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RARE EARTHS AND OTHER TRACE ELEMENTS IN CRETACEOUS CLAYS FROM CENTRAL PORTUGAL

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Eight rare-earth elements (REE), namely La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu, as well as other elements (Na, K, Sc, Cr, Fe, Co, Rb, Cs, Ba, Hf, Ta, and Th), have been determined in fifteen cretaceous clay samples of continental facies by instrumental neutron activation analysis. It was found that the REE contents are variable in absolute and relative values, but the means of these values are similar to those of European shales. Analyses have also been made of the fractions <38 μm and <2 μm (clay-sized). The mineral contents of the clay-sized fraction were determined semi-quantitatively by X-ray diffraction. The results suggest the preferential presence of REE, Hf, and Th in fractions 2–38 μm, which can be explained by the presence of apatite, monazite, and zircon. A correlation study of chemical and mineralogical data of the clay-sized fraction showed that kaolinite is correlated with REE, specially the lighter ones; illite with K, Rb, and Cs; and smectite with Na.

Introduction

The rare-earth element (REE) contents, as well as the concentrations of other elements in sediments, depend obviously on the chemical composition of their constituent minerals, i.e., on the nature of the source rock, weathering and transport processes, and exchange reactions after deposition.

The REE distributions in most shales appear to be quite similar. However, some significant variations have been observed, and the reason for them has not yet been well explained. In many cases no correlation has been found between the REE distribution and clay mineral contents.

In this work, some cretaceous clays from the "Meso-Cenozoic western border of Portugal", and the Lousã Basin, were analysed by neutron activation in order to determine their REE contents, as well as the contents of other trace and major elements. Analyses of the

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fractions <38μm and <2μm (clay-sized) were also carried out, with the view of studying how those elements are distributed in the different-sized grains. On the other hand, the clay-mineral contents of the clay-sized fractions were determined, and the results compared with those of the chemical analyses. For estimating chemical and mineralogical relationships, numerical taxonomy methods, namely cluster analysis and principal components analysis, were applied.

Experimental

Fifteen clay samples from nine different loci were collected from cretaceous clay deposits of continental facies either in the Lousã basin or in the "Figueira da Foz- Coimbra-Pombal" area (Fig.1), which belong to a large coastal basin denominated "Meso-Cenozoic western border". It should be pointed out that these two basins were not separated at the time of deposition, so that both are integrated in the same model of deposition[1].

For each collected clay, three samples were prepared, representing: (i) the whole rock; (ii) the fraction <38μm; and (iii) the clay-sized fraction (<2μm). Sample preparation of whole rocks only involved grinding and homogenizing. For obtaining the fractions <38μm, deionized water was added to the clay samples, and then their constituents were sorted through suitable sieves. The clay-sized fractions were prepared by means of successive centrifugations until one obtained a stable suspension, and then by gravity settling.

The chemical analyses were carried out by using the instrumental neutron activation method developed at our laboratory[2,3]. The clay mineral contents of the clay-sized fractions were determined semi-

