Research Article

Grain-Size Control on the Rare Earth Elements Distribution in the Late Diagenesis of Cretaceous Shales from the Southern Apennines (Italy)

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Different grain-size fractions of samples collected from shales were investigated to determine the role of late diagenetic grade and mineralogy on the rare earth elements (REE) distribution. The samples were collected from Upper Cretaceous varicoloured shales of the Sicilide Unit near the Corleto Perticara villages, Southern Apennines (Italy). The mineralogical and chemical composition of the sample's five fractions (>63 , $32-63$, $2-32$, $0.1-2$, and $<0.1\ \mu\text{m}$) was studied. The data indicate that certain accessory minerals are more important than clay minerals in controlling the REE distribution. In particular, zircon controls the distribution of earth elements in the $0.1-2\ \mu\text{m}$ fraction and is an efficient mechanism in determining the concentration and distribution of REEs in the studied shales.

1. Introduction

The rare earth elements (REE) are considered immobile during diagenesis, hydrothermal processes, and metamorphism (e.g., [1–4]). For this reason, the REEs are useful indicators of provenance of dust aerosol (e.g., [5–10]) and fluvial and marine sediments (e.g., [11–13]). However, some studies have provided evidence of the mobilisation and fractionation of REEs during diagenesis and hydrothermal alteration (e.g., [5, 14–19]) and that these processes depend on the minerals in which the trace elements are hosted. Although it is generally assumed that the rare earth elements are concentrated in the clay-size fraction, a few studies have addressed the role of grain size on REE distribution (e.g., [2, 20–24]), and only some papers have determined the phases in which these elements are mainly hosted [3, 23]. To our knowledge, no investigations have been carried out on the $<0.1\ \mu\text{m}$ grain-size fraction.

Accessory minerals such as monazite, apatite, and zircon, which are common in sedimentary rocks, are known to concentrate and fractionate REEs [11, 25–31]. Other studies,

however, have indicated that these minerals cannot control the REE distribution in the sediments [1, 18, 32, 33]. González López et al. [34] showed that clay minerals have some influence on REE abundance, whereas other authors suggested that kaolinite is the principal REE carrier in the clay fraction [35]. Additionally, Honty et al. [33] considered authigenic mineral phases concentrated in fine and ultrafine fractions as the most appropriate to address potential REE fractionation induced by either diagenetic or hydrothermal processes. The investigations performed by these authors suggest that accessory minerals had no significant impact on the REE contents in the shales and that the distribution patterns of the various analysed size fractions consist mainly, if not exclusively, of mixed layers of illite-smectite, according to the data in the literature [1, 19].

The behaviour of the REEs in clay sediments is not yet completely defined, most likely because such studies were performed on different types of sedimentary rocks with variable amounts of different-sized detrital phases from various geological environments.

Our study aims to contribute to this discussion by evaluating the effect of distinct grain-size fractions of samples subjected to late diagenesis on the distribution of the REEs. In particular, we focus on the clay fraction ($0.1\text{--}2\text{ }\mu\text{m}$ and $<0.1\text{ }\mu\text{m}$) characterised by the presence of mainly I/S mixed layers. The samples studied were collected from shales characterised by a high amount of ordered illite-smectite mixed layers (I/S; I = 70–80%; R1) and showing late diagenesis maturity [36]. Geochemical, mineralogical, and petrographic compositions indicate that a composite crystalline basement, including low- and high-grade metamorphic units, was a major source of these shales, together with some contributions from mafic-ultramafic rocks [37].

2. Samples and Methods

Six samples were collected from the Upper Cretaceous varicoloured shales of the Sicilide Unit near the Corleto Perticara villages in the Southern Apennines (Italy) ([38] and references therein) (Figure 1).

Mineralogical and chemical compositions of the >63 , $32\text{--}63$, $2\text{--}32$, $0.1\text{--}2$, and $<0.1\text{ }\mu\text{m}$ size fractions were studied. Grain-size separation was performed by wet sieving for the $32\text{--}63\text{ }\mu\text{m}$ and $>63\text{ }\mu\text{m}$ fractions and by gravity settling in distilled water for the clay fraction ($<2\text{ }\mu\text{m}$). The splitting of this fraction into two grain-size classes (<0.1 and $0.1\text{--}2\text{ }\mu\text{m}$) was performed by centrifugation, and they were collected by evaporation to avoid any loss of ultrafine particles.

