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TEM Observations and Rare Earth Element Analysis on the Clay Minerals of the CRP-1 Core (Ross Sea, Antarctica)

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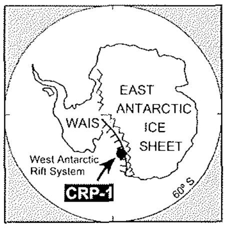
Abstract - TEM observations on smectites and REE analyses on the clay minerals of the sediments of CRP-1 core were carried out to investigate their origin and the source rocks from which they were derive from. Smectites are mostly dioctahedral, but Fe-Mg richer than in other cores from Ross Sea. In addition, small amounts of nontronites and trioctahedral smectites (probably saponites) were found. Smectite microparticles are mainly flaky, but significant percentages of hairy smectites were also recognized. Micromorphologies indicate that smectites were derived from the continent but, in addition, they formed *in situ* through recrystallisation processes. The shale-normalised rare earth elements patterns are very homogeneous, and their features are typical of land-derived sediments. The smectites of CRP-1 formed from parent rocks influenced by volcanic activity, and the source areas are probably represented by both the basaltic rocks of the the McMurdo Volcanic Group and the complex of basement and sedimentary rocks cropping out in the Transantarctic Mountains.



INTRODUCTION

The first hole of the Cape Roberts Project (CRP-1) was drilled to a depth of 147.69 mbsf (metres below sea floor) (Cape Roberts Science Team, 1998). The record of sediments is divided into two sections, the upper being of Quaternary age, the lower of early Miocene. Particularly interesting is the possibility of studying the early Miocene Epoch, which is a very poorly known interval in the Ross Sea region. This period was characterised by the beginning of the formation of Mt. Morning, the oldest stratovolcano of the region (Kyle, 1990).

Clay mineral assemblages are known to be reliable palaeoclimatic indicators, as used by investigators on marine sediment cores from the Southern Ocean. Their study may also provide important information about the source of terrigenous sediments, their main agents of transport and their distribution in the sedimentary basins.

Smectite concentration in the Antarctic sedimentary sequences is considered to be the most relevant mineralogical marker of palaeoclimate. In Cenozoic cores from the Ross and Weddell seas, smectite percentages decrease and illite percentages increase when passing from lower Eocene age to younger strata. Smectite-rich assemblages are believed to characterise warmer climate conditions on the continent, in which chemical weathering prevailed over physical weathering (Chamley, 1989; Claridge & Campbell, 1989; Ehrmann & Mackensen, 1992; Ehrmann et al., 1992; Ehrmann, 1997, 1998; Grobe et al., 1990; Robert & Maillot, 1990).

However, the interpretation of the genesis of smectite in sediments should be approached critically, as this mineral can be either of detrital origin or it may form as halmyrolytic alteration product, both of basaltic basement and of pyroclastic material deposited on the sea floor (authigenic origin); this is particularly evident where a large input of volcanic material is evident (Chamley, 1989; Petschick et al., 1996; Singer, 1984). In addition, the presence of smectite in the cores may also be attributed to the early diagenetic evolution of materials of different composition (Chamley, 1989; Güven, 1988; Velde, 1995).

Discrimination between authigenic/diagenetic and detrital smectites is of great importance for the correct palaeoenvironmental interpretation of the clay mineral assemblages and the determination of the source rocks (Chamley et al., 1985; Chamley, 1989; Singer, 1984). The differentiation is not easy, and is generally based on chemical composition and on the shape of the smectite microparticles. The dominant authigenic smectites in marine sediments are nontronites and trioctahedral ferromagnesian smectites, while the detrital smectites are generally Al-rich montmorillonite and beidellite (Chamley, 1989; Debrabant et al., 1985; Güven, 1988; Velde, 1995). The microparticles of detrital smectites generally show flaky shapes, like those occurring in soils, while the shapes of authigenic or early diagenetic phases are lath or hairy or, sometimes they are transparent (Chamley et al., 1985; Chamley, 1989; López-Galindo et al., 1998; Robert & Maillot, 1990; Setti et al., 1997).

The distribution of the rare earth elements (REE) is also considered a useful tool for determining the origin of the clay minerals and the source rocks, as these elements experience only a reduced fractionation under weathering and diagenetic processes (Chamley, 1989; Courtois & Chamley, 1978; Piper, 1974; Toyoda et al., 1990).

The purpose of this work is to investigate the origin and the provenance of the clay minerals in CRP-1 sediments through a detailed transmission electron microscopy (TEM) study on smectite particles and the geochemical composition of rare earth elements.

