocean [12]. Fig. 8a shows that eolian dust exhibits  $REE_{UCC}$  compositions which match the shadowed area of Patagonian topsoils. Both atmospheric dust and topsoil samples have a similar LREE depletion and enrichment in HREEs relative to the upper crust. Also, both have a striking similarity with the REE riverine patterns (Fig. 2) and with Hudson tephtras (Fig. 6c). Hence, we

conclude that these materials have a clear REE signature mostly controlled by Patagonia's Holocene Andean volcanism.

Grain size analyses in eolian dust samples indicate that a mean of  $86 \pm 4.0\%$  (arithmetic mean  $\pm$  S.D.) of the mass corresponds to particles with diameters less than  $10 \mu m$  [12]. During eolian transport, heavy minerals and quartz are concentrated in the coarse fraction and separated from fine-grained minerals. However, topsoil-normalized eolian dust samples result in a flat REE patterns, suggesting that no fractionation occurs between both types of sediment. In contrast with

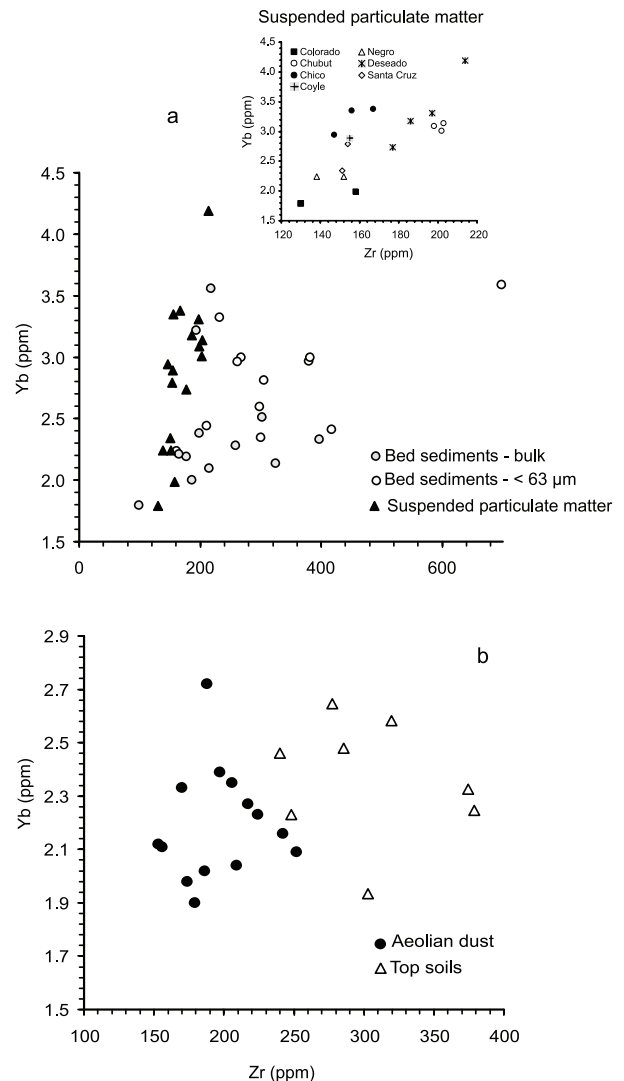


Fig. 7. Relationship between Yb and Zr for Recent Patagonian sediments: (a) riverine materials and (b) topsoil and eolian dust materials.

