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Rare earth element geochemistry of the Late Quaternary tephra and volcano-clastic sediments from the Pachuca sub-basin, north-eastern Basin of Mexico

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Resumen

Este estudio presenta el comportamiento geoquímico de las tierras raras (TR) en tefra y depósitos volcaniclásticos subyacentes del Cuaternario Tardío en la sub-cuenca de Pachuca, ubicada en la parte noreste de la Cuenca de México. Los contenidos totales de TR, así como los patrones normalizados de TR, índices de fraccionamiento de TR ligeras (La/Sm), pesadas (Gd/Yb), total (La/Yb) y anomalía de Eu son comparados con la mineralogía y el contenido de elementos mayores y trazas, con el propósito de encontrar los firmas geoquímicas de la fuente. Las tefras de composición basáltica y basáltica-andesítica, con plagioclasa, piroxeno y olivino, se caracterizan por bajos contenidos de TR, bajos índices de fraccionamiento de TR ligeras y pesadas, así como anomalía positiva de Eu. Los sedimentos subyacentes muestran dos diferentes comportamientos de TR e indican que la proveniencia varía entre rocas félsicas y máficas durante el Cuaternario Tardío. La composición geoquímica y los patrones normalizados de TR del grupo I (15-17 m, 4.6-9.6 m y 2-4.6 m) son comparables a los de las tefras y sugieren una fuente máfica. Además, se caracterizan por una ausencia de anomalía de Eu y bajo contenido en el total de TR, comparada con las muestras del grupo II. Los sedimentos del grupo II (9.6-15 m y 0-2 m) contienen abundante feldespato potásico y los datos geoquímicos muestran altas concentraciones en el total de TR, anomalía negativa de Eu y son enriquecidas en Zr, Y y Th. Esto último indica una contribución de minerales pesados, tales como alanita, monacita y zircón, típica de rocas félsicas.

Palabras clave: Geoquímica, TR, Proveniencia, Sedimento volcán-clastico, Cuenca de México.

Abstract

Chondrite normalized REE patterns, fractionations of light (La/Sm), heavy (Gd/Yb) and total (La/Yb) REE and Eu anomalies of the Late Quaternary multi-layer tephra fall deposits and overlying volcano-clastic sediments deposited in the Pachuca sub-basin (north-eastern Basin of Mexico) are studied to characterize their geochemical signatures. The REE geochemistry is compared with mineralogical abundances and multi-element concentrations to identify the possible source terrains contributing sediments into the basin. The basalt to basaltic-andesite tephra deposits have chemical compositions comparable to the rocks from Apan-Tezontepec volcanic field and consist of plagioclase, pyroxene and olivine. They are characterized by lower total REE abundances, lower light and heavy REE fractionations and a positive Eu anomaly. The overlying sediments show significantly different REE characteristics and can be divided into two different groups (i.e. I and II). The geochemical composition and REE patterns of group I (15-17 m, 4.6-9.6 m and 2-4.6 m depths) are comparable to the tephra deposits and suggest a mafic provenance. They are characterized by the absence of the Eu anomaly and lower total REE concentrations compared to group II. In group II (9.6-15 m and 0-2 m depths), higher total REE, a negative Eu anomaly, abundant K-feldspar and enriched Zr, Y and Th indicate felsic source terrains containing heavy minerals such as allanite, monazite and zircon.

Key words: Geochemistry, REE, Provenance, volcano-clastic sediment, Basin of Mexico.

Introduction

Rare earth elements (REE) are transported in particulate matter (Rollinson, 1993) and regarded as relatively immobile during low-grade metamorphism and hydrothermal alteration (Michard, 1989). They comprise of a coherent group of trace elements (trivalent state) with similar chemical and physical properties. Compared to the signatures of major elements that are modified by the diagenetic history of the sediments, degree of metamorphism and alteration of the sedimentary system (Lee, 2002), the REE are insoluble in aqueous solutions and adsorbed to the sheet silicates (clay minerals) or included in the inter layer cation sites. They are unaffected by chemical alteration and transferred from source rocks to sedimentary basins without significant fractionation (Nesbitt, 1979; Davies, 1980; Girty *et al*., 1994; Bierlein, 1995). So, the studies of Taylor and McLennan (1985), Preston *et al*. (1998), Davies and Pickering (1999), Svendsen and Hartley (2002) and Andersson *et al*. (2004) have emphasized the importance of REE to characterize source terrains.

The mineralogical and chemical composition of source rock is the most important factor that controls the abundance of REE in the clastic sediments. The REE are incompatible in basaltic and andesitic liquids and vice versa (Cox *et al*., 1995). Mineralogical distribution controls the REE abundance and their fractionation. Sediments enriched in quartz and carbonate minerals (i.e. calcite and dolomite) have very low REE abundance (Taylor and McLennan, 1985). Although there is no direct relationship between REE abundance and clay minerals, the studies by Cullers *et al*. (1987, 1988), Sharma and Rajamani (2000) and Singh and Rajamani (2001) show that the bulk REE reside in the finer silt-clay fractions of the sediments. Another significant contributor of REE is the presence of different heavy minerals like zircon, allanite, monazite, sphene and garnet (Gromet and Silver, 1983). For example, addition of zircon and garnet in the sediments increases the Yb abundance and decreases the fractionation of heavy REE (Gd/Yb). Similarly, higher abundance of allanite increases the concentration of light REE and monazite increases the abundance of middle REE compared to heavy REE (McLennan, 1989). REE fractionations are also affected by depositional environment and intensity of chemical weathering. Depositional environment causes change in the valency state of certain REE leading to their fractionation (McLennan, 1989). Under reducing environment, Eu^{+2} precipitates as complexes of SO_4^{-2}, CO_3^{-2} and Cl^- (Sverjensky, 1984; Michard and Alberede, 1986). Similarly, Ce^{+4} precipitates as oxide and carbonate under oxidizing environments (Elderfield and Greaves, 1982; Rollinson, 1993) and alkaline conditions (Moeller and Bau, 1993; Volkova, 1998; Roy and Smykatz-Kloss, 2007). In a profile consisting of granodioritic parent rock and its altered product, Nesbitt (1979) reported that REE abundance of the altered product was higher compared to both parent material and residual clay.