GEOLOGICAL SETTING AND DEPOSITIONAL HISTORY

The CRP-1 core was drilled in the Ross Sea, 15 km east of Cape Roberts, western McMurdo Sound, in a water depth of 150 m. The drillhole was placed at the offshore of the Mackay Glacier, on a western flank of a submarine ridge (Roberts Ridge). Apart from the uppermost 20 m, which remained unsampled, the drillhole penetrated continuously a 147.69 m seaward-dipping sequence of clastic sediments and sedimentary rocks (Cape Roberts Science Team, 1998).

Diatom biostratigraphy showed that the lower sequence (43.55 to 147.69) belongs to the early Miocene Epoch; while the upper part of the core (up to 43.55 mbsf) is of early Pleistocene age. The two sections are separated by an unconformity at 43.55 mbsf. The lithostratigraphy of the sequence consists of an alternation of diamicton and other clastic sedimentary facies (Cape Roberts Science Team, 1998).

The Quaternary section is made up especially of diamicton. A variety of depositional environments, including open marine with or without the presence of sea ice was recognized.

The lithologies of the Miocene sequence are consolidated and dominated by diamictites. About eight cycles of relative sea-level have been recorded; grounded ice probably passed across the drill site several times, leaving the record of glacial retreat and the subsequent relative sea-level rise. Like the Quaternary sequence, the depositional environments of the Miocene section probably remained entirely marine (Cape Roberts Science Team, 1998).

Preliminary petrographical investigations on extraformational clasts indicate that the main provenance was in the Transantarctic Mountains. The mineralogy of the sand fraction is made up mainly of quartz and feldspar with minor amounts of biotite, tourmaline, zircon, garnet and pyroxene; this assemblage indicates provenance from the crystalline basement and the Beacon Supergroup. The upper part of the core is characterised by abundant volcanic detritus, which decreases sharply below 62 mbsf. Volcanic components comprise glass shards, fragments of oxidised lava flows with fluidal plagioclase microlites, sharp fragments of labradorite to bytownite plagioclase, augite and aegirinic clinopyroxene. The abrupt influx of volcanic detritus is probably due to the onset of McMurdo Volcanic Group activity (Cape Roberts Science Team, 1998).

CLAY MINERALOGY

Clay mineral investigations of the sediments of CRP-1 core were performed by Ehrmann (1998b). The clay mineral assemblage of the lower CRP-1 sequence, belonging to the early Miocene, is mainly made up of illite, while chlorite and smectite are present in smaller amounts. Quartz and feldspars were sometimes detected in significant quantities. The clay mineral assemblage resembles the composition of sediments of Miocene age in other cores from the Ross Sea and indicates a wide source area that includes the basement and the sedimentary rocks cropping out in the Transantarctic Mountains and on the East Antarctic Craton.

In the upper sequence of Miocene and Quaternary age (above 65 mbsf), smectite is more abundant, while chlorite and illite are present in smaller amounts than in the lower sequence. Quartz and feldspars are also present in all samples. Smectite percentages reach three maxima at 59, 45 and 33 mbsf. The source of the large amount of smectite is probably local and represented by the basaltic volcanic rocks belonging to the McMurdo Volcanic Group; these crop out widely in the area between Ross Island and Mt. Morning. This origin for smectite is also supported by the composition of the volcanic detritus present in the sediments of CRP-1.

METHODS

The TEM observations and microanalyses were carried out on the clay fraction of selected samples of CRP-1, using a PHILIPS CM 20 (coupled with the EDS X-ray spectrometry). Rare earth elements were measured in the same samples and fraction, using an ICP-MS Perkin Elmer SCIEX Elan-5000 equipment, with detection limits 10 ppb.

SMECTITE COMPOSITION

Crystal-chemical formulae of smectites were obtained from the TEM microanalyses of individual particles; the average composition of the smectites occurring in each core level are reported in table 1.

Figure 1 illustrates the octahedral composition field of smectites, considered on the typical $(Al^{3+} + Fe^{3+})^{VI}$ *vs.* Mg^{VI} plot. The plot allows the distinction between dioctahedral and trioctahedral smectites. Most CRP-1 smectite microparticles fall within the dioctahedral domain, *i.e.* $(Al^{3+} + Fe^{3+}) > 1.3$ and $Mg^{VI} < 1.83$ per half unit cell, but minor amounts fall into the intermediate and the trioctahedral domains (Paquet et al., 1987; Weaver & Pollard, 1975).

Tab. 1 - Average composition of smectites (calculated with O=10 and OH=2) obtained by TEM-EDAX microanalyses.