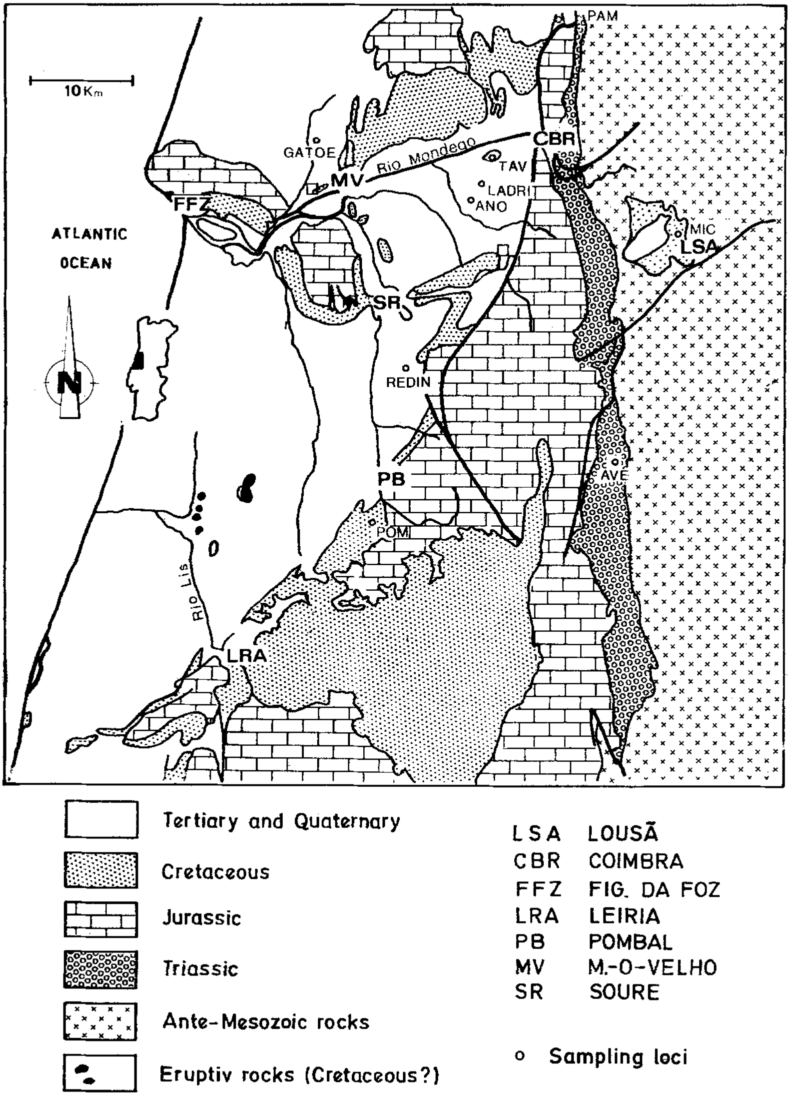

Fig. 1. Location of the sampling loci

quantitatively by X-ray diffraction (oriented aggregates). Computations of cluster and principal components analysis were performed by employing the NTSYS programs system[4].

Results and discussion

The results of the chemical analyses for the whole sediment, the fraction <38µm, and the clay-sized fraction are presented in Tables I, II and III, respectively.

The REE diagrams of two selected samples (GATOE and MIC-2) of the whole rocks, and the corresponding fractions <38µm and <2µm, relative to condrites[5] and to European shales (ES)[6], are shown in Fig.2. In the bottom of the same Figure, the clay mineral contents in the clay-sized fraction are also shown.

As seen in Table I, the REE contents for the analysed whole rock samples have been found to be variable either in absolute value (range of ΣREE = 107-233 ppm, taking into account only the elements determined) or in relative value (range of La/Lu=57-110). The Eu/Sm ratio was used as a criterion for the anomalous behaviour of Eu (Eu/Sm=0.17-0.24). The means of these values are very similar to the corresponding values in the ES.

As expected, the REE contents in the fractions <38µm are higher than in the whole sediment (sample GATOE is a typical example). However, the REE contents in the clay-sized fraction are smaller than in the fraction <38µm , particularly as far as the heavier REE are concerned. This is an indication of the preferential presence of these elements in the fraction 2µm-38µm. However, some exceptions were found, as for instance the MIC-2 sample, where the REE contents, particularly those of the light and intermediate REE, are higher in the clay-sized fraction. It should be pointed out that kaolinite is the dominant clay mineral in the observed exceptional cases.