The mineralogy of the whole rock and of the five grain size fractions on random specimens prepared by the side-loading method was determined by X-ray powder diffraction (XRD) using a Siemens D5000 diffractometer (Cu-K α radiation; graphite secondary monochromator; sample spinner; step size 0.02° ; speed $0.6^\circ/\text{min}$). Oriented mounts were prepared by settling a suspension (concentration: 10 mg/cm^2) on a glass slide after being saturated with Mg^{++} cations using a 1 N MgCl_2 solution. Each specimen was analysed in an air-dried state, glycolated at 60°C for 8 h, and heated at 375°C for 1 h [39]. The mixed layer I/S was identified following the indications of Moore and Reynolds [39], and a very good agreement exists between our experimental profile and the theoretical profile calculated with Newmod [40]. The comparison showed that there is an excellent agreement between profiles.

Semiquantitative mineralogical analyses of the different fractions, except for the >63 and $0.1\text{ }\mu\text{m}$ fractions, were performed on random powders and orientated specimens using the WINFIT computer program [41]. The strongest reflection of each mineral was considered. An exception was made for quartz, for which the $4.26\text{ \AA}$ line was used instead of the peak at $3.34\text{ \AA}$ because of its superimposition with $10\text{ \AA}$ -minerals and the I-S mixed layer series. The amount of phyllosilicates was estimated by measuring the $4.5\text{ \AA}$ peak area. The percentage of phyllosilicates, determined on the oriented specimens, was split according to the following peak areas: $10\text{--}15\text{ \AA}$ (illite-smectite), $10\text{ \AA}$ (illite + micas), and $7\text{ \AA}$ (kaolinite + chlorite) minerals. The amount of these latter phases was estimated on the basis of the intensity of

FIGURE 1: Geological sketch map of Southern Apennine (modified after [47]) with indication of studied area.

the lines at $3.58\text{ \AA}$ and $3.54\text{ \AA}$, respectively. A quantitative analysis of the mineralogical phases in the sand fraction was performed only on random powders, whereas the <0.1 fraction was studied only on the oriented mounts. The quantitative mineralogical composition of the bulk samples was determined by Σ clay minerals following the method of Laviano [42]. The morphological analyses were performed using scanning electron microscopy (SEM).

The chemical analyses of all samples were performed using ICP-AES (major and minor elements) and ICP-MS (REE, Y, Zr, Nb, Th) after fusion of the samples by LiBO_2 and HNO_3 dissolution.

TABLE 1: Mineralogical composition of the bulk sample and different fractions.

Sample	Qtz	Feld	Cal	Dol	Hem	I/S	Ill	Chl	Kao
Bulk sample									
2T	12	1	tr	0	0	50	5	20	12
4T	11	1	tr	1	0	62	2	11	12
6T	14	7	24	3	0	30	4	14	4
7T	14	3	2	0	tr	58	12	11	tr
8T	18	1	0	0	1	40	6	12	22
9T	14	1	2	0	tr	46	1	15	21
Fractions									
<0.1 μm									
2A	0	0	0	0	0	100	0	0	tr
4A	0	0	0	0	0	100	0	0	tr
6A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7A	0	0	0	0	0	100	0	0	0
8A	0	0	0	0	0	100	0	0	0
9A	0	0	0	0	0	100	0	0	tr
(0.1–2) μm									
2B	4	tr	0	0	0	62	3	14	17
4B	7	tr	1	0	0	74	1	6	11
6B	6	tr	11	0	0	56	3	21	3
7B	3	1	0	0	0	82	7	6	1
8B	7	tr	0	0	4	58	2	15	14
9B	3	tr	0	0	0	51	5	19	21
(2–32) μm									
2C	18	2	0	0	0	37	6	28	10
4C	18	3	1	0	tr	37	2	20	18
6C	16	6	25	4	tr	21	12	9	6
7C	23	5	0	0	1	34	16	20	1
8C	31	5	0	0	1	15	6	9	33
9C	27	2	0	3	0	22	2	13	31
(32–63) μm									
2D	20	3	0	0	0	26	7	35	9
4D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6D	15	10	51	7	0	tr	5	5	7
7D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8D	27	8	0	0	0	18	3	20	24
9D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
>63 μm									
2E	21	2	2	0	0	0	2	60	13
4E	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6E	18	3	64	0	0	0	0	14	0
7E	41	5	23	0	0	0	0	30	0
8E	24	3	2	0	0	0	9	30	32
9E	24	tr	43	0	0	0	0	14	19