The Basin of Mexico is a topographically closed, high altitude (2240 m asl) sedimentary basin, located in the central-eastern part of the Trans Mexican Volcanic Belt (TMVB) (Bradbury, 1989; Lozano–Garcia *et al*., 1993). The topographically closed nature of the basin is associated with the formation of the Chichinautzin volcanic field during 7.8 Ma (Mooser *et al*., 1974; Urrutia-Fucugauchi and Martín del Pozzo, 1993). The basin presently hosts a number of sub-basins, i.e. Xochimilco and Chalco in the south, Texcoco in the centre, Zumpango and Xaltocan in the north and Tecocomulco and Pachuca in the north-east (Fig. 1). The sediments of the basin are thoroughly investigated for its biological (pollen and diatom contents) and physical (magnetic) properties by Bradbury (1989),

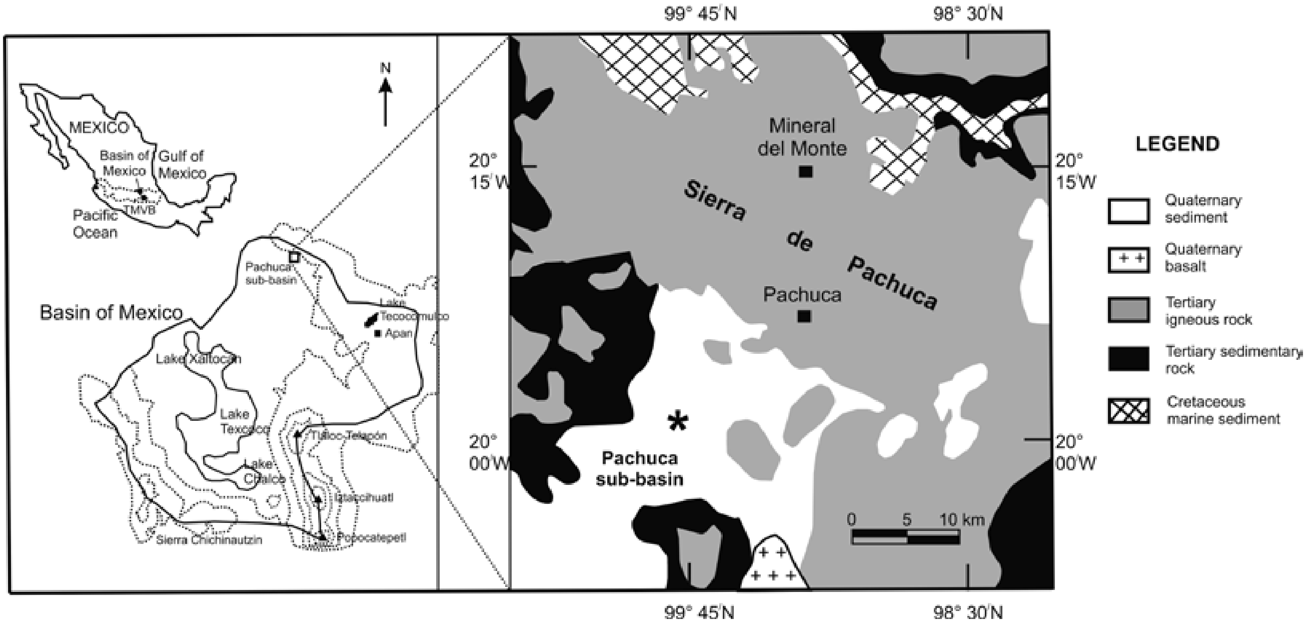

Fig. 1 Location map of the Pachuca sub-basin at the north-eastern part of the Basin of Mexico (location of the studied profile is marked with asterisk).

Lozano–García *et al.* (1993), Caballero (1997), Caballero and Ortega-Guerrero (1998), Lozano-García and Ortega-Guerrero (1998) and Caballero *et al.* (1999). Geochemical investigations are relatively scarce, except for the works by Geyne *et al.* (1963), García-Palomo *et al.* (2002) and Roy *et al.* (2008, 2009). Geyne *et al.* (1963) and García-Palomo *et al.* (2002) have reported the geochemical compositions of the volcanic deposits in the Sierra de Pachuca and Apan regions, respectively. Recently, Roy *et al.* (2008, 2009) studied the geochemical properties of the lacustrine sediments from the Tecocomulco sub-basin to understand the Pleistocene-Holocene paleo-environmental conditions.

In this study, we present new geochemical data on REE systematic of the Late Quaternary multi-layered tephra fall deposits and overlying volcano-clastic sediments deposited in the Pachuca sub-basin to strengthen the geochemical investigations in the region. The abundance and fractionations of REE were compared with mineralogy and major and trace element geochemistry to characterize the possible source terrains of the volcano-clastic sedimentary sequence.

Regional setting

The Pachuca sub-basin has a temperate climate (average temperature 13-15 °C) and receives an average annual precipitation of ca. 680 mm. Cretaceous marine limestone, shale, sandstone and evaporite deposits are present in the south and north of the basin, respectively. Low temperature shallow depth hydrothermal vein deposits of pyrite, sphalerite, chalcopyrite and chalcosite are present in the mining district of Real de Monte (Dueñas-García *et al.*, 1992). The Tertiary granodiorite to diorite are present at Zimapan and Jacala located at ca.100 km north-west of the sub-basin. The sub-basin is surrounded by Tertiary sedimentary and igneous rocks in the vicinity. The sedimentary rocks consist of sandstones, gravels and conglomerates (Dueñas-García *et al.*, 1992) and the igneous rocks comprise inter-layering of felsic and mafic volcanics exposed in the Sierra de Pachuca (Fig. 1). These rocks belong to the Santiago (rhyolite), Corteza (andesite), Pachuca (andesite-dacite), Real de Monte (andesite), Santa Gertrudis (dacite), Vizcaína (andesite) and Cerezo (rhyolite-dacite) Formations (Geyne *et al.*, 1963). The overlying lithologies exposed in the vicinity are constituted by basaltic-andesites of the Zumate Formation, rhyolites of the Tezuantla Formation and basaltic-andesite of the San Cristóbal Formation (Geyne *et al.*, 1963).