Fig. 3 and Table IV show the results of principal components analysis using the chemical composition data of whole rock and of the

Table I

Concentrations of elements in clay samples

		ANO-1	ANO-2	AVE-1	AVE-2	TAV-1	TAV-2	REDIN	GATOE
Na_2O	%	0.281	0.200	0.242	0.172	0.134	0.136	0.226	0.202
K_2O	"	4.01	2.73	5.93	4.35	2.57	2.11	3.07	2.84
Sc	ppm	19	11	19	19	12	10	15	14
Cr	"	102	60.0	98.1	98.5	70.4	53.6	75.7	80.9
Fe_2O_3T	%	8.04	5.39	5.66	10.2	4.02	3.54	6.34	5.72
Co	ppm	28	14	39	12	12	10	19	17
Rb	"	217	141	220	248	139	101	172	145
Cs	"	13.1	10.7	69.4	74.6	8.15	6.32	12.5	9.67
Ba	"	601	466	561	542	430	461	814	425
La	"	42.7	51.0	43.2	27.8	48.7	41.4	38.7	42.5
Ce	"	71.8	87.6	73.2	58.1	76.3	71.6	72.3	76.9
Nd	"	34.5	41.8	35.7	27.2	38.4	34.1	32.6	36.7
Sm	"	7.8	8.5	9.4	6.9	9.4	7.8	7.0	7.9
Eu	"	1.7	1.8	1.9	1.4	1.9	1.3	1.5	1.6
Tb	"	1.2	1.2	1.0	0.92	1.3	1.2	0.83	1.0
Yb	"	3.32	3.27	3.12	2.87	3.71	3.46	2.67	3.45
Lu	"	0.53	0.52	0.43	0.49	0.60	0.53	0.40	0.52
Hf	"	5.4	7.9	3.8	4.4	8.3	11	5.1	6.3
Ta	"	2.0	1.7	1.9	2.0	1.8	2.0	2.4	1.9
Th	"	15	14	13	13	15	14	13	14
Σ TR		163.6	195.7	168.0	125.7	180.3	161.4	156.0	170.6
La/Lu		80.6	98.1	100.5	56.7	81.2	78.1	96.8	81.7
Eu/Sm		0.218	0.212	0.202	0.203	0.202	0.167	0.214	0.203

		LADRI	PAM-1	PAM-2	POM-1	POM-2	MIC-1	MIC-2
Na_2O	%	0.142	0.119	0.154	0.0958	0.112	0.414	0.060
K_2O	"	2.93	2.05	5.24	1.70	2.55	3.33	0.71
Sc	ppm	15	10	18	11	14	15	5.3
Cr	"	97.1	63.5	95.6	60.2	80.2	90.8	34.4
Fe_2O_3T	%	6.57	1.81	7.93	4.39	1.66	5.05	1.99
Co	ppm	7.7	19	19	11	6.2	8.3	2.3
Rb	"	169	131	239	97.2	127	114	27.9
Cs	"	11.4	8.71	15.7	13.6	17.1	5.58	2.38
Ba	"	555	394	443	413	473	561	172
La	"	52.5	41.7	41.1	52.9	41.6	32.7	28.3
Ce	"	86.1	84.6	72.2	106	71.0	69.6	46.7
Nd	"	43.9	42.7	35.0	55.2	36.7	34.6	23.0
Sm	"	10	8.5	8.2	12	8.4	5.9	5.1
Eu	"	2.2	1.7	1.7	2.0	1.6	1.4	0.93
Tb	"	1.2	1.2	1.1	1.3	1.3	0.88	0.60
Yb	"	3.48	3.64	3.24	3.09	3.55	2.91	1.84
Lu	"	0.52	0.59	0.51	0.48	0.61	0.52	0.31
Hf	"	7.4	8.0	5.0	8.0	6.5	5.1	4.9
Ta	"	1.9	2.1	2.1	1.8	1.9	1.1	1.1
Th	"	16	14	15	14	13	10	9.6
Σ TR		199.9	185.0	163.1	233.0	164.8	148.5	106.8
La/Lu		101.0	70.7	80.6	110.2	68.2	62.9	91.3
Eu/Sm		0.220	0.200	0.20	0.167	0.190	0.237	0.182