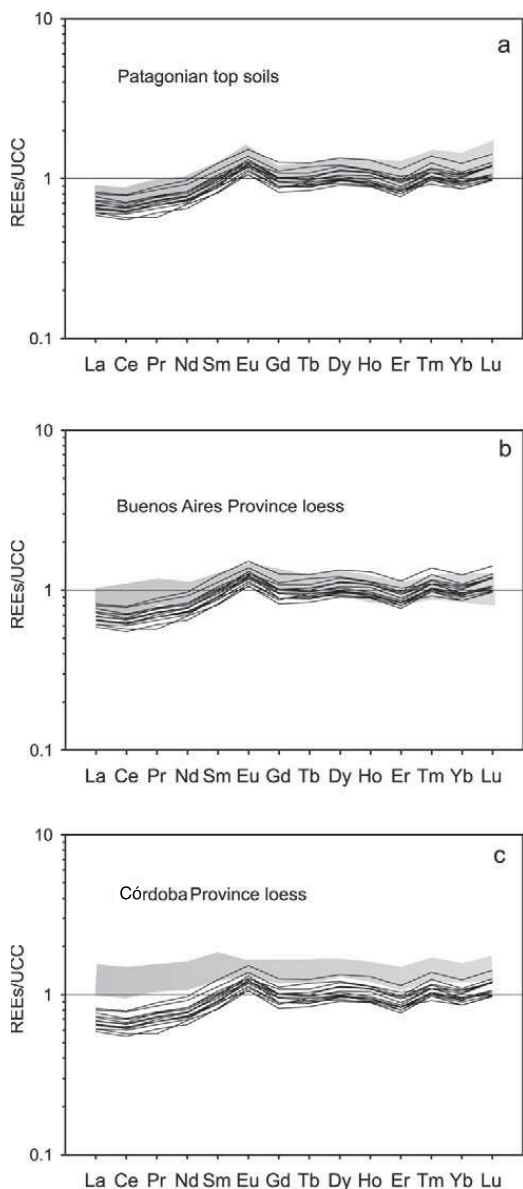


Fig. 8. Comparison of REE abundance patterns of Patagonian eolian dust with different potential sources (shaded areas): (a) Patagonian topsoils, (b) Buenos Aires Province loess [46], and (c) Córdoba Province loess.

riverine materials, topsoil and eolian dust samples show a low correlation between Zr and Yb concentrations (Fig. 7b). In the study of Chinese eolian deposits of loess–paleosol sequences, Gallet et al. [46] concluded that heavy minerals do not significantly control REE patterns. Consequently, and in agreement with the observations made by other authors [38,46,47], the bulk of REEs in dust

seems to reside largely in clay minerals, which have also been identified as potential major carriers of REEs in shales [45].

Similarly to riverine sediments, the Eu\* anomaly in topsoil samples seems mainly controlled by clay/plagioclase ratios and, in general, it shows low values with increased percentages of smectite (Fig. 6 and inset). Usually, dust is dominated by fine particles containing a high percentage of clay minerals [12]. Therefore, a lower Eu\* anomaly is to be expected in far-travelled and fractionated eolian dust derived from Patagonian topsoils.

#### 4.4. Other probable sources of dust supplied to the Patagonian coastal zone

Fig. 8b,c shows the REE<sub>UCC</sub> composition of eolian dust. It can be contrasted with shadowed areas representing REE compositions of other surficial sediments from potential source areas that ultimately can reach the Patagonian coast. Recently, Prospero et al. [48] showed that Patagonia, along with western Argentina and Bolivia's Altiplano, is South America's most persistent dust source. Besides Patagonia, the second largest dust source in Argentina is bounded between the eastern Andean slopes and the western side of Sierra de San Luis, and Sierra de Córdoba [48]. From the three dust sources mentioned above, only the Altiplano has no available information on the REE compositions of Recent sediments. It must be noted that chemical information reveals that the composition of ignimbrites from this area is homogeneous. They were emplaced during the Neogene and the late Quaternary, and cover large areas of the Altiplano. Ignimbrites have a dacite and rhyodacite composition, and their isotopic signature suggests a dominantly crustal origin [49,50]. Furthermore, Clapperton [29] suggests that the southern Altiplano of Bolivia could have been a potential source area for the eolian deposits of the Chaco region (northern Argentina). The mineral composition of sediments deposited in the Chaco is markedly different from Pampean eolian deposits; quartz is dominant (60–80%) and volcanic glass is completely absent [51]. Then, a significant contribution from this region to Patagonian dust is ruled out as it should

confer compositions that characterize evolved rocks.