The endorreic nature of the Pachuca sub-basin occurred through an intensive eruptive period of mafic eruptions in the Apan-Tezontepec volcanic field (ATVF) during Pliocene-Pleistocene (Dueñas-García *et al.*, 1992; García-Palomo *et al.*, 2002). The rocks of ATVF are characterised by presence of basalt to basaltic-andesites with aphanitic texture and phenocrysts of olivine and plagioclase (García-Palomo *et al.*, 2002).

Material and methods

A total of 42 samples were collected from a 20 m thick exposed profile in the central part of the Pachuca sub-basin (Fig. 1). The profile consists of fining upward tephra fall deposits (17.0 and 20.0 m depths) at the base and overlying volcano-clastic sediments. The tephra deposits consist of at least 6 different layers containing black-brown lapilli and coarse ash scoria. Each layer begins with lapilli and terminates with coarse ash. The overlying clastic sediments are characterized by massive silty-clay (15.0 - 17.0 m), medium to fine sand (9.6 – 15.0 m), intercalations of silt and silty-clay (4.6 - 9.6 m) and massive fine sand (2.0 - 4.6 m) and conglomerates (0 – 2.0 m). For geochemical analysis, 12 different samples were collected from the tephra layers and 30 samples from the overlying clastic sediments (Fig. 2).

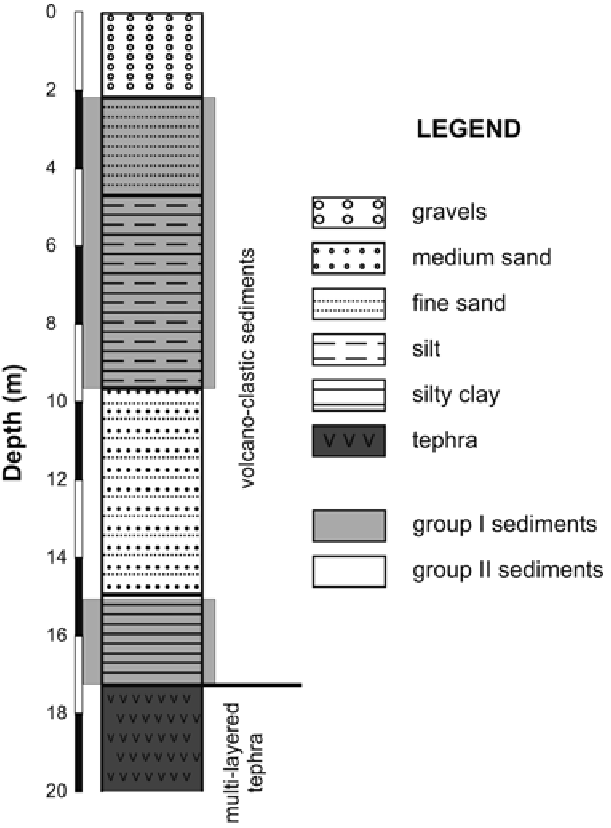

Fig. 2 Schematic diagram showing stratigraphy of the studied profile at the Pachuca sub-basin. The profile consists of multi-layered tephra fall deposits at the base overlain by volcano-clastic sediments.

The samples were subjected to oven drying at 40°C, homogenizing and grinding in an agate mortar. The concentrations of REE were analyzed in a VG Elemental PlasmaQuad3 ICP-MS following the procedure of Morton-Bermea *et al.* (1997). Analytical precision of the REE is < 10 %. Mineralogy was determined on a Philips 1130/96 X-ray diffractometer with digital data collection using Cu target from 4° to 70° (2θ) at a speed of 1°/min in the bulk powder samples. The oxides of 10 major elements (Si, Al, Ti, Fe, Ca, Mg, Na, K, Mn and P) were measured in fused discs and trace elements (Zr, Y, Zn and Th) were measured in pressed pellets after the methods of Verma *et al.* (1996) and Lozano and Bernal (2005) in a Siemens SRS 3000 wavelength dispersive X-ray fluorescence (XRF) spectrometer. The precision of the analysis is < 10 % for both major and trace elements.

Results

Rare earth elements

The REE concentrations of the tephra, sediments and upper continental crust (Taylor and McLennan, 1981) are normalized to the chondrite meteorite (Taylor and McLennan, 1985) to eliminate the abundance variations between elements with even and odd atomic numbers and to compare their normalized REE patterns and fractionations of light REE (La/Sm), heavy REE (Gd/Yb) and total REE (La/Yb) and Eu anomaly ($Eu/Eu^* = Eu/\sqrt{[Sm \times Gd]}$).

The REE patterns of the tephra fall deposits are more homogeneous compared to the overlying sediments (Fig. 3). They are characterized by comparable and low light (La/Sm = 1.53-2.02) and heavy (Gd/Yb = 1.12-1.73) REE fractionations and a positive Eu anomaly (Eu/Eu* = 0.99-1.30). The tephra are relatively less fractionated in total REE compared to rest of the sediments. The La/Yb of the tephra varies between 2.25 and 5.22 (Table 1).

Based on their REE patterns and Eu anomalies, the overlying sediments are divided into two different groups (i.e. I and II). The first group (I) includes sediments from the depths of 15.0-17.0 m (massive silty-clay), 4.6-9.6 m (intercalations of silt and silty-clay) and 2.0-4.6 m (massive fine sand). The group II comprises samples from depths of 9.6-15.0 m (massive medium to fine sand) and 2.0-0 m (conglomerates) (Fig. 2).

The REE patterns of group I samples (Fig. 3) are characterized by slightly enriched light REE (La to Sm) compared to heavy REE (Gd to Lu). However, they differ among themselves in terms of their total REE abundances and Eu anomalies (Table 1). They are characterized by relatively higher light REE fractionation (La/Sm = 2.07-3.83) compared to heavy REE (Gd/Yb = 1.15-1.64) and variable Eu anomaly (Eu/Eu* = 0.82-1.12). Table 1 presents the REE concentrations and chondrite normalized REE ratios of group I samples and upper continental crust (UCC).