Table II

Concentrations of elements in the fraction <38 μm

		ANO-1 < 38μm	ANO-2 < 38μm	AVE-1 < 38μm	AVE-2 < 38μm	TAV-1 < 38μm	TAV-2 < 38μm	REDIN < 38μm	GATOE < 38μm
Na_2O	%	0.309	0.250	0.226	0.218	0.145	0.175	0.263	0.230
K_2O	"	3.30	2.40	4.50	4.47	2.43	1.68	2.70	2.31
Sc	ppm	20	16	21	19	14	12	17	17.8
Cr	"	97.6	76.3	100	95.9	76.5	63.2	79.9	85.9
Fe_2O_3T	%	7.64	5.78	5.90	9.93	4.23	4.42	6.71	5.81
Co	ppm	23	16	40	11	12	11	15	17
Rb	"	204	165	216	222	139	105	185	154
Cs	"	12.7	13.2	72.2	69.3	8.80	7.88	13.7	10.8
Ba	"	498	633	454	473	439	323	440	451
La	"	42.9	70.6	45.4	35.5	52.7	51.9	42.0	47.8
Ce	"	75.2	114	83.1	60.6	88.6	89.3	67.6	89.8
Nd	"	38.3	57.9	45.7	31.1	49.5	45.1	37.9	45.4
Sm	"	7.4	11	11	6.1	9.9	8.8	7.2	8.7
Eu	"	1.6	2.2	2.0	1.4	2.0	1.7	1.6	1.8
Tb	"	1.1	1.4	1.2	1.0	1.4	1.3	1.0	1.2
Yb	"	2.99	3.74	3.13	2.99	4.37	4.76	2.75	4.00
Lu	"	0.52	0.62	0.53	0.44	0.64	0.67	0.47	0.60
Hf	"	4.7	9.0	4.0	3.9	8.9	13	5.6	7.6
Ta	"	1.7	2.1	1.7	1.8	2.0	2.0	2.7	2.1
Th	"	13	16	12	12	15	16	13	15
Σ TR		170.0	261.5	192.1	139.1	209.1	203.5	160.5	199.3
La/Lu		82.5	113.9	85.7	80.7	82.3	77.5	89.4	79.7
Eu/Sm		0.216	0.200	0.182	0.230	0.20	0.193	0.222	0.207

		LADRI < 38μm	PAM-1 < 38μm	PAM-2 < 38μm	POM-1 < 38μm	POM-2 < 38μm	MIC-1 < 38μm	MIC-2 < 38μm
Na_2O	%	0.158	0.129	0.156	0.148	0.131	0.512	0.0884
K_2O	"	2.38	2.12	3.36	1.90	2.22	3.10	0.99
Sc	ppm	17	13	18	17	18	18	12
Cr	"	90.4	63.5	89.5	90.5	96.1	104	43.1
Fe_2O_3T	%	6.60	2.26	7.12	6.76	2.01	5.20	4.87
Co	ppm	7.57	23	17	12	7.2	5.9	5.4
Rb	"	156	148	230	117	128	116	60.8
Cs	"	12.4	10.7	14.5	17.8	19.6	6.27	4.78
Ba	"	600	329	422	573	499	578	329
La	"	60.2	49.5	39.6	76.8	49.1	42.1	45.3
Ce	"	105	102	72.7	148	85.7	70.9	80.4
Nd	"	56.0	49.8	36.8	80.8	48.8	35.9	42.2
Sm	"	11	10	7.3	16	8.9	6.8	7.4
Eu	"	2.42	2.0	1.5	3.0	1.9	1.4	1.9
Tb	"	1.5	1.5	0.99	1.3	1.4	0.96	1.1
Yb	"	3.21	4.76	3.34	4.40	4.43	3.55	3.26
Lu	"	0.58	0.73	0.51	0.69	0.71	0.54	0.52
Hf	"	7.3	10	4.7	8.8	8.3	5.3	7.0
Ta	"	2.0	2.5	1.9	1.8	2.0	1.2	1.4
Th	"	16	16	13	16	15	11	12
Σ TR		239.9	220.8	161.4	331.0	200.0	162.2	182.1
La/Lu		103.8	67.8	75.1	111.3	69.2	78.0	87.1
Eu/Sm		0.220	0.200	0.205	0.188	0.213	0.206	0.257

