

## Crystal-Chemistry of Smectites in Sediments of CRP-3 Drillcore (Victoria Land Basin, Antarctica): Preliminary Results

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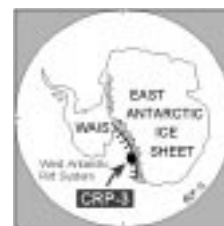
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**Abstract** - The aim of this work is to evaluate the origin of smectites in sediments of CRP-3 core (Victoria Land Basin, Antarctica), through TEM observations and microanalyses on smectite microparticles and XRD analyses of clay fractions.

Smectites in the lower sedimentary section (between 602.05 and 815.86 mbsf), and in some levels of the central section of the core, are intermediate members of the beidellite-saponite series, with lower K and higher Mg contents in interlayer and higher crystallinity values. The clay fraction largely consists of smectite, that is regarded as authigenic. Smectites in the upper (between 6.60 and 101.69 mbsf) and in some other levels of the central section of the core are Al-Fe beidellites, with higher K and lower Mg contents in interlayer sites and lower values of crystallinity. In the clay fraction illite and chlorite also occur. These characteristics suggest that smectites in these sediments are detrital.

Smectites in an igneous body (between 901.20 and 919.06 mbsf) have a homogeneous composition and are Al-rich beidellite-montmorillonites; the clay fraction is mostly composed by kaolinite with mixed-layer smectite-illite or kaolinite-smectite.

Authigenic smectites probably formed from the alteration of volcanic material (pyroxenes, glasses) and/or through precipitation from fluids of possible hydrothermal origin.



### INTRODUCTION

In this work preliminary results on the composition of smectite in sediments of the CRP-3 core are discussed.

The CRP-3 drillhole was carried out in 1999 and is situated about 12 km east of Cape Roberts in the Victoria Land Basin, Ross Sea (Antarctica). The aim of the drilling project was to investigate the Palaeogene climatic and tectonic history of the area (Cape Roberts Science Team, 2000).

The drilling collected a sequence of sediments from 3 to 939 mbsf (meters below sea floor). Down to 823 mbsf the sediments are mainly composed of glacially-influenced marine sediments of Oligocene age, with possibly some latest Eocene sediments at the lowest levels. From 823 mbsf to basement at the bottom of the hole the sediments are mainly made up of light-reddish brown sandstones probably comparable with the Arena sandstone formation of the Beacon Supergroup. In particular, a body of highly altered intrusive rock of unknown age was found in the interval from 901 to 920 mbsf. For further details, see Cape Roberts Science Team (2000) and in other papers in this volume.

The distribution of smectite (and other clay minerals) in the Cenozoic and Quaternary sequences off Antarctica has been successfully used to describe

paleoclimatic changes, to infer source rocks of the sediments and stratigraphic correlations (Chamley, 1989; Ehrmann & Mackensen, 1992; Ehrmann et al., 1992; Ehrmann, 1998; Robert & Maillot, 1990).

Interpretation of the genesis of smectite in marine sediments can be controversial, as this mineral may be detrital or authigenic. Detrital smectites are inherited from continental soils and rocks, while authigenic smectites often form in sea floor sediments. It is generally assumed that only detrital minerals are indicative of the paleoenvironments and/or provenance and transport, while authigenic phases provide information on geochemistry of the sedimentary environment (Chamley, 1989; Hillier, 1995; Singer, 1984).

Differentiation between detrital and authigenic smectites is typically based on chemical composition and habit (Chamley, 1989; Güven, 1988; Hillier, 1995; Setti et al., 1997, 1998, 2000; Singer, 1984). As a general rule, in marine environments detrital smectites usually belong to the aluminous montmorillonite-beidellite series, while authigenic smectites are Fe or Fe-Mg -rich and are classified as nontronites or saponites.

Preliminary investigations on clay mineral distribution in the CRP-3 core showed that smectite is particularly abundant in the clay fraction of the

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sediments below 400 mbsf (Ehrmann, this volume; Cape Roberts Science Team, 2000). In this study the microchemical and morphological characters of smectite are used to elucidate its origin and the provenance.

## MATERIALS AND METHODS

Twenty samples were collected from different levels along the sequence; investigations included mineralogical analyses to evaluate the relative abundances of clay minerals and smectite crystallinity, and microchemical and morphological analyses on smectite microparticles.