Qtz: quartz; Feld: K-feldspar + plagioclase; Cal: calcite; Dol: dolomite; Hem: hematite; I/S: illite-smectite mixed layers; Ill: illite and/or muscovite; Chl: chlorite; Kao: kaolinite and dickite; n.a.: not analysed; tr: trace.

3. Result

The XRD analysis shows that the bulk samples are mainly composed of clay minerals and quartz (Figure 2); one sample (#6) is also rich in secondary calcite. Feldspars, dolomite, and

hematite are minor constituents. I/S ($\chi = 40\%$) R1 with $I\% = 70\text{--}80$ prevails over chlorite ($\chi = 15\%$), kaolinite ($\chi = 14\%$), and illite (Ill; $\chi = 5\%$) (Table 1). I/S is the main constituent of the finest grain-size fraction, and it decreases as grain size increases; it is absent in the coarser fraction. Quartz,

TABLE 2: Chemical composition (wt%) of the bulk sample and different fractions.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
Bulk sample											
2T	54.38	0.86	20.26	8.01	0.03	2.89	0.51	0.86	2.48	0.30	9.17
4T	54.87	1.06	19.39	7.43	0.07	1.89	1.63	0.90	2.68	0.16	9.71
6T	41.35	0.60	13.05	6.11	0.21	2.30	15.90	1.20	1.67	0.29	17.12
7T	56.14	0.78	18.79	7.38	0.03	2.63	0.94	1.06	4.27	0.14	7.61
8T	58.54	0.93	19.90	7.53	0.02	2.11	0.24	1.06	2.03	0.17	7.28
9T	52.54	1.20	21.23	7.78	0.07	1.59	2.47	1.24	1.51	0.16	9.99
Fractions											
<0.1 μm											
2A	46.65	0.04	23.46	4.75	0.00	2.69	0.46	4.26	3.74	0.62	13.06
4A	41.08	0.07	20.63	4.01	0.00	1.95	1.82	7.60	4.55	0.05	18.00
6A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7A	41.51	0.05	19.42	5.02	0.00	2.16	0.57	7.24	5.20	0.05	17.70
8A	45.92	0.04	25.65	4.96	0.00	2.62	0.32	2.84	4.05	0.35	13.05
9A	37.72	0.04	22.65	1.62	0.00	1.24	1.47	11.37	3.01	0.05	19.68
(0.1–2) μm											
2B	48.69	1.10	24.87	7.06	0.02	2.90	0.66	0.64	3.37	0.37	10.04
4B	52.59	1.34	22.83	5.67	0.03	1.74	0.95	0.43	4.08	0.16	9.94
6B	43.50	0.95	20.77	7.87	0.08	2.85	6.98	0.44	3.39	0.42	12.52
7B	50.71	0.84	23.18	7.21	0.00	2.86	0.47	0.41	5.72	0.16	8.18
8B	47.65	1.27	24.57	10.47	0.02	2.91	0.29	0.65	3.18	0.19	8.56
9B	47.40	1.61	26.87	7.39	0.02	1.64	0.58	0.94	2.45	0.17	10.66
(2–32) μm											
2C	58.85	0.77	17.92	8.88	0.03	2.89	0.39	0.66	1.96	0.20	7.21
4C	56.75	0.96	17.68	9.45	0.09	2.04	1.63	0.82	1.85	0.13	8.43
6C	46.92	0.60	12.63	6.48	0.18	2.44	12.90	1.42	1.34	0.27	14.63
7C	63.53	0.82	15.13	7.94	0.02	2.43	0.35	1.15	2.71	0.11	5.61
8C	65.66	0.82	17.10	6.15	0.00	1.59	0.16	1.10	1.25	0.10	5.88
9C	58.62	1.10	18.64	8.54	0.07	1.58	1.11	0.87	0.90	0.14	8.26
(32–63) μm											
2D	50.62	0.64	19.64	13.08	0.05	3.84	0.52	0.50	1.87	0.24	8.72
4D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6D	33.04	0.17	5.92	4.22	0.24	1.43	28.64	0.84	0.44	0.11	24.80
7D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8D	62.23	0.65	16.32	9.06	0.03	2.32	0.43	1.04	1.39	0.14	6.21
9D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
>63 μm											
2E	46.02	0.53	19.54	16.38	0.23	4.57	1.00	0.37	1.60	0.21	9.33
4E	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6E	20.06	0.19	4.88	3.43	0.36	1.16	37.46	0.39	0.55	0.14	31.16
7E	50.38	0.43	10.64	8.57	0.37	2.77	11.43	0.71	1.30	0.12	13.04
8E	53.52	0.54	17.45	13.47	0.17	3.24	1.60	0.56	1.23	0.15	7.87
9E	28.52	0.42	9.43	10.91	0.42	1.04	23.85	0.33	0.54	0.11	22.97