Table III

Concentrations of elements in the clay-sized fraction

		ANO-1 < 2μm	ANO-2 < 2μm	AVE-1 < 2μm	AVE-2 < 2μm	TAV-1 < 2μm	TAV-2 < 2μm	REDIN < 2μm	GATOE < 2μm
Na_2O	%	0.256	0.254	0.166	0.147	0.158	0.220	0.245	0.219
K_2O	"	4.07	2.82	5.40	4.96	3.17	2.44	3.10	3.03
Sc	ppm	23	18	21	17	19	18	20	20
Cr	"	116	99.2	122	100	120	95.9	95.0	104
Fe_2O_3T	%	9.31	8.03	6.66	12.0	7.12	7.81	8.67	8.39
Co	ppm	28	23	26	11	19	17	17	20
Rb	"	247	197	243	250	202	163	226	180
Cs	"	5.5	15.8	107	104	12.7	12.3	16.7	13.3
Ba	"	537	571	440	344	556	524	376	443
La	"	34.0	57.1	59.5	39.0	44.7	37.1	36.4	34.3
Ce	"	62.4	88.9	97.2	61.0	69.4	64.3	54.9	61.7
Nd	"	33.2	47.7	39.4	24.5	44.4	34.0	31.9	31.8
Sm	"	6.3	8.8	5.6	4.1	9.0	6.6	6.4	6.3
Eu	"	1.5	2.3	1.3	1.2	2.3	1.4	1.6	1.6
Tb	"	0.91	1.0	0.64	0.64	1.1	0.77	0.66	0.56
Yb	"	2.06	2.12	2.72	1.82	3.07	2.29	2.1	1.9
Lu	"	0.37	0.27	0.39	0.33	0.53	0.41	0.31	0.32
Hf	"	3.4	2.5	4.0	3.2	3.3	3.8	4.2	3.2
Ta	"	1.6	1.3	1.7	1.7	1.3	1.8	2.7	1.6
Th	"	13	13	13	12	12	12	13	13
Σ TR		140.7	208.3	206.8	132.6	174.5	146.9	134.3	138.5
La/Lu		91.9	211.5	152.6	118.2	84.3	90.5	117.4	107.2
Eu/Sm		0.238	0.261	0.232	0.293	0.256	0.210	0.250	0.254

		LADRI < 2μm	PAM-1 < 2μm	PAMP-2 < 2μm	POM-1 < 2μm	POM-2 < 2μm	MIC-1 < 2μm	MIC-2 < 2μm
Na_2O	%	0.209	0.134	0.144	0.121	0.156	0.222	0.148
K_2O	"	4.02	3.01	4.14	2.78	3.32	4.58	2.50
Sc	ppm	31	19	20	21	24	23	31
Cr	"	170	113	106	144	143	149	154
Fe_2O_3T	%	14.2	4.28	8.82	13.4	2.80	9.20	17.5
Co	ppm	13	48	21	23	16	8.8	13
Rb	"	304	219	270	185	192	160	161
Cs	"	22.1	19.0	18.1	26.8	33.0	14.8	12.8
Ba	"	1253	512	432	794	699	791	1067
La	"	69.3	45.2	35.1	72.3	35.9	29.2	73.1
Ce	"	135	9.6	66.7	146	59.6	48.0	121
Nd	"	75.5	55.0	36.6	83.5	34.3	25.8	63.9
Sm	"	15	10	6.8	16	6.1	5.4	12
Eu	"	4.0	2.3	1.5	3.3	1.6	1.2	3.7
Tb	"	2.1	1.4	0.65	1.6	0.91	0.82	1.5
Yb	"	3.0	2.9	2.28	3.20	3.37	3.19	4.75
Lu	"	0.51	0.50	0.40	0.57	0.63	0.60	0.63
Hf	"	4.1	3.7	3.8	4.4	5.5	6.3	4.3
Ta	"	2.2	1.7	1.7	1.5	1.7	1.5	2.1
Th	"	20	15	13	14	12	13	20
Σ TR		304.1	216.9	150.0	326.5	142.4	114.2	280.6
La/Lu		135.2	90.4	87.8	126.8	57.0	48.7	116.0
Eu/Sm		0.267	0.230	0.221	0.206	0.262	0.222	0.308