Depth (m)	Tetrahedral sheet		Octahedral sheet				Interlayer		
	Si	Al^{IV}	Al^{VI}	Mg^{VI}	Fe^{3+}	Ti	K	Ca	Mg
20.84	3.51	0.49	0.72	0.78	0.70	0.04	0.30	0.03	0.07
25.83	3.51	0.49	0.56	0.98	0.69	0.07	0.20	0.05	0.09
27.66	3.63	0.37	0.94	0.57	0.56	0.07	0.29	0.04	0.04
46.60	3.69	0.31	0.59	0.77	0.71	0.10	0.22	0.10	0.02
61.60	3.67	0.33	1.01	0.40	0.60	0.05	0.21	0.08	0.05
69.96	3.53	0.47	0.94	0.40	0.71	0.06	0.20	0.01	0.14
82.58	3.50	0.50	0.41	0.80	0.93	0.08	0.28	0.04	0.09
92.77	3.48	0.52	0.67	0.53	0.91	0.05	0.27	0.02	0.11
97.39	3.37	0.63	0.33	0.55	1.29	0.04	0.07	0.10	0.25
99.95	3.59	0.41	0.60	0.92	0.68	0.07	0.11	0.04	0.12
109.09	3.51	0.49	0.66	0.45	0.93	0.07	0.28	0.02	0.11
122.23	3.74	0.26	1.16	0.34	0.54	0.06	0.20	0.01	0.03
134.31	3.74	0.26	0.83	0.58	0.63	0.07	0.24	0.10	0.00
142.34	3.55	0.45	0.51	0.90	0.80	0.07	0.24	0.04	0.07
147.03	3.71	0.29	0.62	0.77	0.80	0.03	0.28	0.01	0.04

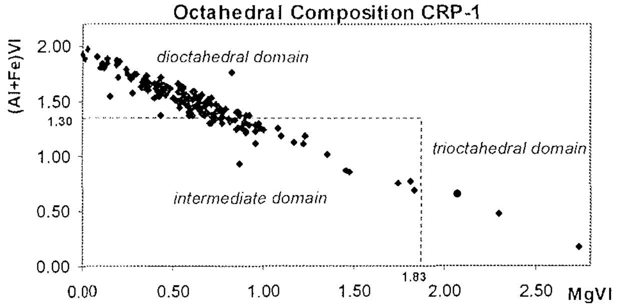


Fig. 1 - Octahedral composition of individual particles of smectites: (Al+Fe^{3+}) *v.s.* Mg. The compositional fields of dioctahedral, intermediate and trioctahedral domains are reported (after Paquet et al., 1987).

In figure 2a, Al-Fe-Mg variations in the CRP-1 smectite microparticles are plotted (Weaver & Pollard, 1975). In this ternary diagram, the different compositional domains of nontronites, trioctahedral smectites (saponite, stevensite, hectorite), montmorillonite and illite-smectite mixed layer are illustrated. For comparison, the microchemical composition of some different smectites reported in literature are plotted in figure 2b (Chamley, 1989). The plot 2a shows that most of smectites in the CRP-1 core are widely scattered, and their composition exceeds the typical fields for beidellite and montmorillonite. Most CRP-1 smectites are placed in the central part of the diagram and can be generally classified as Fe-Mg-rich and dioctahedral, with small amounts of nontronites and trioctahedral smectites (probably saponites).

The composition of CRP-1 smectites (Fig. 2a) is also compared with those from other sequences in the Ross Sea, belonging to older ages: CIROS-1, DSDP 270 and 274 (Fig. 2b; López-Galindo et al., in press; Setti et al., 1997). The CIROS-1 sequence belongs to Eocene and Oligocene, DSDP 274 to Oligocene and DSDP 270 to Oligocene and, probably, early Miocene time. Little or no evidence of volcanogenic detritus in these cores is given, except in the lowermost part of CIROS-1 (López-Galindo et al., in press; Setti et al., 1997). CRP-1 smectites are considerably less aluminiferous than those in the other sequences from the Ross Sea; this suggests that the CRP-1 smectites formed from compositionally more femic parent rocks.

Lastly, the smectites in the two upper units (20.84 and 25.83 mbsf) have a more homogeneous composition, and are slightly less aluminiferous, than in the underlying core section; this may be because of the larger abundance of volcanic material in the Quaternary sequence.

SMECTITE MORPHOLOGY

TEM investigations showed that the smectites of CRP-1 sediments generally display both hairy and flaky shapes (Fig. 3a, b & d). Flaky shapes are generally typical of alkaline smectites or beidellites, and are considered to be of detrital origin. Hairy smectites appear as finely folded layers, are generally ferromagnesian, and indicate that the sediments were partly influenced by volcanic activity. Because of their delicate morphology, hairy shapes are considered to be of authigenic origin (Chamley et al., 1985; Chamley, 1989).