On the other hand, Fig. 8b shows the REE<sub>UCC</sub> composition from a sediment core that reached a depth of 60 m in loess sequences from Buenos Aires Province [47]. Although Buenos Aires Province is not recognized as an active dust supplier, loess samples from this area were extensively used by many authors to demonstrate the likely origin of terrigenous materials found in ice cores from Antarctica [9,10] and on sediment cores in the Southern Ocean [5,6]. The relevance of this material for paleoclimatic interpretations will be discussed later on.

The upper crustal signal depicted by the REE<sub>UCC</sub> of Córdoba Province loess is surely determined by the mineralogy derived from central Pampean ranges (dominated by metamorphic and igneous rocks) [52] (Fig. 8c). Similarly to Altiplano's material, a significant contribution to Patagonian dust of Recent sediments from this region should be ruled out.

From the above argumentation, we conclude that dust reaching the Patagonian coast bears a clear signature, characterized by materials of mafic to intermediate composition of common occurrence in the region.

#### 4.5. *The southernmost South American REE signature in sediments of the southern South Atlantic and east Antarctica*

##### 4.5.1. *Redefining Patagonia as a source*

Grousset et al. [9] and Basile et al. [10] recognized that during Late Pleistocene glacial events, Patagonia was identified as a source of wind-blown dust deposited on east Antarctica. For convenience, Basile et al. [10] employed the term Patagonia to refer to the whole southern South America desert/arid/semi-arid continental area east of the Andes. However, isotopic evidence for a Patagonian source of dust in Antarctica is supported by only one sample (i.e., taken from the Central Patagonian plateau). The other samples correspond to Tierra del Fuego (with a less significant influence, as the complete area was ice-covered during the Last Glacial Maximum (LGM) [53]), and to Buenos Aires Province, fur-

ther north (ca. 35°S), with dominant illite [54] and heterogeneous isotopic compositions [10,47]. As stated by Zárate [52], Basile et al. [10], when referring to Patagonia, also included the Chaco-pampean plains, where the loess records of southern South America are found. Conversely, no significant loess records are reported for Patagonia. The environmental conditions of the Chaco-pampean plain during the glacial stages were different from those found in Patagonia. Both areas are very different in terms of geomorphology, climate, and biogeography, and it is misleading to consider them as a rather uniform region [52].

On the other hand, based on isotopic and mineralogical evidence, the studies of terrigenous sediment sources that supplied dust to the South Atlantic provided two different models for glacial–interglacial stages [5,6]. Following Basile et al. [10], Walter et al. [5] and Diekmann et al. [6] also used the term Patagonia to refer to the continental area east of the Andes. One way or another and due to confusing information, both models underestimate the role played by Patagonia as a sediment supplier to the nearby ocean during the Late Pleistocene (especially during the LGM). Besides the isotopic evidence supplied by Basile et al. [10], Walter et al. [5] and Diekmann et al. [6] based part of their conclusions, for example, on the rate of dust deposition for the South Atlantic Ocean estimated by Duce et al. [55], and mineralogical information from Buenos Aires Province's loess rather than a Patagonian source. Recently, the model of Tegen and Fung [56] and direct dust measurements performed by Gaiero et al. [12] imply that this region is a much larger supplier (about 100-fold) of dust to the southern South Atlantic Ocean than originally estimated by Duce et al. [55].

We now have the possibility to compare REE patterns of ice core dust samples from Antarctica and sediment cores from the Southern Ocean with different likely sources located in the eastern Andes sector of southern South America, especially with those characterizing the authentic Patagonian signature (Figs. 9 and 10). Plots (Fig. 10) showing normalized Yb/La ratios vs. the Eu\* anomaly are considered to be useful for the recognition of potential source areas (e.g., [6]).