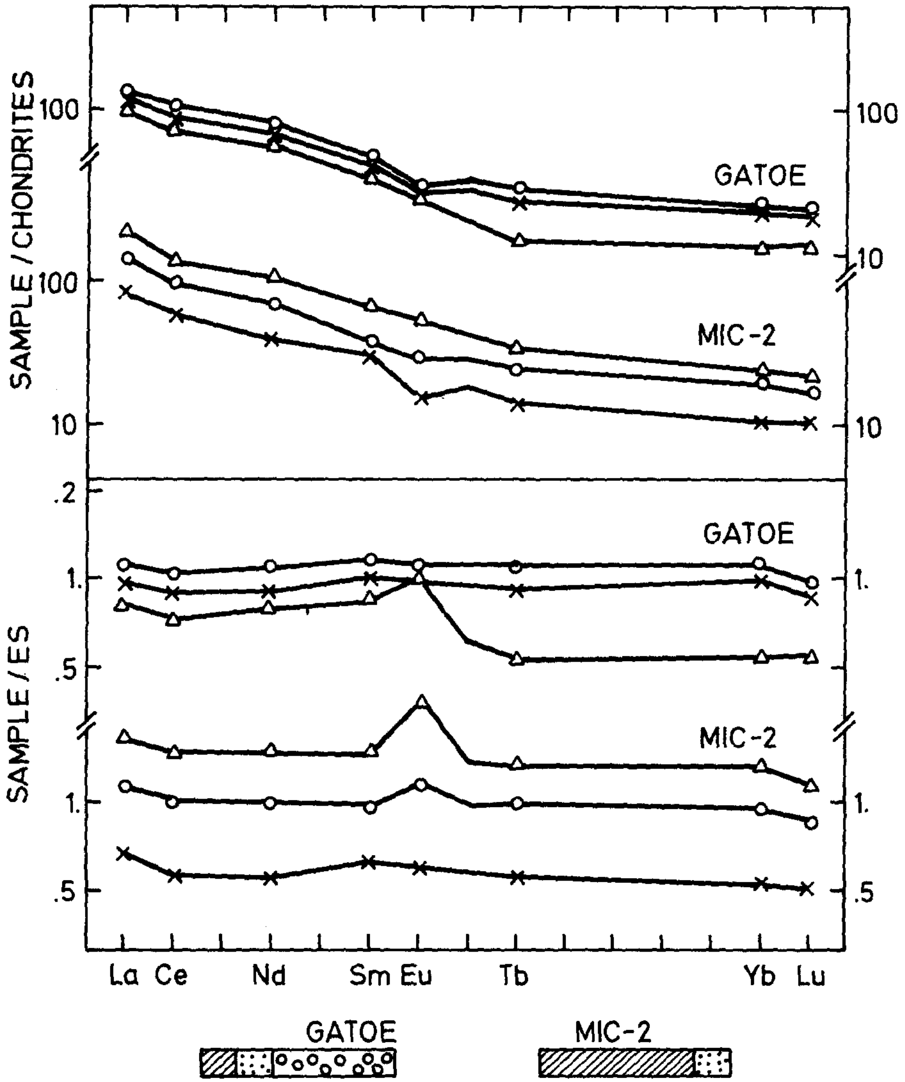

Fig. 2. REE distributions and clay mineral contents of the clay-sized fraction in the selected samples GATOE and MIC-2. X whole rock; o fraction <38 µm; Δ clay-sized fraction; ▨ kaolinite; ⊡ illite, ▦ smectite

fractions <38µm and <2µm. These results indicate (1) an increase in REE and Th after the separation of the fraction >38µm, and (2) an enrichment in K, Rb, Sc, Cr, and Fe and a decrease in Hf after removing the grains >2µm. The decrease in Hf, which has a strong affinity with Zr,