Hairy smectites in CRP-1 sediments were observed below the 20.28 mbsf level; this indicates these shapes formed after the deposition of the sediments on the sea floor, and that their formation was induced by the early diagenesis. In addition, the percentage of hairy smectites in the CRP-1 core is higher than in the sediments of CIROS-1, DSDP 270 and 274 cores (López-Galindo et al., 1998; Setti et al., 1997); this may confirm the stronger influence of volcanic material in CRP-1. No particular compositional differences between hairy and flaky smectites were observed.

In the sequence between 97.4 and 103 mbsf, TEM observations highlighted the presence of abundant grains of pyrite (Fig. 3c), whose occurrence is also confirmed by XRD powder diffraction results. Possibly, particular anoxic and reducing conditions, resulting from the accumulation of organic matter and early diagenesis, or from volcanic activity, allowed the formation of this mineral.

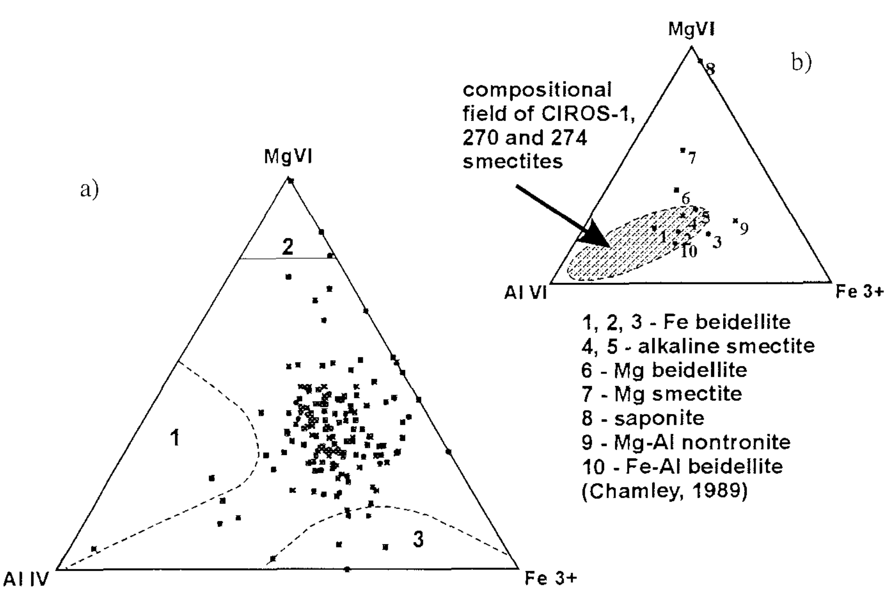


Fig. 2 - *a)* Ternary plot of the octahedral sheet of the smectites of CRP-1; field 1 = montmorillonite-beidellite and mixed-layer illite-smectite, field 2 = trioctahedral smectite, field 3 = nontronite.
b) Ternary plot showing the octahedral compositions of different smectites reported in literature (Chamley, 1989) and the compositional field of smectites of cores CIROS-1, 270, 274 (Setti et al., 1997; López-Galindo et al., in press).