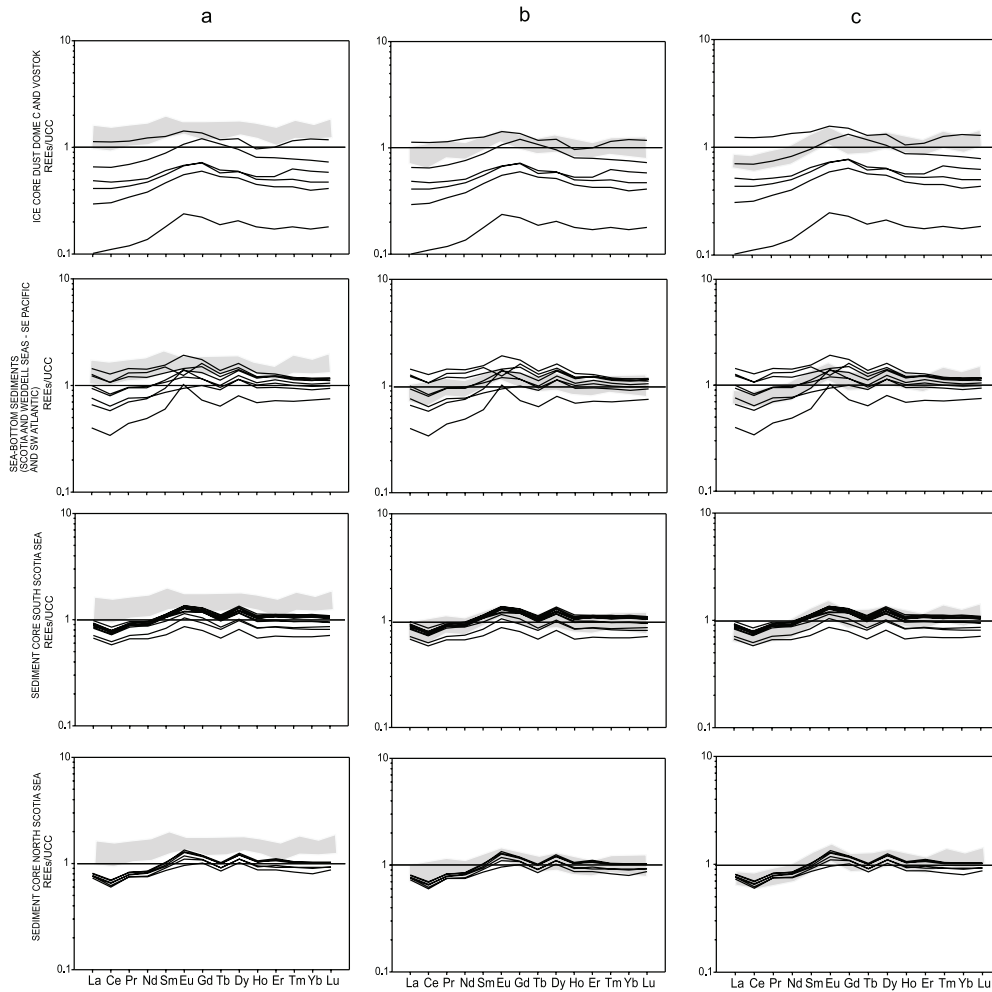


Fig. 9. REE compositions of Quaternary sediments from Antarctica [9,10], bottom sediments from Scotia and Weddell seas and SE Pacific Ocean [6], and sediment cores from the Scotia Sea [6], compared to shadowed areas corresponding to probable sources in southern South America: (a) Córdoba Province loess, (b) Buenos Aires Province loess [47], and (c) Patagonian eolian dust.

Clearly, this figure indicates that the shadowed areas that represent potential continental sources (we also included the Hudson tephtras) are distributed along two poles: one with slight REE fractionation (lower  $Yb/La_{UCC}$ ) and low  $Eu^*$  anomaly (upper crust-like) and the other pole with enriched HREEs and a high  $Eu^*$  anomaly, representing terrigenous materials of basic to intermediate composition.

#### 4.5.2. Dust from east Antarctic ice cores

Regardless of differing concentrations, the pattern of  $REE_{UCC}$  composition of most ice core dust samples [9,10] matches reasonably well with the shadowed area representing the mean

$REE_{UCC}$  composition of Patagonian eolian dust and the Buenos Aires loess (Fig. 9). Nevertheless, data in Fig. 9 are in clear conflict with what is shown in Fig. 10, where a group of dust samples from Antarctic ice cores plot within the compositional area corresponding to the loess from central Argentina (Córdoba Province). Furthermore, another group of dust samples from Antarctic ice cores plots outside the field of any of these potential source areas.