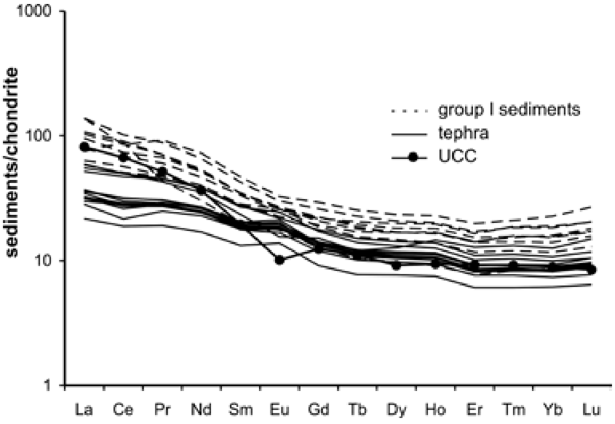

Fig. 3 Chondrite normalized REE diagrams of tephra, group I sediments and UCC (upper continental crust, Taylor and McLennan, 1981). The solid lines show REE patterns of tephra and dotted lines show REE patterns of group I sediments.

The group II sediments show REE patterns similar to UCC (Fig. 4): enriched light REE, flat heavy REE and negative Eu anomaly. They are highly fractionated in light REE (La/Sm = 2.19-4.66) compared to heavy REE (Gd/Yb = 0.52-1.75) and their Eu anomaly varies between 0.24 and 0.97. Table 2 presents REE concentrations and chondrite normalized REE ratios of group II samples and UCC. The sediments of both the groups have similarly fractionated total REE contents: La/Yb vary between 4.12 and 8.71 in group I sediments and ranges from 3.57 to 8.89 in sediments of group II. Fig. 5 shows fractionations of (a) light REE, (b) heavy REE, and (c) total REE with increasing REE abundance in tephra deposits and overlying sediments.

The tephra deposits and sediments can also be differentiated in terms of their total REE (TREE) concentrations. The tephra deposits have the lowest (TREE = 55-128 ppm), group I sediments have intermediate (TREE = 82-248 ppm) and group II sediments have the highest (TREE = 126-392 ppm) REE concentrations. The tephra have lower TREE abundance compared to UCC (Table 1). Sediments show a large TREE variation and most of them have higher TREE concentrations than UCC (Tables 1 and 2). The samples of both the groups have higher Eu concentration compared to UCC.

Table 1

Concentration of rare earth elements (ppm) and chondrite* normalized REE ratios for the tephra and group I sediments of the Pachuca sub-basin and UCC**.

	Samples	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	TREE	$(Eu/Eu^*)_N$	(La/Sm)N	$(Gd/Yb)_N$	$(La/Yb)_N$
Tephra	S1	19.7	13.25	30.41	4.17	18.75	4.67	1.84	4.16	0.68	4.32	0.95	2.26	0.34	2.24	0.36	88.39	1.27	1.79	1.51	4.00
	S2	19.5	7.93	18.06	2.62	12.03	3.06	1.20	2.79	0.45	2.92	0.64	1.51	0.22	1.52	0.24	55.17	1.25	1.63	1.48	3.51
	S3	19.3	10.98	26.76	3.76	17.44	4.50	1.77	3.84	0.63	3.96	0.86	2.02	0.30	2.04	0.33	79.19	1.30	1.53	1.53	3.64
	S4	19.1	19.00	44.89	6.12	27.12	6.22	2.13	5.25	0.81	5.01	1.07	2.51	0.37	2.46	0.40	123.36	1.14	1.92	1.73	5.22
	S5	19.0	20.31	47.40	6.20	27.04	6.34	1.90	5.42	0.87	5.40	1.18	2.73	0.40	2.66	0.45	128.31	0.99	2.02	1.65	5.16
	S6	18.9	13.10	30.24	4.20	19.10	4.73	1.70	4.33	0.71	4.46	0.98	2.29	0.33	2.21	0.37	88.75	1.15	1.74	1.59	4.01
	S7	18.8	11.51	26.17	3.73	17.17	4.25	1.60	3.87	0.64	4.04	0.90	2.06	0.30	2.02	0.33	78.60	1.21	1.70	1.55	3.84
	S8	18.6	11.98	26.16	3.83	17.58	4.37	1.61	4.05	0.66	4.13	0.91	2.13	0.32	2.10	0.36	80.19	1.17	1.72	1.57	3.86
	S10	18.5	11.73	24.97	3.83	17.78	4.39	1.64	4.04	0.66	4.15	0.91	2.12	0.32	2.07	0.34	78.94	1.19	1.68	1.58	3.83
	S11	18.3	12.67	26.58	4.01	18.56	4.52	1.69	4.19	0.68	4.34	0.96	2.31	0.33	2.17	0.36	83.37	1.19	1.76	1.57	3.95
	S13	18.0	11.83	27.73	3.83	17.34	4.21	1.59	3.88	0.64	4.08	0.89	2.12	0.31	2.05	0.35	80.84	1.20	1.77	1.53	3.91
	S15	17.5	10.37	20.67	3.41	16.26	4.14	1.55	4.30	0.70	4.84	1.24	3.19	0.48	3.12	0.57	74.83	1.12	1.58	1.12	2.25
Group I	S16	16.7	13.55	28.69	3.96	17.42	4.07	1.45	3.64	0.59	3.70	0.80	1.89	0.27	1.82	0.29	82.14	1.15	2.10	1.62	5.04
	S18	15.9	21.85	47.85	5.87	25.12	5.41	1.35	4.64	0.69	4.30	0.96	2.30	0.33	2.29	0.40	123.35	0.82	2.54	1.64	6.46
	S41	7.7	39.27	86.65	9.65	38.13	7.99	2.32	6.82	1.07	6.42	1.39	3.48	0.50	3.47	0.59	207.77	0.96	3.09	1.59	7.64
	S43	7.3	34.94	70.23	9.15	36.42	8.03	2.22	6.79	1.13	6.89	1.52	3.80	0.56	3.86	0.65	186.20	0.92	2.74	1.43	6.12
	S44	6.8	50.42	81.12	12.65	51.37	10.82	2.84	8.94	1.47	8.88	1.95	4.92	0.75	5.60	1.02	242.75	0.88	2.93	1.29	6.09
	S45	6.3	27.47	84.34	5.97	21.53	4.51	1.53	3.89	0.60	3.70	0.77	1.91	0.30	2.13	0.35	158.99	1.12	3.83	1.48	8.71
	S46	5.5	37.74	81.95	9.62	36.93	7.97	2.31	6.30	1.04	6.37	1.41	3.54	0.55	3.94	0.68	200.36	1.00	2.98	1.30	6.47
	S47	4.8	50.58	97.32	12.12	46.45	9.78	2.60	7.96	1.31	7.87	1.70	4.25	0.66	4.55	0.78	247.91	0.90	3.25	1.42	7.52
	S50	3.4	23.18	54.32	6.57	26.94	6.49	1.95	5.88	0.98	6.38	1.43	3.50	0.57	3.80	0.65	142.64	0.96	2.25	1.25	4.12
	S51	3.0	28.69	65.37	8.23	32.86	7.69	2.10	6.64	1.18	7.54	1.66	4.10	0.67	4.67	0.77	172.18	0.90	2.35	1.15	4.15
	S53	2.4	21.42	48.43	6.46	28.38	6.52	2.25	5.65	0.90	5.57	1.17	2.90	0.43	2.89	0.49	133.48	1.13	2.07	1.59	5.01
	UCC		30.00	64.00	7.10	26.00	4.50	0.88	3.80	0.64	3.50	0.80	2.30	0.33	2.20	0.32	146.37	0.65	4.20	1.40	9.21