calcite, and chlorite are concentrated in the coarser fraction (>63 μm), whereas kaolinite, illite, feldspars, and dolomite are more abundant in the silt fractions (2–32 μm and 32–63 μm) (Table 1).

The major element abundance is given in Table 2. The chemical compositions of the bulk samples are close to those

of the PAAS (Post-Archean Average Australian Shale; McLennan, 1989) (Figure 3), except for CaO and MnO, which are scattered. In fact, although the general chemical composition of the bulk samples is quite uniform, the amount of CaO is variable (min. = 0.42%, max. = 15.90%) according to the presence of secondary calcite identified in some samples. The

TABLE 3: The trace elements abundance (ppm) of the bulk sample and different fractions.

Sample	Ba	Be	Co	Cr	Cu	Ga	Nb	Ni	Rb	Sc	Sr	Th	Y	Zn	Zr
Bulk sample															
2T	303.0	3.4	20.7	187.0	72.5	30.1	27.5	69.3	124.0	12.1	297.0	13.7	26.7	145.0	197.0
4T	189.0	4.3	19.3	122.0	33.8	31.7	28.7	51.3	147.0	12.6	181.0	13.8	34.0	106.0	198.0
6T	143.0	2.3	11.5	133.0	45.7	19.1	11.2	38.6	79.5	12.6	353.0	8.4	20.6	89.0	86.6
7T	272.0	3.8	17.8	148.0	81.4	26.7	13.5	65.1	184.0	13.3	190.0	12.2	21.3	93.9	128.0
8T	153.0	3.7	17.7	145.0	56.2	26.8	17.0	55.2	96.4	12.3	126.0	11.2	20.8	92.8	140.0
9T	131.0	3.2	21.6	128.0	38.5	29.8	33.8	63.1	75.2	13.1	249.0	14.4	29.7	113.0	237.0
Fractions															
<0.5 μm															
2A	353.0	4.2	15.9	207.0	103.0	39.3	1.9	65.9	184.0	13.8	382.0	5.4	18.2	139.0	161.0
4A	237.0	4.0	10.8	124.0	47.6	42.6	2.0	34.4	223.0	11.8	507.0	5.1	15.3	83.2	101.0
6A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7A	205.0	4.1	8.4	151.0	77.1	27.7	0.8	36.7	196.0	12.1	222.0	2.0	3.9	82.3	30.8
8A	150.0	3.9	12.1	226.0	114.0	46.9	0.8	62.0	180.0	19.1	193.0	2.6	6.1	110.0	31.4
9A	176.0	4.3	8.0	132.0	43.0	47.5	1.1	24.6	124.0	12.2	726.0	5.0	17.4	78.7	148.0
(0.5–2) μm															
2B	356.0	3.7	17.7	210.0	71.9	37.8	36.3	65.9	171.0	15.1	385.0	19.6	36.9	139.0	234.0
4B	278.0	5.1	18.2	135.0	32.9	41.9	35.1	42.6	219.0	13.6	235.0	17.5	42.1	81.7	241.0
6B	265.0	3.1	16.9	219.0	64.3	34.9	18.1	54.2	159.0	13.1	266.0	13.1	28.5	141.0	132.0
7B	351.0	3.3	15.0	178.0	49.8	34.0	14.8	56.6	251.0	15.6	215.0	13.5	24.2	96.7	141.0