Clearly, the upper crust-like spidergrams in Fig. 9 lead to discarding central Argentina as a likely main source of ice core dust. On the other hand, the clay mineral composition of Córdoba's loess samples (determined by X-ray diffraction) indicate

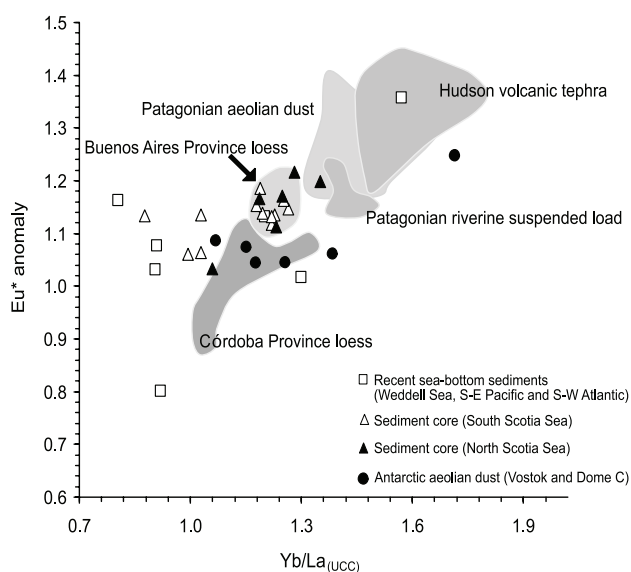


Fig. 10. Relationship between  $Eu^*$  anomaly and  $Yb/La_{(UCC)}$  for Quaternary sediments from east Antarctica [9,10], bottom sediments from Scotia and Weddell seas and SE Pacific Ocean [6], and sediment cores from the Scotia Sea [6]. They are contrasted to shadowed areas corresponding to possible sources located in southern South America: major rivers suspended load and eolian dust from Patagonia, Buenos Aires Province loess [47], Córdoba Province loess and Hudson volcanic tephtras ([23,25], this work).

a dominance of illite (mean  $\pm$  S.D.,  $53 \pm 9\%$ ), followed by smectite ( $39 \pm 15\%$ ) and traces of kaolinite (Table 3), and Antarctic dust appears to be dominantly illitic ( $\sim 70\%$ ) with a lesser proportion of smectite ( $\sim 20\%$ ) and traces of chlorite [57]. It must be stressed at this point that the mineralogical analyses performed by Gaudichet et al. [57] (by means of transmission electron microscopy) include significant proportions of unidentified particles (i.e., ‘colloidal’+‘unidentified’ reaching a total of  $\sim 28\%$  in Vostok) and that most of the same authors believe these results to be statistically insignificant [58].

Considering the uncertainties of ice core mineralogical analyses, the spidergrams (Fig. 9) and the isotopic signature of the calc-alkaline volcanic rocks [9,10], allow us to single out Buenos Aires loess and Patagonian sediments (see Section 4.5.1) as the most probable source of dust in Antarctica during the LGM. As will be mentioned later on, in the coastal plains of Buenos Aires Province,

loess shows a mixture of smectite, illite and kaolinite in approximately equal amounts [54]. If Patagonia, Buenos Aires Province, and even Córdoba Province were important sources of sediment, we should expect a higher proportion of smectite in Antarctic dust samples. The most remarkable feature of ice core dust samples is the low mean  $Eu^*$  anomaly (1.09), when compared to mean Patagonian dust (1.21), and mean Buenos Aires loess (1.18). Fig. 6 demonstrates that a high proportion of smectite in Patagonian riverine suspended matter and topsoils promotes a low  $Eu^*$  anomaly in sediments. This could also explain the low  $Eu^*$  anomaly in dust from Antarctic ice cores: a higher proportion of smectite in a dominant clay size fraction could lower the  $Eu^*$  anomaly and thus locate Antarctic dust composition in the field characterizing sediments from Córdoba Province (Fig. 10). Future studies will further assist in clarifying this issue.