Subscript N denotes chondrite normalized values
*Taylor and McLennan (1985)
**Taylor and McLennan (1981)

Table 2

Concentration of rare earth elements (ppm) and chondrite* normalized REE ratios for the group II sediments of the Pachuca sub-basin and UCC**.

Sample	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	TREE	$(Eu/Eu^*)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$	$(La/Yb)_N$
S19	14.8	40.44	95.97	11.47	46.30	11.61	0.85	10.25	1.84	11.61	2.61	6.29	0.98	6.30	1.02	247.54	0.24	2.19	1.32	4.34
S21	14.2	46.03	108.12	11.95	47.40	10.45	2.13	9.68	1.70	11.23	2.63	6.52	1.04	7.00	1.21	267.08	0.65	2.77	1.12	4.45
S22	14.1	75.65	129.26	19.38	77.70	16.33	2.78	13.65	2.22	13.43	2.98	7.01	1.07	6.94	1.16	369.55	0.57	2.92	1.59	7.36
S23	13.8	55.01	122.41	13.94	56.55	12.44	2.44	11.01	1.85	11.66	2.66	6.56	1.00	6.19	1.01	304.74	0.64	2.78	1.44	6.00
S24	13.5	61.82	117.17	16.44	67.68	14.16	2.68	11.82	1.93	12.02	2.69	6.62	1.05	6.93	1.18	324.18	0.63	2.75	1.38	6.02
S25	13.2	23.95	45.78	6.60	25.92	5.55	0.99	4.60	0.76	4.87	1.07	2.65	0.40	2.75	0.46	126.35	0.60	2.72	1.35	5.87
S27	12.5	62.18	109.64	16.62	64.57	13.88	2.44	11.16	1.92	11.95	2.59	6.42	1.03	7.23	1.24	312.89	0.60	2.82	1.25	5.81
S28	12.1	68.31	137.34	16.84	64.40	13.69	2.23	11.28	2.01	12.51	2.71	6.68	1.09	8.02	1.40	348.51	0.55	3.14	1.14	5.75
S29	11.9	47.96	121.76	11.41	43.54	9.05	1.77	7.72	1.33	8.34	1.85	4.57	0.71	4.86	0.80	265.68	0.65	3.34	1.29	6.66
S30	11.7	51.22	108.71	12.61	49.47	10.24	2.21	8.64	1.47	9.25	2.04	5.05	0.79	5.40	0.92	268.02	0.72	3.15	1.30	6.41
S32	11.3	60.59	134.20	15.24	60.08	12.68	3.13	10.39	1.73	10.72	2.36	5.74	0.91	6.19	1.03	325.00	0.83	3.01	1.36	6.61
S34	10.5	71.17	150.35	19.47	80.66	17.04	3.28	13.27	2.25	13.93	2.95	7.03	1.12	7.81	1.33	391.65	0.67	2.63	1.38	6.15
S35	10.0	73.35	149.43	19.22	76.30	16.29	2.73	13.52	2.26	14.21	3.12	7.50	1.17	7.83	1.33	388.26	0.56	2.83	1.40	6.33
S36	9.3	66.99	143.58	17.61	69.22	14.63	3.00	11.99	2.03	12.74	2.75	6.60	1.03	6.87	1.18	360.23	0.69	2.88	1.42	6.59
S38	8.6	44.61	94.47	10.77	39.62	8.03	1.99	6.60	1.07	6.56	1.33	3.23	0.46	3.39	0.54	222.68	0.84	3.50	1.58	8.89
S40	8.3	35.14	58.40	8.58	33.14	7.06	2.04	5.82	0.93	5.50	1.14	2.71	0.38	2.70	0.44	164.00	0.97	3.13	1.75	8.80
S48	4.3	52.68	112.89	12.50	45.90	9.62	2.28	7.80	1.23	7.65	1.65	4.13	0.64	4.51	0.77	264.24	0.80	3.45	1.40	7.89
S49	3.8	38.07	91.37	10.04	36.63	8.87	1.86	7.95	1.48	9.60	2.25	5.89	0.96	6.65	1.14	222.75	0.68	2.70	0.97	3.87
S55	1.0	50.57	89.57	9.68	32.70	6.84	1.16	6.19	1.11	8.03	2.12	6.28	1.24	9.57	1.77	226.84	0.55	4.66	0.52	3.57
UCC		30.00	64.00	7.10	26.00	4.50	0.88	3.80	0.64	3.50	0.80	2.30	0.33	2.20	0.32	146.37	0.65	4.20	1.40	9.21

Subscript N denotes chondrite normalized values

*Taylor and McLennan (1985)

**Taylor and McLennan (1981)

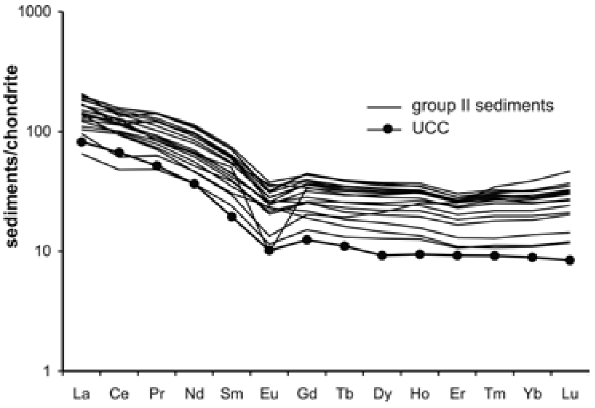

Fig. 4 Chondrite normalized REE diagrams of group II sediments and UCC (upper continental crust, Taylor and McLennan, 1981).