8B	229.0	3.2	23.0	210.0	70.6	38.2	24.4	67.7	157.0	17.7	195.0	14.8	27.9	128.0	180.0
9B	200.0	3.9	23.0	161.0	38.3	43.7	44.9	63.3	123.0	14.1	377.0	20.1	42.2	131.0	334.0
(2–32) μm															
2C	232.0	2.2	20.4	156.0	68.9	23.1	23.5	68.0	93.1	10.0	218.0	10.3	20.8	162.0	162.0
4C	150.0	2.8	23.4	113.0	35.1	25.0	25.3	63.9	93.4	11.8	118.0	10.8	28.4	136.0	163.0
6C	131.0	2.0	12.5	120.0	47.8	16.9	11.2	39.6	59.3	11.8	225.0	8.4	18.0	95.8	89.5
7C	218.0	2.4	21.2	120.0	70.7	20.4	14.0	76.1	109.0	9.3	106.0	10.2	19.9	104.0	129.0
8C	122.0	2.0	15.8	109.0	36.7	19.5	15.4	41.9	58.8	8.1	93.7	8.8	19.6	86.0	136.0
9C	102.0	1.8	20.8	111.0	36.1	22.0	31.4	67.4	45.2	11.3	136.0	11.1	24.9	118.0	195.0
(32–63) μm															
2D	470.0	2.4	31.5	194.0	179.0	26.4	19.3	96.7	84.0	10.8	294.0	9.6	20.7	219.0	139.0
4D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6D	56.5	0.6	8.6	54.3	58.7	6.5	3.3	23.5	21.5	12.8	421.0	2.8	15.0	54.0	25.7
7D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8D	127.0	2.0	23.3	117.0	133.0	22.0	11.5	55.1	63.4	9.6	138.0	7.8	16.8	120.0	96.3
9D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
>63 μm															
2E	327.0	2.2	32.2	164.0	178.0	26.8	16.2	105.0	72.8	11.8	249.0	7.9	16.7	278.0	119.0
4E	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6E	54.3	1.1	5.0	48.0	26.9	7.5	4.0	23.4	26.4	11.8	940.0	3.3	20.0	39.9	32.4
7E	281.0	1.3	22.6	62.1	272.0	14.4	8.1	73.1	56.7	14.6	324.0	5.5	26.0	134.0	102.0
8E	117.0	1.6	35.2	101.0	346.0	26.1	10.7	69.7	61.8	12.1	133.0	6.3	14.6	181.0	100.0
9E	72.4	1.1	53.6	48.7	65.8	13.7	12.5	87.8	29.2	17.8	422.0	4.6	30.6	173.0	94.9

slightly higher Fe content is most likely due to the presence of Fe-chlorite and the lower amount of K_2O to a scarcity of feldspars, illite, and/or micas. The chemical compositions of the different grain-size fractions indicate that SiO_2 is concentrated in the 2–32 μm fraction; Al_2O_3 is concentrated

in the fine fraction (<2 μm), in accordance with the higher amount of clay minerals; and TiO_2 and P_2O_5 are concentrated in the 0.1–2 μm fraction. Fe_2O_3 , MnO , MgO , CaO , and LOI show higher values in the >63 μm fraction than in the finer fractions, corresponding to the higher amount of Fe-chlorite