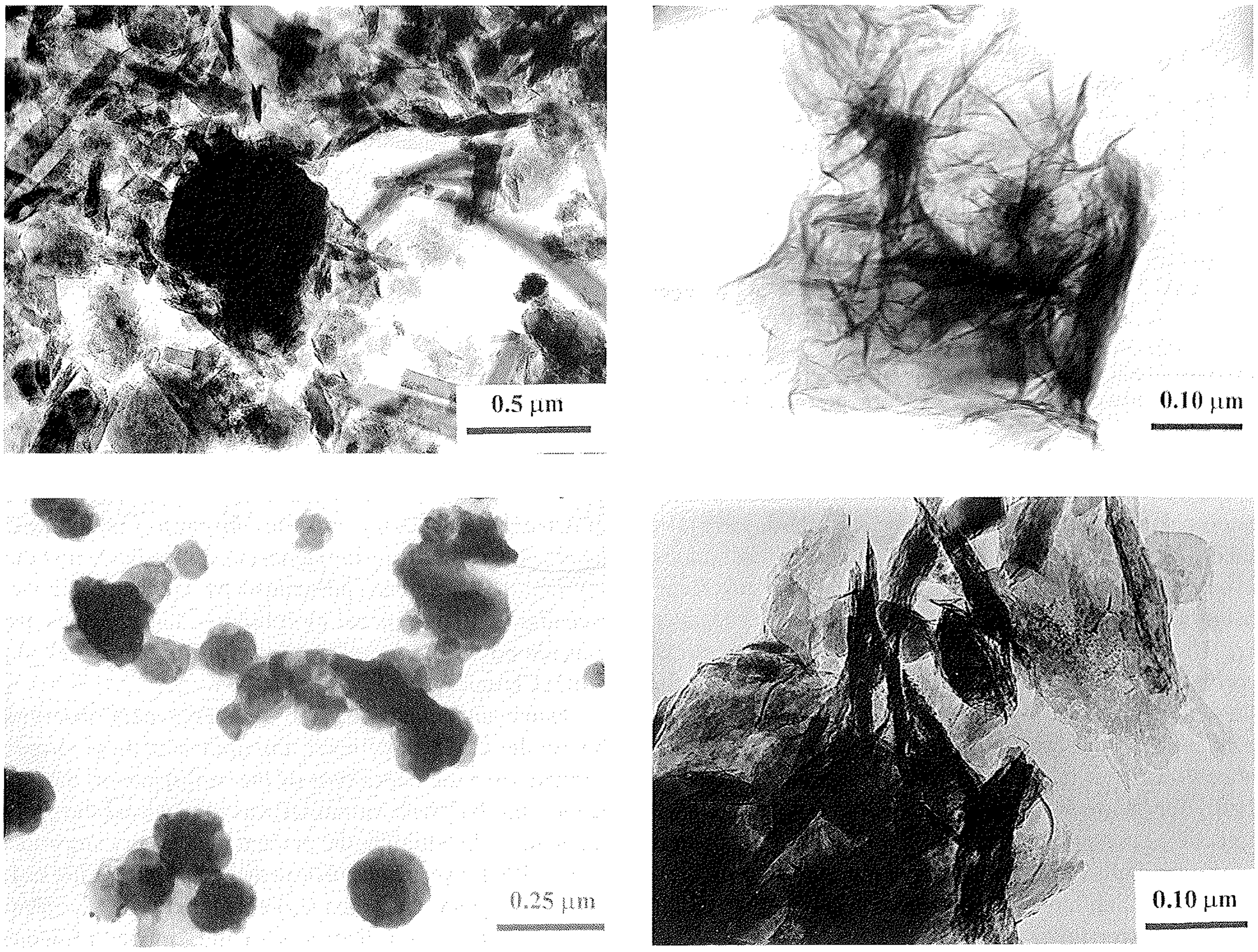


Fig. 3 - a) Core level 20.83-20.84 mbsf, TEM image showing an assemblage of detrital phases (mica, chlorite and smectite). In the middle of the photo a flaky smectite is visible. *b)* Core level 46.59-46.60 mbsf, TEM image showing a typical hairy smectite. *c)* Core level 99.94-99.95 mbsf, TEM image showing pyrite grains. *d)* Core level 142.33-142.34 mbsf, TEM image showing an assemblage of hairy and flaky smectites.

RARE EARTH ELEMENT COMPOSITION

The rare earth element content of the clay fraction of some selected samples (in ppm) is reported in table 2. REE distribution, when normalised to NASC (North American Shales; Piper, 1974), shows a very homogeneous pattern (Fig. 4).

The Sm content is generally used to represent the REEs, because Sm does not show anomalous behaviour typical of other elements, such as Ce or Eu; Sm contents of CRP-1 clay fractions give very similar results to those reported for average shale (Piper, 1974; Toyoda et al., 1990).

The REE patterns of sediments equilibrated with seawater, or related to hydrothermal activity near active spreading centres, generally display a negative Ce anomaly, while a strong impact of volcanic activity (especially of tholeiitic basalts) on the sediments is recorded by a clear

Tab. 2 - Rare earth element content of the clay fractions of selected samples.