Table IV
Relative contribution of attributes to first principal components and relative importance of these

Attributes	FACT 1	FACT 2	FACT 3
Na_2O	.208	-.287	.248
K_2O	.229	-.731	.341
Sc	-.352	-.820	.338
Cr	-.379	-.721	.276
Fe_2O_3T	-.292	-.768	.009
Co	-.041	-.419	.005
Rb	.026	-.850	.162
Cs	.185	-.493	-.010
Ba	-.608	-.523	.262
La	-.909	-.005	-.275
Ce	-.929	.029	-.246
Nd	-.850	-.028	-.087
Sm	-.917	.069	-.155
Eu	-.930	-.227	-.121
Tb	-.868	.206	.135
Yb	-.610	.541	.432
Lu	-.582	.533	.524
Hf	-.300	.849	.176
Ta	-.267	.097	.363
Th	-.839	-.007	.199
Σ REE	-.951	.024	-.235
La/Lu	-.304	-.448	-.730
Eu/Sm	-.074	-.661	-.029
Eigenvalue	8.30	5.86	1.92
% variance	36.1	25.5	8.3
Cumulative % variance		61.6	69.9

together with the decrease of the heavy REE after the separation of the fraction >38µm, suggest the presence of zircon in the fraction 2µm-38µm.

In order to investigate any possible correlation between the clay minerals and the elements determined in the clay-sized fraction, cluster analysis (UPGMA), using the R technique and the correlation

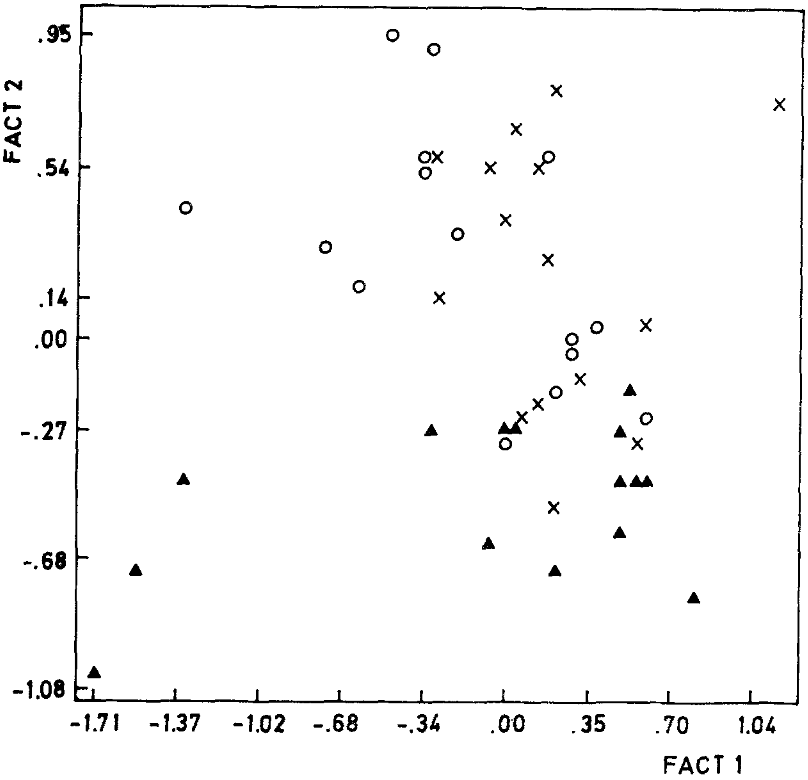

Fig. 3. Ordination plot of the whole sediments (X) and the fractions <38 μm (o) and <2 μm (▲) from principal components analysis. The proportion of the variance accounted for by the two first principal components is 61.6%

coefficient to estimate the similarity between characters, was employed. Chlorite was not taken into account in this analysis, since it is present only in two samples (AVE-1 and AVE-2). The resulting phenogram is presented in Fig.4. The corresponding cophenetic correlation coefficient was 0.89.