TABLE 4: The REE abundance (ppm) of the bulk sample and different fractions.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Bulk sample														
2T	50.2	101.8	10.6	40.9	7.7	1.7	6.4	0.9	5.0	1.0	2.7	0.4	2.6	0.4
4T	47.9	98.5	11.2	43.7	8.8	2.0	7.6	1.2	6.4	1.4	3.3	0.5	3.2	0.4
6T	32.3	55.7	6.9	25.9	4.7	1.0	3.8	0.6	3.3	0.8	2.0	0.3	1.8	0.3
7T	33.3	71.0	8.1	30.4	5.4	1.1	4.4	0.7	3.7	0.8	2.2	0.4	2.4	0.4
8T	31.1	72.9	7.4	28.4	5.3	1.2	4.2	0.7	3.7	0.9	2.1	0.3	2.3	0.3
9T	51.0	107.5	12.3	47.5	8.9	1.8	7.1	1.1	6.2	1.3	3.2	0.5	3.4	0.5
Fractions														
<0.1 μm														
2A	18.8	35.0	3.5	12.2	2.3	0.6	2.2	0.4	2.6	0.7	1.9	0.3	2.3	0.4
4A	14.6	27.0	2.8	9.6	1.7	0.4	1.6	0.3	2.3	0.6	1.5	0.3	1.5	0.2
6A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7A	4.4	7.3	0.7	2.3	0.4	0.1	0.5	0.1	0.6	0.2	0.4	0.1	0.5	0.1
8A	7.1	14.0	1.3	4.7	1.0	0.3	1.0	0.1	0.9	0.2	0.6	0.1	0.6	0.1
9A	7.8	14.8	1.4	4.6	0.9	0.2	1.1	0.3	2.4	0.7	2.0	0.3	2.0	0.3
(0.1–2) μm														
2B	75.4	148.1	15.8	60.8	11.0	2.4	9.0	1.3	7.4	1.5	3.9	0.6	3.6	0.6
4B	73.2	143.9	15.4	61.9	12.1	2.5	9.8	1.4	8.4	1.8	4.4	0.6	3.9	0.6
6B	64.5	107.0	12.7	43.9	7.3	1.5	6.0	0.9	5.2	1.0	2.7	0.4	2.8	0.4
7B	45.4	90.6	10.0	37.5	6.6	1.3	5.0	0.7	4.3	0.9	2.5	0.4	2.9	0.4
8B	55.2	122.5	12.1	46.2	7.7	1.5	5.8	0.9	5.3	1.1	2.8	0.4	3.3	0.5
9B	83.8	167.0	18.1	70.2	12.5	2.2	8.5	1.3	8.2	1.8	4.9	0.7	5.0	0.7
(2–32) μm														
2C	38.3	77.4	8.7	32.4	6.0	1.3	4.7	0.7	4.1	0.8	2.2	0.3	2.3	0.3
4C	38.2	76.7	8.7	32.8	7.4	1.7	6.5	1.0	5.3	1.1	2.6	0.4	2.5	0.4
6C	27.5	47.9	6.0	22.4	4.6	0.9	3.7	0.5	3.1	0.7	1.6	0.2	1.6	0.2
7C	27.9	56.8	6.3	24.1	4.9	1.0	4.0	0.6	3.4	0.8	2.0	0.3	2.1	0.3
8C	23.0	53.0	5.3	19.4	4.6	1.0	3.6	0.6	3.5	0.8	1.9	0.3	1.9	0.3
9C	39.3	79.1	9.2	36.4	7.5	1.6	6.3	1.0	5.1	1.0	2.6	0.4	2.3	0.3
(32–63) μm														
2D	36.5	71.0	8.1	30.8	5.4	1.3	4.4	0.7	3.8	0.8	2.0	0.3	1.9	0.3
4D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6D	11.6	20.6	2.9	10.8	2.3	0.6	2.1	0.3	2.1	0.5	1.2	0.2	1.2	0.2
7D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8D	20.2	44.0	4.7	18.3	4.0	0.9	3.5	0.6	3.1	0.7	1.6	0.2	1.5	0.2
9D	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
>63 μm														
2E	30.1	58.6	6.6	25.0	4.5	1.0	3.6	0.5	3.1	0.7	1.6	0.3	1.6	0.2
4E	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6E	12.9	23.9	3.2	12.9	2.8	0.7	2.8	0.4	2.5	0.6	1.5	0.2	1.3	0.2
7E	12.7	29.3	3.5	15.0	4.7	1.2	4.5	0.8	4.4	0.9	2.2	0.3	2.0	0.3
8E	16.1	37.9	3.7	13.9	2.9	0.6	2.4	0.4	2.4	0.5	1.3	0.2	1.4	0.2
9E	18.1	39.1	4.4	17.5	5.5	1.7	6.8	1.2	5.8	1.1	2.3	0.3	1.7	0.2

and calcite. Instead, Na_2O and K_2O are concentrated in the fine fraction (<0.1 μm), in accordance with the presence of natroiarosite and a higher amount of I/S, respectively.