#### 4.5.3. Sediment cores in the Southern Ocean

The study of two sediment cores from the northern and southern Scotia Sea reveal a typical variability in magnetic susceptibility, indicating compositional variations of the terrigenous sediment fraction that reflect glacial–interglacial stages [6]. The sources of terrigenous sediments in the Scotia Sea may derive from South America, from Antarctica or from offshore islands. Probably, they were introduced through interbasinal sediment transfer from the adjacent Weddell Sea and SE Pacific [6]. The magnetic susceptibility pattern of the sediment cores studied by Diekmann et al. [6] roughly matches the deuterium and dust record of the Antarctic Vostok ice core. Hence, an increased dust supply from the ‘pampas’ to the Scotia Sea is likely during cold stages and stadials [59]. Isotopic evidence in cores from the northern Scotia Sea indicates the Argentinean shelf and loess samples from Buenos Aires Province as possible sources [5]. Using the same data as Basile et al. [10], Walter et al. [5] ruled out a possible continental Patagonian origin.

Mineralogical and isotopic evidence reveals that sediments were supplied to the Scotia Sea from different sources, depending on climatic conditions [5,6]. However, a common feature is the in-

put of basic and undifferentiated crustal material and the increase of the smectite/chlorite ratio during interglacial time in the north Scotia Sea [6]. It must be noted that tephra from the moderately explosive 1991 eruption of Mount Hudson was dispersed widely southeastward, falling on Puerto San Julián, the Malvinas (Falkland) Islands (several centimeters of accumulation) and it was detected in the South Georgia archipelago, > 2700 km distant from Mount Hudson [60]. These observations sustain the importance of a significant contribution of South American tephras, distributed over a wide area of the Scotia Sea [60] and found in the Antarctic continent [61].

The comparison of REE concentrations and compositions from sediment cores of the Scotia Sea with eastern Andean sources indicates that most of the samples match the Buenos Aires Province loess composition and, to a lesser extent, Patagonian sources (Fig. 9). Normalized REE patterns of core samples from the northern Scotia Sea indicate a rather homogeneous source of terrigenous material similar to Patagonian dust. In contrast, only sediment samples from the southern Scotia Sea that correspond to the LGM period have REE<sub>UCC</sub> similar to both Buenos Aires Province loess and Patagonian eolian dust samples. Furthermore, Fig. 10 indicates that most of these samples plot within the compositional area corresponding to Buenos Aires Province loess. Noticeably, samples identified as deposited during the LGM in the northern Scotia Sea plot within the Patagonian data field. An older sample of this core (of ca. 59–71 kyr BP), which also depicts a high terrigenous rate accumulation, falls on the limit of the shadowed areas between Buenos Aires Province loess and Patagonian materials. However, sediments deposited during interglacial periods, on the southern sector of the Scotia Sea, have compositions that differ from materials found in the eastern Andean sector of southern South America. Interglacial samples from this area indicate a signature derived from the old crust as the one found in the Weddell Sea [5]. This suggests that southern South American materials are less significant in high-latitude ocean where hydrographic transport could dominate.

#### 4.6. A model for the sediment sources of southern latitudes

Fig. 9 indicates that, although the patterns of REEs characterizing Patagonian eolian dust are comparable to loessic material from Buenos Aires Province, they are depleted in LREEs. Isotopic evidence indicates the dominance of very ancient continental rocks on world loess composition [47]. Notably, the Buenos Aires loess depicts an intermediate REE<sub>UCC</sub> composition between Patagonian topsoils and Córdoba Province loess. Accordingly, Gallet et al. [47] found that the Buenos Aires loess composition is explained by a combination of factors, like the nature of the source, where the volcanic contributions determine a relatively high  $\epsilon_{Nd}$  and young model ages. These observations are in agreement with Zárate and Blasi [62], who established that the main provenance area of the southern Buenos Aires Province loess seems to be the distal segments of the river-transported volcanoclastic material of the Colorado and Negro river floodplains derived from the Andean piedmont, and from northern Patagonia. A simple estimate indicates that, to reproduce the mean REE<sub>UCC</sub> composition of loess from Buenos Aires Province, it is necessary to combine about 80% of the mean REE compositions of dust from Patagonia and 20% of materials with an upper crustal signature similar to that of Córdoba Province.