As seen in this phenogram, it appears that: (1) kaolinite is correlated with the REE, particularly the light and intermediate REE; (2) illite is correlated with K, Cs, and Rb; and (3) smectite is correlated with Na.

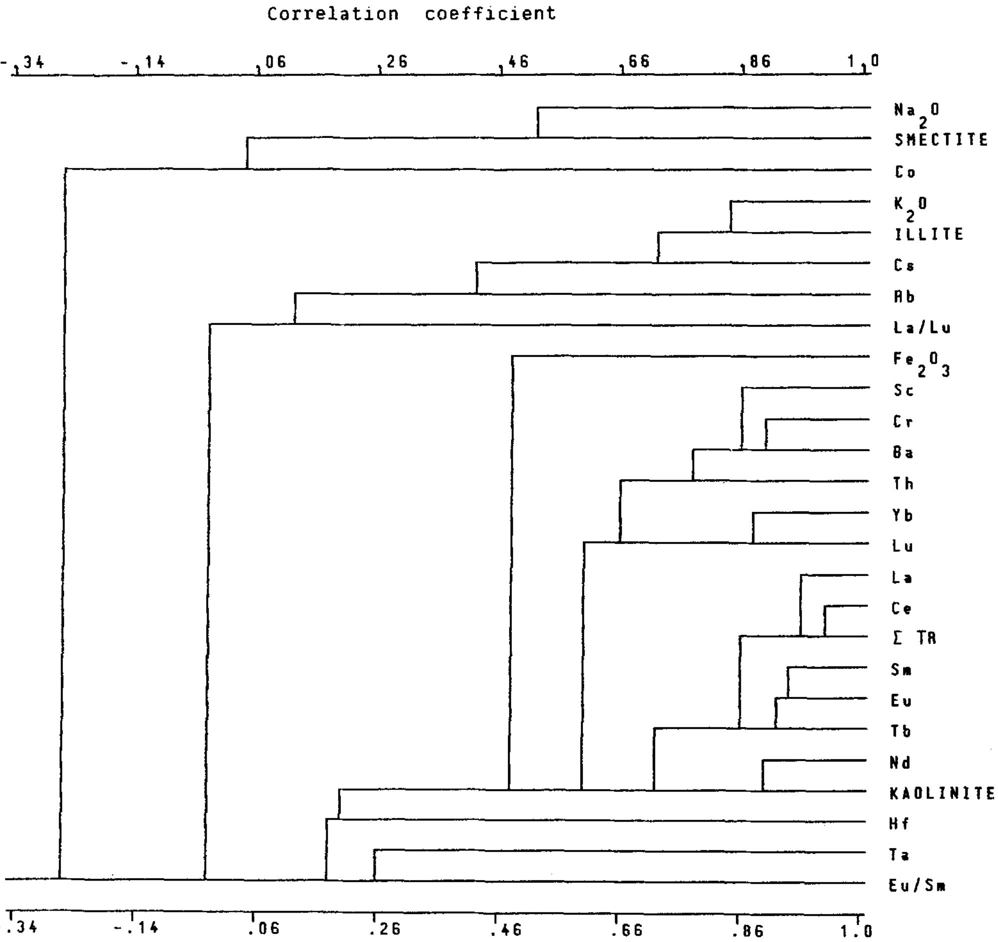

Fig. 4. Phenogram of characters (constituent elements and clay-minerals), based on UPGMA cluster analysis of correlation coefficients. The cophenetic correlation coefficient was 0.89

It is interesting to note that the Eu anomaly is generally smaller, or even absent, in the clay-sized fraction than in the others. On the other hand, it seems not to be correlated with any of the constituent clay minerals. The heavy REE are mostly correlated with Hf, probably due to their affinity with zircon.

A correlation between REE (and also ΣREE) and kaolinite had already been observed in the clay-sized fraction of some American shales, which was explained as due to the low ion-exchange capacity of that mineral[7]. Smectites, with a higher exchange capacity, can lose these elements more easily, explaining the low REE contents observed in the clay-sized fraction when this mineral group is the dominant mineral in that fraction.

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