Mineralogy

Table 3 presents the semi-quantitative estimation of the bulk mineralogy of the tephra deposits and sediments. The tephra deposits consist of plagioclase as the most abundant mineral followed by pyroxene. Olivine is present in minor amounts. The mineralogical distribution and their abundance in the sediments of groups I and II are different from tephra. In group I, plagioclase and polymorphs of quartz (i.e. tridymite and cristallobalite) are the most abundant minerals. Quartz, K-feldspars, amphiboles, mica and clay minerals are present in minor amounts. Both pyroxene and olivine are absent. Group II consists of K-feldspar, plagioclase, tridymite/cristobalite and mica in minor amounts.

Major and trace elements

The tephra layers have comparable chemical composition and basalt to basaltic-andesite in nature (SiO_2 = 49.9-57.1%). They show variable concentrations of Al_2O_3 (13.0-18.5 %), TiO_2 (0.9-1.6 %), Na_2O (0.9-3.1 %), K_2O (0.4-1.3 %), CaO (1.7-9.7 %), MgO (2.7-7.5 %), Fe_2O_3 (6.0-9.0 %) and relatively homogeneous concentrations of P_2O_5 (0.15-0.39 %), Zr (142-215 ppm), Y (17-39 ppm), Zn (69-89 ppm) and Th (3 ppm).

Except for a few elements, the chemical composition of group I sediments is comparable to tephra (SiO_2: 52.6-61.7 %, Al_2O_3: 16.4-19.0 %, TiO_2: 0.8-1.7 %, Na_2O: 1.9-3.3 %, K_2O: 1.0-1.8 %, CaO: 2.2-6.9 %, Fe_2O_3: 5.6-9.2 %, P_2O_5: 0.04-0.31 %, Y: 24-42 ppm). They are depleted

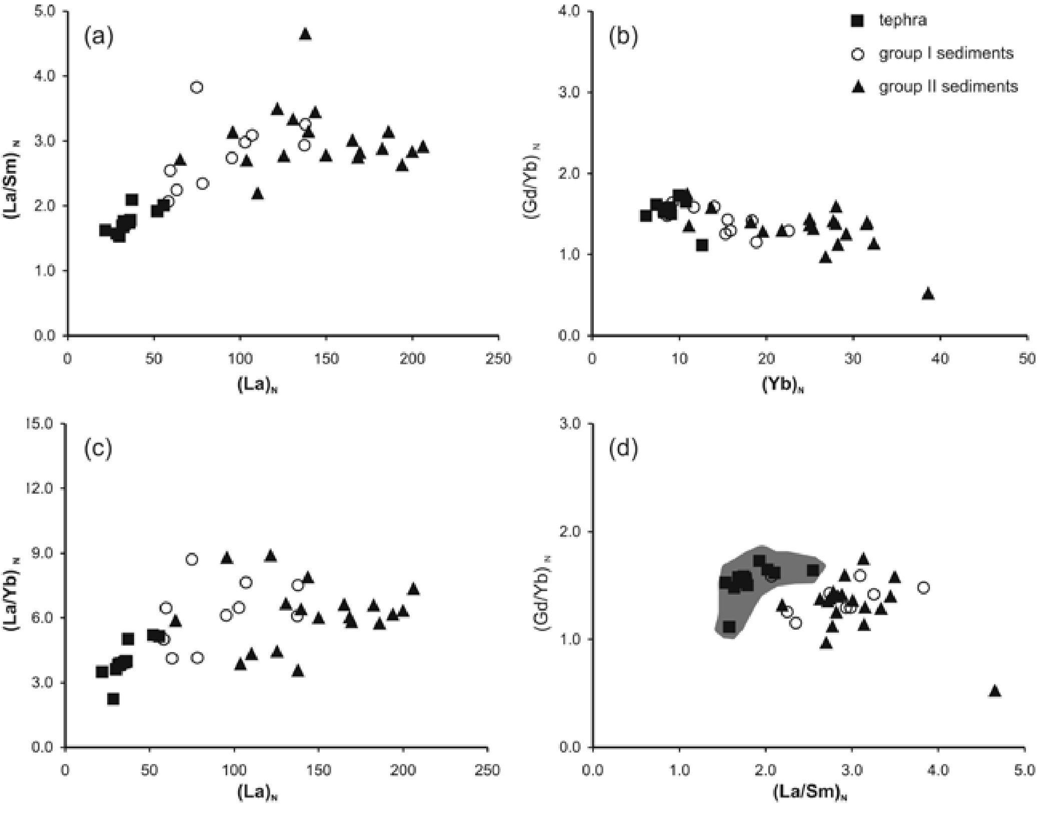

Fig. 5 Chondrite normalized (a) light REE, (b) heavy REE, (c) total REE fractionations with changing REE contents and (d) distribution of light REE and heavy REE fractionations in tephra and sediments from the Pachuca sub-basin.

Table 3

Bulk mineralogy of tephra deposits and sediments of the Pachuca sub-basin.

	Tephra	**Sediment**	
		Group I	**Group II**
Quartz	-	+	-
Tridymite/Cristobalite	-	++	++
Plagioclase	++++	+++	++
K-feldspar	-	+	++
Pyroxene	+++	-	-
Amphibole	-	+	-
Olivine	+	-	-
Mica	-	+	+
Amorphous (Non crystalline)	+	++	++
Clay minerals	-	+	-

++++, very abundant, +++, abundant, ++, major, +, minor, -, absent

Table 4

Average elemental concentrations and CIA values in tephra deposits and sediments of the Pachuca sub-basin.