Depth (m)	20.84	25.83	27.66	46.60	61.60	69.96	82.58	92.77	97.39	99.95	109.09	122.23	134.31	142.34	147.03
La	33.54	40.40	39.53	57.69	47.51	28.19	52.60	55.33	38.54	55.28	29.67	32.83	45.75	43.95	48.72
Ce	66.08	78.78	76.55	116.65	94.20	57.12	106.39	112.47	76.07	111.10	58.34	63.14	89.13	84.41	94.54
Pr	7.61	8.95	8.90	13.79	10.95	6.59	12.34	12.67	8.81	12.78	6.68	7.25	10.28	9.70	10.78
Nd	27.62	31.91	31.60	52.23	39.73	24.32	45.37	46.01	32.49	47.64	23.97	26.43	37.32	34.87	38.67
Sm	5.20	5.75	6.30	9.82	7.76	4.88	8.25	8.62	5.91	8.82	4.49	4.95	7.02	6.57	7.14
Eu	1.18	1.36	1.57	2.38	1.66	1.05	1.78	1.79	1.30	1.98	1.00	1.12	1.61	1.47	1.53
Gd	4.47	4.90	4.82	8.08	6.41	3.97	6.87	7.15	5.13	7.74	3.90	4.23	5.74	5.64	5.89
Tb	0.71	0.74	0.72	1.23	0.99	0.63	1.05	1.09	0.80	1.12	0.63	0.67	0.89	0.87	0.91
Dy	4.18	4.18	4.11	7.07	5.80	3.75	6.11	6.48	4.76	6.62	3.61	3.94	5.19	5.06	5.24
Ho	0.85	0.87	0.81	1.40	1.20	0.77	1.23	1.29	0.96	1.36	0.77	0.84	1.05	1.03	1.08
Er	2.33	2.34	2.18	3.83	3.19	2.03	3.24	3.53	2.69	3.48	2.05	2.14	2.73	2.73	2.83
Tm	0.34	0.35	0.33	0.53	0.48	0.31	0.49	0.53	0.39	0.52	0.31	0.33	0.43	0.41	0.41
Yb	2.18	2.12	2.06	3.15	2.98	1.91	3.07	3.17	2.43	3.15	1.96	2.14	2.62	2.48	2.58
Lu	0.34	0.34	0.32	0.48	0.46	0.30	0.46	0.48	0.37	0.48	0.29	0.34	0.40	0.38	0.39
La/Sm	6.45	7.02	6.27	5.87	6.12	5.78	6.38	6.42	6.52	6.27	6.60	6.63	6.51	6.69	6.82

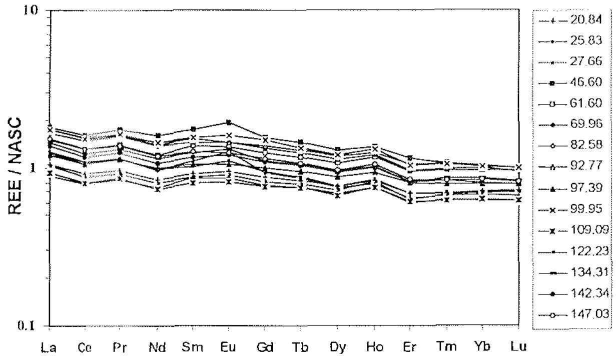


Fig. 4 - NASC-normalised REE patterns of the analysed samples.

enrichment in heavy REE, such as europium, gadolinium, terbium, thulium, yterbium, lutetium (Chamley, 1989; Courtois & Chamley, 1978; Hoffert et al., 1980; Toyoda et al., 1990). The degree of Ce anomaly can be expressed by the value of Ce/Ce* ($=5Ce_n/4La_n+Sm_n$; Toyoda et al., 1990); this value in the CRP-1 clay fraction is about 0.9, so indicating that only a little negative Ce anomaly is present. Also, the La/Sm ratio, which shows the degree of enrichment or depletion of LREE (light rare earth element; lantanium, cerium, neodymium, samarium), is about 1.2; this indicates light enrichment in LREE (Toyoda et al., 1990). Very similar REE patterns were found in the sediments, considered of continental origin, at other DSDP sites (Chamley, 1989; Courtois & Chamley, 1978).

The features of the REE patterns of the CRP-1 clay fraction highlight a composition that reflects the average composition of the source rocks; therefore clay minerals are mostly of continental origin and represent reliable indicators of past continental environments and provenance. The authigenic hairy smectites do not affect the overall REE composition.

DISCUSSION AND CONCLUSIONS

The combined investigations of the microchemical and micromorphological characters of CRP-1 smectites, together with the analysis of rare earth elements of the clay fraction, give insight into the provenance and the source rocks of the sediments.

The presence of both flaky and hairy micromorphologies indicate that smectites in the sediments of CRP-1 are derived from the continent but, also, that they formed *in situ* through recrystallization processes. It would be interesting to try to quantify the different proportions of authigenic and detrital smectites through an evaluation of the ratio between hairy and flaky shapes.

It is know as, during its formation, smectite inherits a significant compositional character from the parent mineral. Pyroxene and amphibole generally produce trioctahedral Mg-rich smectites and nontronites, while olivine is believed to form Fe-saponite with low Al-content. Feldspars weather into dioctahedral aluminous smectites. Lastly, smectite derived from muscovite has little or no Fe, and its composition is close to pure montmorillonite (Banfield & Eggleton, 1990; Eggleton et al., 1991).

Most CRP-1 smectites can be classified as ferromagnesian and dioctahedral, but their composition is very variable, thus indicating that they formed from parent rocks of different composition.