Mineralogical evidence also points to an admixed provenance for coastal plains Buenos Aires Province loess from two defined areas: central western Argentina and Patagonia. Soils in central Argentina exhibit a clear mineralogical gradient from northwest to southeast. Southeast of Córdoba Province, illite dominates the mineralogical composition of loess located in the Upper Pampa, while the coastal plains Lower Pampa (further southeast) depicts a mixture of smectite, illite and kaolinite in approximately equal amounts [54]. On the other hand, the acidic Neogene–Quaternary volcanic tuffs in the Bolivian Altiplano are characterized by enrichment of LREEs (mean Yb/La<sub>N</sub> = 0.34) [45]. Their contribution to Recent sediments of Buenos Aires Province may be important. Nevertheless, sediments examined in Fig.

10 indicate that materials with this composition could have a minor role as possible contributors of terrigenous material to the Southern Ocean and east Antarctica.

Therefore, ruling out Buenos Aires province as a major source of sediments, their chemical signature in different southern environments (i.e., the Scotia Sea and east Antarctica) may be explained by a combination of sources. Many clues allocate the LGM as the major factor defining Argentinian loess deposition [51]. Although it is not possible to identify active dust sources during the LGM, it is likely that the sites identified today (e.g., Bolivia's Altiplano, Patagonia, and western Argentina) were much more active during the LGM than they are today [48]. For the particular case of eolian deposits found in southern Buenos Aires Province, they are defined as proximal facies and attributed to a medium-distance transport of dust [51]. Similarly to Buenos Aires loess, it is likely that the REE composition of most sediment cores of the Scotia Sea and Antarctica reflect a distal transport of dust with an admixed composition from two main sources: a major contribution from Patagonia (the closest land mass) and a minor proportion from source areas containing sediments with upper crustal signature, like western Argentina and Bolivia's Altiplano.

## 5. Conclusions

Riverine and wind-borne materials being delivered from Patagonia to the South Atlantic Ocean exhibit a homogeneous REE signature that can be used to identify their past and present occurrence on various depositional environments of the southern latitudes. This signature matches well with the REE compositions of Recent tephra from the Hudson volcano and suggests a dominance of material supplied by this source. Moreover, the importance of Quaternary volcanic activity as a supplier of particles to the southern latitudes must be highlighted.

The original Patagonian Andes REE signature is slightly modified in riverine sediments as they flow along their pathway to the ocean. This is particularly important for the suspended matter

transported by Patagonian rivers, where the dominance of smectites determines a REE signature with a low Eu\* anomaly, when compared to the bulk of bed and topsoil materials. Moreover, due to the trapping effect of proglacial and reservoir lakes, the larger Patagonian rivers deliver to the ocean a suspended load with a REE compositions which is poorer in HREEs. In spite of a present low riverine sediment supply to the sea, it must be noted that the 'original' Patagonian Andes signature could have been dominant during pre-glacial times.

In this paper we evaluate the chemical composition of Recent sedimentary materials from areas of southern South America, which have been considered as past and current important sources of sediment to southern latitudes. Most Quaternary sediments deposited in the northern and, to a lesser extent, in the southern Scotia Sea have REE compositions very similar to those shown by loess from Buenos Aires Province and to Patagonian dust. Similarly, most of the dust in ice cores of east Antarctica shows a REE pattern that matches well with those characterizing Buenos Aires Province loess and Patagonian dust. The evidence indicates that Buenos Aires Province loess derives from a mixed origin, with a preponderance of Patagonian material and a minor contribution from areas dominated by evolved rocks (e.g., Sierras Pampeanas range or Altiplano?). Moreover, Buenos Aires Province is defined as a depositional area of medium-distance transport from its sources. Probably, the same environmental conditions that allow the thick accumulation of Buenos Aires loess also contributed to distal facies, supplying sediments to the Southern Ocean and even to Antarctica. It seems that only during the LGM, Patagonian materials predominated in the transport of sediments to southern latitudes as is indicated by a higher rate of terrigenous deposition in cores of the Scotia Sea displaying a Patagonian signature.

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