The trace element distributions are given in Tables 3 and 4. The 32–63 μm fraction shows enrichment in Cu compared to the other fractions, whereas the <0.1 and 0.1–2 μm fractions

are more enriched in Ba, Be, Cr, Ga, Rb, and Sr than the coarser fractions, most likely because of the adsorption of these elements by clay minerals. The amounts of Co, Ni, and Zn are comparable to each other, with a downward trend in the fine fraction (0.1 μm). Sc shows enrichment in the fine-ultrafine fraction, but Nb, Th, Y, and Zr are characterised by

TABLE 5: Correlation matrix for same elements. LREE = (La-Nd); MREE = (Sm-Tb); HREE = (Dy-Lu). Bold numbers indicate $P > 0.001$; italic numbers indicate $0.01 < P < 0.001$.

(a) Bulk sample								
	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
LREE	1.0000							
MREE	<i>0.9675</i>	1.0000						
HREE	<i>0.9319</i>	0.9848	1.0000					
Nb	0.9841	<i>0.9624</i>	<i>0.9424</i>	1.0000				
Th	<i>0.9177</i>	0.8762	0.8677	0.8792	1.0000			
Y	0.8764	<i>0.9681</i>	<i>0.9617</i>	0.8740	0.7702	1.0000		
Zr	0.9780	<i>0.9376</i>	<i>0.9270</i>	0.9851	<i>0.9370</i>	0.8263	1.0000	
P ₂ O ₅	-0.1173	-0.2067	-0.3540	-0.1509	-0.3922	-0.2184	-0.2546	1.0000
(b) Fraction >63 μm								
	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
LREE	1.0000							
MREE	0.1925	1.0000						
HREE	0.0126	<i>0.9684</i>	1.0000					
Nb	0.9244	0.3873	0.2330	1.0000				
Th	0.8284	-0.0548	-0.1273	0.8314	1.0000			
Y	-0.2724	0.8817	0.9307	-0.0929	-0.4784	1.0000		
Zr	0.6876	0.3704	0.3398	0.8569	0.8661	-0.0261	1.0000	
P ₂ O ₅	0.7896	-0.4188	-0.5561	0.5486	0.7451	-0.7425	0.3369	1.0000
(c) Fraction (32–63) μm								
	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
LREE	1.0000							
MREE	0.9839	1.0000						
HREE	0.9895	0.9994	1.0000					
Nb	0.9930	0.9981	0.9996	1.0000				
Th	0.9336	0.9826	0.9756	0.9694	1.0000			
Y	0.9943	0.9592	0.9684	0.9747	0.8901	1.0000		
Zr	0.9704	0.9979	0.9951	0.9921	0.9925	0.9391	1.0000	
P ₂ O ₅	0.9803	0.9292	0.9415	0.9501	0.8445	0.9958	0.9036	1.0000
(d) Fraction (0.1–2) μm								
	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
LREE	1.0000							
MREE	<i>0.9337</i>	1.0000						
HREE	<i>0.9620</i>	<i>0.9666</i>	1.0000					
Nb	0.9858	<i>0.9272</i>	<i>0.9672</i>	1.0000				
Th	<i>0.9375</i>	0.9037	0.9086	<i>0.9667</i>	1.0000			
Y	<i>0.9501</i>	0.9848	0.9897	<i>0.9380</i>	0.8780	1.0000		
Zr	<i>0.9364</i>	0.8526	<i>0.9447</i>	<i>0.9715</i>	<i>0.9265</i>	0.8899	1.0000	
P ₂ O ₅	-0.0469	-0.1090	-0.2443	-0.1808	-0.1185	-0.1601	-0.3380	1.0000
(e) Finest fraction (<0.1) μm								
	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
LREE	1.0000							
MREE	0.9931	1.0000						
HREE	0.7402	0.7521	1.0000					
Nb	<i>0.9308</i>	0.8860	0.7233	1.0000				
Th	0.8038	0.8041	<i>0.9788</i>	0.8193	1.0000			

(e) Continued.

	LREE	MREE	HREE	Nb	Th	Y	Zr	P ₂ O ₅
Y	0.7535	0.7628	0.9972	0.7483	0.9905	1.0000		
Zr	0.6996	0.7172	0.9867	0.6567	0.9349	0.9717	1.0000	
P ₂ O ₅	0.6115	0.6755	0.2555	0.2913	0.2263	0.2350	0.2990	1.0000

FIGURE 2: XRD patterns of bulk sample. Chl = chlorite; Kao = kaolinite; Ill = illite; I/S = illite-smectite mixed layers; Qtz = quartz; Kfs + Pl = K-feldspar + plagioclase; Cal = calcite.