Although aluminiferous phases are present, most CRP-1 smectites are generally more Mg- and Fe-rich than those of the older CIROS-1, DSDP 270 and 274 sequences from the Ross Sea (López-Galindo et al., 1998; Setti et al., 1997). The composition of CRP-1 smectites highlights the importance of volcanic influence on the origin of these minerals; therefore the difference with the smectites of the other Cenozoic sequences might be related to the different stratigraphy and to the volcanic events documented in CRP-1 levels. This is also supported by the sporadic occurrence of trioctahedral smectites (saponites) and nontronites, which are typical alteration products of volcanic glass and basaltic rocks (Chamley, 1989; Singer, 1984; Velde, 1995).

No marked smectite compositional difference was observed between the sequences of Miocene and Quaternary age but, in the most smectite-rich levels (25.83, 27.60, 46.60 mbsf levels), the microparticle composition is more concentrated in the central part of the Al-Fe-Mg triangular plot. This could be due to the larger abundance of volcanic detritus in the upper core section.

The occurrence of abundant grains of pyrite in the sequence between 97.4-103 mbsf may be due to a warmer climate, which allowed the formation of organic matter or, more likely, to volcanic activity. This level could be used as a lithostratigraphic marker between cores.

The REE distribution patterns of the clay fraction of the CRP-1 sediments are generally very flat, and only a slight enrichment in light elements is observed. The curves do not show features characteristic of smectite-rich sediments formed from the alteration of basaltic detritus, or of minerals equilibrated with sea water. The REE patterns are typical of terrigenous sediments.

This apparent discrepancy between the conclusions gained from REE analysis and the TEM observations on smectites is probably due to the high percentages of chlorite and illite present in the clay fraction; such minerals are of detrital origin and the products of physical weathering. In addition, the abundance of flaky shapes emphasises that a large proportion of smectite particles formed on the continent and is of detrital origin; its composition is therefore inherited from that of the parent rocks. The content of authigenic hairy smectites, observed by TEM, is probably not high enough to affect the overall REE composition that is distinctive of land-derived sediments. Therefore, clay mineral assemblage distribution in the CRP-1 core can be used as an indicator of the provenance of the sediments.

Considering the large compositional variations, the source areas for the smectites of CRP-1 core are probably represented by both the basaltic rocks of the McMurdo Volcanic Group and by the complex of basement and sedimentary rocks cropping out in the Transantarctic Mountains.

It seems more problematic to describe the process which led to the formation of the detrital ferromagnesian smectites present in the Quaternary part of the core, as cold climate conditions were surely unfavourable to advanced chemical weathering on the continent. However, in the soils of the Transantarctic Mountains, formed on tills derived from dolerites, the occurrence of iron-rich smectites has been described (Campbell & Claridge, 1989; Claridge & Campbell, 1984). This iron-rich smectite in soil is believed to be a secondary mineral, formed through the recrystallization of iron and magnesium, previously released by chemical weathering processes operating on basic igneous rocks. A xerous moisture regime and availability of water are the conditions that allow chemical weathering of the parent rocks to take place. Considering the large abundance of volcanic detritus in the upper core, a similar model could also explain the formation of at least a part of the detrital smectites of the Quaternary section of CRP-1.

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REFERENCES

Banfield J.F. & Eggleton R.A., 1990.Analytical transmission electron microscope studies of plagioclase, muscovite, and K-feldspar weathering. *Clays and Clay Minerals*, **38**, 77-89.

Barrett P.J., 1996. Antarctic palaeoenvironment through Cenozoic times-a review. *Terra Antartica*, **3**, 103-119.

Campbell I.B. & Claridge G.G.C., 1989. *Antarctica: Soils, Weathering Processes and Environments*. Elsevier, 368 p.

Cape Roberts Science Team, 1998. Summary of Results from CRP-1, Cape Roberts Project, Antarctica. *Terra Antartica*, **5**(1), 125-137.

Chamley H., 1989. *Clay Sedimentology*. Springer, 623 p.

Chamley H., Coulon H., Debrabant P. & Holtzapffel T., 1985. Cretaceous interactions between volcanism and sedimentation in the east Mariana Basin, from mineralogical, micromorphological and geochemical investigations (Site 585, Deep Sea Drilling Project). *Init. Repts. DSDP*, **89**, 413-429.

Claridge G.C.C. & Campbell J.B., 1984. Mineral transformation during the weathering of dolerite under cold arid conditions. *N.Z.J. Geol. Geophys.*, **27**, 537-545.

Claridge G.C.C. & Campbell J.B., 1989. Clay mineralogy. In: Barrett P.J. (ed.), *Antarctic Cenozoic history from the CIROS-1 Drillhole, McMurdo Sound, DSIR Bull.*, **245**, 186-200.