	Elements	**Tephra (n=12)**	**Sediment**	
			Group I (n=11)	**Group II (n=19)**
	Major elements (%)			
	SiO_2	51.63	58.29	66.83
	TiO_2	1.41	1.11	0.39
	Al_2O_3	17.27	17.55	14.49
	$Fe2O_3$	8.30	6.86	4.01
	MnO	0.12	0.11	0.08
	MgO	5.38	1.65	0.44
	CaO	8.51	3.11	1.43
	Na_2O	2.65	2.37	2.80
	K_2O	0.61	1.37	3.54
	P_2O_5	0.23	0.11	0.04
Trace elements (ppm)				
	Zr	162	352	491
	Y	23	33	50
	Zn	78	99	141
	Th	3	6	13
CIA	46	62	57	

CIA = chemical index of alteration

Table 5

Coeficiente of correlation between rare earth elements (REE) and total REE (TREE) with different major and trace elements at 95% confidence level ($p<0.05$).

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Zr	Y	Zn	Th
La	0.84	-0.82	-0.60	-0.79	-0.52	-0.84	-0.83	-	0.76	-0.72	0.84	0.68	0.71	0.67
Ce	0.84	-0.83	-0.60	-0.80	-0.57	-0.85	-0.84	-	0.79	-0.72	0.85	0.64	0.72	0.66
Pr	0.80	-0.79	-0.59	-0.75	-0.49	-0.80	-0.78	-	0.74	-0.68	0.79	0.66	0.72	0.59
Nd	0.76	-0.75	-0.58	-0.70	-0.47	-0.76	-0.73	-	0.70	-0.63	0.74	0.62	0.71	0.53
Sm	0.75	-0.74	-0.59	-0.69	-0.45	-0.74	-0.71	-	0.71	-0.62	0.72	0.63	0.72	0.52
Eu	0.34	-	-	-	-	-0.43	-0.38	0.36	-	-	0.48	-	-	-
Gd	0.76	-0.75	-0.63	-0.69	-0.48	-0.73	-0.71	-	0.73	-0.62	0.72	0.64	0.74	0.53
Tb	0.77	-0.76	-0.64	-0.71	-0.47	-0.74	-0.72	-	0.75	-0.64	0.74	0.68	0.77	0.56
Dy	0.77	-0.77	-0.65	-0.71	-0.48	-0.73	-0.72	-	0.77	-0.65	0.76	0.71	0.79	0.59
Ho	0.78	-0.78	-0.68	-0.72	-0.48	-0.72	-0.72	-	0.79	-0.65	0.78	0.73	0.80	0.64
Er	0.79	-0.79	-0.68	-0.74	-0.48	-0.74	-0.74	-	0.81	-0.67	0.82	0.77	0.81	0.70
Tm	0.78	-0.78	-0.65	-0.73	-0.45	-0.73	-0.74	-	0.81	-0.67	0.84	0.79	0.81	0.76
Yb	0.77	-0.77	-0.61	-0.73	-0.43	-0.73	-0.74	-	0.79	-0.67	0.86	0.81	0.80	0.79
Lu	0.75	-0.75	-0.59	-0.72	-0.41	-0.71	-0.73	-	0.77	-0.66	0.85	0.81	0.78	0.81
TREE	0.83	-0.82	-0.61	-0.78	-0.53	-0.83	-0.81	-	0.77	-0.70	0.83	0.67	0.74	0.64

in MgO (1.0-3.2%) and enriched in Zr (226-512 ppm), Zn (68-152 ppm) and Th (3-11 ppm) compared to tephra. Both the tephra deposits and group I sediments have higher concentrations of TiO_2, Al2O3, Fe2O3, MnO, MgO, CaO and P2O5 compared to group II sediments.

Group II sediments show higher concentrations of SiO_2 (62.2-70.9 %), K_2O (1.9-5.4 %) and Na_2O (2.1-4.2 %). The distributions of Zr (293-698 ppm), Y (31-71 ppm), Zn (84-181 pm) and Th (5-32 ppm) show large variations and most of the samples have higher concentrations of these elements than the sediments of group I. Table 4 presents the average concentrations of major and trace elements in the tephra deposits and overlying sediments.

The degree of chemical alteration of the samples is estimated by the calculation of the chemical index of alteration (CIA) using the formula of Nesbitt and Young (1984), where

$$CIA = [Al_2O_3 / (Al_2O_3+CaO+Na_2O+K_2O)] \times 100.$$

The CIA of tephra deposits (44 – 51) suggests the absence of chemical weathering. The CIA values of the sediments vary between 49 and 77. The sediments of group I (49-77) and group II (51-65) have comparable CIA values which indicate low to intermediate chemical weathering in the source terrains (Table 4).

Statistical analysis

Table 5 presents the coefficient of correlation between the REE and different major and trace elements at 95% significant level ($p<0.05$). Among the compositional variables, TiO_2, Fe_2O3, MgO and CaO show strong negative correlations and Al_2O_3, MnO and P_2O_5 show significant negative correlations with the REE and TREE. Constituents like SiO_2, K_2O, Zr, Y, Zn and Th show positive correlations. Zr shows a strong correlation with both light REE (LREE) and heavy REE (HREE) and an intermediate correlation with middle rare earth elements. The correlation coefficient of K_2O, Y, Zn and Th are stronger with HREE compared to LREE. Similarly, SiO_2 shows stronger correlation with LREE compared to HREE. Na_2O show significant positive correlation with Eu.

Discussion

The tephra fall deposits of the Pachuca sub-basin are basalt to basaltic-andesite in nature and have chemical and mineralogical compositions comparable to the volcanic products from the Apan-Tezontepec volcanic field (ATVF). Both of them also have equivalent SiO_2 concentrations. The rocks of ATVF consist of basalt to basaltic-andesites that are characterized by the occurrence of olivine and plagioclase (García-Palomo *et al*., 2002).