FIGURE 3: PAAS-normalized major elements patterns.

a higher value of the clay fraction (0.1–2 μm) compared with the other grain-size fractions, particularly with the <0.1 μm fraction. The REE distribution in the whole rock is similar to that of the PAAS, except for a slight enrichment in MREEs (Sm–Tb) and a depletion in HREEs (Dy–Lu) (Figure 4). The elemental concentration in the 5 grain-size fractions, normalised to the whole rock, shows that the concentration decreases rapidly from the 0.1–2 μm fraction (up to 1.5X) to the 2–32 μm (0.8X), 32–63 μm , and >63 μm fractions (approximately 0.5X); the lowest concentration was observed in the finest fraction (<0.1 μm ; 0.2X).

4. Discussion

The samples studied show a highly homogeneous chemical composition comparable with the PAAS. The mineralogical

composition is typical of clays that underwent a late diagenetic grade. The very low content of REEs measured in the finest grain-size fraction ($\Sigma\text{REE} = 17\text{--}83\text{ ppm}$) clearly indicates that this fraction is not the carrier of REEs and that only very small amounts of these elements, if any, are hosted by the I/S mixed layer. This hypothesis is not in accordance with some literature data indicating REEs are essentially concentrated in kaolinite minerals ([20] and references therein). A strong linear correlation (probability P varying from 0.01 to 0.001) exists between the HREEs (Dy to Lu) and Zr, Th, and Y (Table 5), suggesting that the presence and distribution of HREEs in the fine fraction of the studied shales are controlled by zircon (e.g. [26, 29]). The similarity between the pattern of this mineral and that of the finest fraction confirms this hypothesis. Thus, an enrichment of REE content does not correspond to the high specific surface of the finest fraction, suggesting that adsorption is not an efficient mechanism for determining the concentration and distribution of these elements in the studied shales.

The highest REE content in the 0.1–2 μm grain-size fraction does not appear to be related to the clay minerals, but there is a strong correlation between REEs and Zr (not observed in the finest grain-size fraction) and between Y, Zr, REEs, and Nb. This result suggests that accessory phases may be more important than clay minerals in controlling the distribution of the REEs in shales, which is particularly evident from the comparison of the REE–Nb–Th–Zr–Y distribution in the distinct grain-size fractions of the studied shales (Figure 4). The higher the concentration of the REE contents, the higher the concentration of the other trace elements. In addition, strong similarities exist between the Y, HREE, and MREE profiles and between the Th and LREE profiles.

The data are also confirmed by the abundance of isolated zircon (1–2 μm) sometimes associated with kaolinite crystals (Figure 5). In our opinion, the presence of kaolinite with zircon could be explained taking into account that this clay mineral is an alteration product of zircon carrying phyllosilicates.

Some studies have suggested an influence of REE-rich phosphate on the REE distribution in fine-grained sediments [43, 44]. Rasmussen [45], for instance, documented the presence of REE-phosphate in marine sandstone and suggested a diagenetic origin. Di Leo and Fiore [46], using selective chemical dissolution techniques, deduced the presence of phosphate containing REEs in shales. Although the studied shales underwent late diagenetic processes, phosphates did not play a significant role in the REE fine fraction distribution. Thus, it appears that the elucidation of the presence/absence of REE-rich phosphate minerals in shales requires further investigation.

FIGURE 4: Bulk sample-normalized REE patterns of fractions.

FIGURE 5: SEM images of (a) single particle of zircon (Zr) and (b) zircon (Zr) and kaolinite (kao) crystals.

5. Concluding Remarks

Mineralogical and chemical data of grain-size fractions of 6 samples collected from shales affected by late diagenesis maturity indicate that distribution of REEs in the fine fraction is mainly controlled by zircon. Phosphates did not play an important role in the fine fraction distribution of the REE.

This result is not in accordance with some data available in the literature that indicate the fundamental role assumed by illite-smectite mixed layers or phosphates.

Conflict of Interests

The authors declare that there is no conflict of interests.

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