Courtois C. & Chamley H., 1978. Terres rares et minéraux argileux dans le Crétacé et le Cénozoique de la marge atlantique orientale. *C.R. Acad. Sci., Paris*, D, **286**, 671-674.

Debrabant P., Delbart S. & Lemaguer D., 1985. Microanalyses géochimiques de mineraux argileux de sediments preleves en Atlantique Nord (forages du DSDP). *Clay Minerals*, **20**, 125-145.

Eggleton R.A. & Wang Qiming., 1991. Smectites formed by mineral weathering. *PROC. 7th EUROCLAY Conf.*, Dresden, **91**, 313-318.

Ehrmann W.U., 1997. Smectite Concentrations and Crystallinities: Indications for Eocene Age of Glaciomarine Sediments in the CIROS-1 Drill Hole, McMurdo Sound, Antarctica. In: Ricci C.A. (ed.), *The Antarctic Region: Geological Evolution and Processes*, Terra Antartica Publication, Siena, 771-780.

Ehrmann W.U., 1998. Implications of late Eocene to early Miocene clay mineral assemblages in McMurdo Sound (Ross Sea, Antarctica) on paleoclimate and ice dynamics. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, **139**, 213-331.

Ehrmann W.U. & Mackensen A., 1992. Sedimentological evidence for the formation of an East Antarctic ice sheet in Eocene/Oligocene time. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, **93,** 85-112.

Ehrmann W., Melles M., Kuhn G. & Grobe H., 1992. Significance of clay mineral assemblages in the Antarctic Ocean. *Marine Geology*, **107**, 249-273.

Grobe H., Futterer D.K. & Spiess V., 1990. Oligocene to Quaternary sedimentation processes on the Antarctic continental margin, ODP LEG 113, Site 693. *Proc. ODP. Sci. Results*, **113**, 121-131.

Güven N., 1988. Smectites. In: Bailey S.W. (ed.), *Hydrous Phyllosilicates. Reviews in Mineralogy, Min. Soc. America*, 497-552.

Hoffert M., Person A., Courtois C., Karpoff A.M. & Trauth D., 1980. Sedimentology, mineralogy and geochemistry of hydrothermal deposits from holes 424, 424A, 424B and 424C (Galapagos spreading center). *Init. Repts. DSDP*, **54**, 339-376.

Kyle P.R., 1990. McMurdo Volcanic Group, Western Ross Embayment. In: Baker P.E., Kyle P.R., Rowley P.D., Smellie J.L. & Verwoerd W.J. (eds.), *Volcanoes of the Antarctic Plate and Southern Ocean, Antarctic Res. Ser.*, **48**, 19-46.

López-Galindo A., Marinoni L., Ben Aboud A. & Setti M., 1998. Morfologia, fabrica y quimismo en esmectitas de los sondeos Ciros-1, 270 y 274 (Mar de Ross, Antartida). *Revista de la Sociedad Española de Mineralogía*, **21**, 1-15.

Paquet H., Duplay J., Valleron-Blanc M. & Millot G., 1987. Octahedral compositions of individual particles in smectite-palygorskite and smectite-sepiolite assemblages. *Proc. Int. Clay Conference*, AIPEA, Denver, 73-77.

Petschick R., Kuhn G. & Gingele F., 1996. Clay mineral distribution in surface sediments of the South Atlantic: sources, transport, and relation to oceanography. *Marine Geology*, **130**, 203-229.

Piper D.Z., 1974. Rare earth elements in sedimentary cycle: a summary. *Chem. Geology*, **4**, 285-304.

Robert C. & Maillot H., 1990. Paleoenvironment in the Weddel Sea area and Antarctic climates, as deduced from clay mineral association and geochemical data, ODP Leg 113. *Proc. ODP. Sci. Results*, **113**, 51-70.

Setti M., Marinoni L., López-Galindo A. & Ben Aboud A., 1997. XRD, SEM and TEM Investigation of Smectites of the Core Ciros-1 (Ross Sea, Antarctica). *Terra Antartica*, **4**(2), 119-125.

Singer A., 1984. The paleoclimatic interpretation of clay minerals in sediments: a review. *Earth-Science Reviews*, **21**, 251-293.

Toyoda K., Nakamura Y. & Masuda A., 1990. Rare earth element of Pacific pelagic sediments. *Geochim et Cosmochim. Acta*, **54**, 1093-1103.

Velde B., 1995. *Origin and mineralogy of clays*. Springer, 334 p.

Weaver C.E. & Pollard L.D., 1975. *The chemistry of Clay Minerals*. Elsevier, 213 p.