The tephra deposits have SiO_2 concentrations of 49.9-57.1% and the rocks of ATVF have concentration of SiO2 varying between 50.0 and 56.0% (García-Palomo *et al*., 2002). This suggests that the tephra layers present at the base of the studied profile are possibly sourced from different eruptive events at ATVF. The K/Ar dates constrained the volcanic activities at ATVF between 1.50 Ma and 0.47 Ma (Cantagrel and Robin, 1979; López-Hernández and Castillo-Hernández, 1997; Carrasco *et al*., 1997). So the overlying sediments were likely deposited after 0.47 Ma.

In order to understand the REE systematic (abundance and pattern) of the tephra deposits and overlying sediments, chondrite normalized light REE (Fig. 5a), heavy REE (Fig. 5b) and total REE (Fig. 5c) fractionations are taken into consideration. The samples do not show any heavy REE fractionation but indicate varying degrees of light REE fractionation. With increasing REE abundance (La), the light REE fractionation (La/Sm) of group II sediments remains relatively constant. The tephra deposits and group I sediments show gradually increasing light REE fractionation. This feature is similar for their total REE fractionations (Fig. 5c). So, the differences in REE patterns are mainly caused by variations in the La/Sm ratios (Fig. 5d). The absence of authigenic minerals (i.e. carbonates and evaporites) both in the tephra deposits and overlying sediments rules out the effect of inflow geochemistry on REE fractionations. Similarly, intermediate and comparable CIA values (Table 4) also rule out the effect of chemical weathering on REE abundance and their fractionations. This suggests that the REE abundance and their fractionations are controlled mainly by the source rock composition and clastic mineralogy including heavy minerals. In the absence of heavy mineral data, concentrations of elements associated with heavy minerals are considered. For example, higher concentration of Zr is related to zircon, Th with both monazite and allanite and Ti to sphene.

The tephra deposits consisting of pyroxene and olivine show lower total REE abundance. The REE are incompatible in basaltic and andesitic liquids and are only slightly fractionated (Rollinson, 1993). This is mirrored by the lower light and heavy REE fractionations (Fig. 3 and Table 1) and the negative coefficient of correlation between TiO_2, Fe_2O_3, MnO, CaO, MgO, P_2O_5 and TREE (Table 5). The positive Eu anomaly mirrors the higher abundance of plagioclase (Table 3). The higher concentration of P_2O_5 (0.15-0.39 %) in the tephra could be from the accessory phases such as apatite and monazite. However, lower Th concentration (Table 4) and light REE (La to Sm) rule out the presence of monazite. So, the higher concentrations of middle REE (Gd to Ho) in tephra layers compared to UCC (Table 1) is mainly caused by the occurrence of apatite. Apart from plagioclase, a part of the CaO in the tephra is associated with apatite.

The sediments overlying the tephra deposits show comparable LREE and HREE fractionations (Fig. 5d) but variable REE patterns (Figs. 3 and 4), TREE contents and Eu anomalies (Tables 1 and 2). Most of the group I sediments have lower TREE concentrations and absence of Eu anomalies compared to group II sediments. This variable REE systematic is also mirrored by their different mineralogical assemblages and geochemical compositions. Group I sediments have plagioclases and amphibole and geochemical composition comparable to the tephra layers (Table 4). The comparable REE systematic and geochemical composition between group I sediments and tephra and presence of mafic minerals (plagioclases and amphibole) suggest that the group I sediments are possibly sourced from mafic rocks with chemical composition similar to the tephra deposits.

The sediments of group II have higher concentrations of SiO_2, K_2O, Na_2O, Zr, Y, Zn and Th (Table 4), higher abundance of K-feldspar (Table 3) and higher TREE concentrations (Table 2). The REE are preferentially partitioned into melts during crystallization and are enriched in felsic rocks compared to mafic rocks (Feng and Kevrich, 1990). The higher concentrations of SiO_2, K_2O, Na_2O, Zr, Y, Zn and Th (Table 4), their positive correlation with REE and TREE (Table 5) and higher abundance of felsic mineral K-feldspar in group II sediments point to a source terrain comprising of felsic rocks. Higher concentrations of both Th and Zr in group II sediments suggest that the higher LREE abundance could be due to presence of monazite and allanite and higher HREE abundance could be due to presence of zircon. The provenance of the sediments that varies between mafic and felsic source terrains is supported by the surrounding geology. The sierra de Pachuca consists of alternated layers of mafic and felsic rocks (Geyne *et al*., 1963). So the sediments from depths of 15-17 m, 4.6-9.6 m and 2-4.6 m (group I) could be derived from the erosion of mafic to intermediate rocks consisting of basaltic-andesite, andesite and andesite-dacite, whereas the sediments from depths of 9.6-15 m and 0-2 m (group II) are possibly sourced from dacite, dacite-rhyolite and rhyolites. The geochemical characteristics of group II sediments suggest the presence of heavy minerals (monazite and allanite) that are typical of intrusive plutonic rocks, e.g. granodiorite, granite and pegmatite. However detail geochemical analysis of the surrounding geology is required to point out the exact source terrains contributing sediments to the Pachuca sub-basin.

Conclusions

The tephra fall deposits and overlying volcano-clastic sediments from the Pachuca sub-basin located at the north-eastern Basin of Mexico show significantly different REE patterns, fractionations and Eu anomalies. The basalt to basaltic-andesite tephra layers present at the base of the sequence were likely sourced from the Apan-Tezontepec volcanic field and characterized by lower TREE, lower light and heavy REE fractionations and positive Eu anomaly. The positive Eu anomaly reflects the higher abundance of plagioclase. Similarly, the higher concentrations of middle REE suggest presence of apatite. Based on the REE abundances and Eu anomalies, the sediments overlying the tephra are divided into two different groups and show comparable light, heavy and total REE fractionations. However, group I sediments have geochemical compositions and Eu anomalies comparable to the tephra. They are characterized by the absence of Eu anomaly and lower TREE abundances compared to group II sediments and suggest a mafic provenance possibly from the basaltic-andesite and andesites exposed in the Sierra de Pachuca. Group II show a negative Eu anomaly comparable to UCC, but their TREE concentrations are higher than UCC. Higher concentrations of light REE and Th in group II suggest the occurrence of trace minerals (allanite and monazite). Similarly, higher abundances of heavy REE and Zr suggest presence of zircon. All of these are indicative of a provenance comprising of plutonic igneous rocks or felsic volcanic rocks, e.g. dacite and rhyolite.

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