Mineralogical analyses were carried out on < 2  $\mu\text{m}$  fraction of the sediments, using a Philips PW 1800 diffractometer with  $\text{CuK}\alpha$  radiations (50 kV, 30 mA) and a scan speed of  $1^\circ 2\theta/\text{min}$ . The < 2  $\mu\text{m}$  fraction was separated by settling in a water column and samples were mounted as oriented aggregates on glass slides. X-ray traces were recorded under natural conditions (air-drying) and after ethylene glycol solvation. The XRD patterns were obtained between  $2^\circ$  to  $65^\circ 2\theta$ . Semi-quantitative analysis was performed by measuring the integrated peak areas of the main basal reflections on glycolated samples: smectite at 17  $\text{\AA}$ , illite at 10  $\text{\AA}$  and kaolinite/chlorite at 7  $\text{\AA}$ . The values of peak areas were converted into relative concentrations using the weighting factors of Biscaye (1965). The degree of crystallinity for smectite (v/p) was evaluated according to the methods of Biscaye (1965) and Thorez (1976). Observations and microanalyses of smectites were carried out by transmission electron microscopy (AEM/TEM) using a PHILIPS CM 20 TEM/STEM fitted with an EDAX energy dispersive X-ray detector operated at 100  $\text{\AA}$  beam diameter and a 200 x 1000  $\text{\AA}$  scanning area. In particular, the smectite-richest levels have been

investigated in detail. TEM microanalyses have been performed on several individual smectite micro particles, and the average compositions of smectites occurring in each core level have been calculated (Table 1).

## MINERALOGICAL ANALYSES OF THE CLAY FRACTION

Mineralogical analyses indicates that the clay fraction of CRP-3 core consists of smectite, chlorite and illite (mica). Typical XRD patterns (glycolated samples) of the clay fraction of the core are given in figure 1. Interpretations on smectite distribution and crystallinity in CRP-3 are reported in the paper of Ehrmann (this volume).

In the part of the upper sequence, above 522.73 mbsf, clay mineral contents show considerable fluctuations. At 6.60 and 52.61 mbsf, illite is the most abundant phase with respect to chlorite and smectite. At levels between 101.69 and 522.73 mbsf, smectite contents vary from about 30 to nearly 100%, and illite contents are generally higher than chlorite. Between 602.05 and 815.86 mbsf the clay fraction is almost exclusively smectite, while chlorite and mica are either absent, or present in very low amounts. The results of analyses of three samples of the intrusive body (levels 901.20, 918.53 and 919.06 mbsf) are not very clear, probably because of the extensive alteration that characterised these lithologies (Cape Roberts Science Team, 2000). However, the clay fraction appears to be dominated by kaolinite with variable amount of a slightly expandable phase, possibly a mixed-layer phase (illite-smectite or kaolinite-smectite).

Evaluation of smectite crystallinity index (v/p) indicated that it is generally well crystallised in all samples examined. The v/p ratio increases with the

Tab. 1 - Average composition of smectites from each analysed core levels (calculated with O=10 and OH=2) obtained by TEM-EDS microanalyses.

n.	depth (mbsf)	Tetrahedral sheet		Octahedral sheet				Interlayer		
		Si	Al <sup>IV</sup>	Al <sup>VI</sup>	Mg <sup>VI</sup>	Fe <sup>3+</sup>	Ti	K	Ca	Mg
1	6.60	3.63	0.37	1.14	0.69	0.38	0.00	0.23	0.06	0.04
2	52.61	3.59	0.41	1.01	0.66	0.55	0.00	0.27	0.04	0.04
3	101.69	3.58	0.42	1.06	0.65	0.50	0.00	0.16	0.03	0.11
4	154.45	3.28	0.72	0.05	1.42	1.01	0.00	0.05	0.02	0.32
5	200.25	3.39	0.61	0.58	1.10	0.69	0.00	0.13	0.04	0.20
6	255.83	3.59	0.41	1.56	0.19	0.31	0.00	0.20	0.02	0.08
7	313.83	3.52	0.48	0.89	0.87	0.53	0.00	0.08	0.03	0.18
8	341.46	3.37	0.63	0.80	0.61	0.77	0.02	0.21	0.06	0.14
9	406.34	3.65	0.35	0.68	0.63	0.81	0.03	0.22	0.12	0.03
10	435.34	3.18	0.82	0.11	1.38	0.94	0.03	0.04	0.05	0.34
11	522.73	3.71	0.29	1.39	0.32	0.36	0.02	0.21	0.03	0.03
12	602.05	3.81	0.19	0.63	1.10	0.63	0.00	0.04	0.03	0.05
13	680.65	3.48	0.52	0.09	1.19	1.11	0.01	0.04	0.09	0.16
14	710.81	3.45	0.55	0.24	1.37	0.84	0.00	0.06	0.06	0.19
15	735.71	3.36	0.64	0.08	1.67	0.81	0.00	0.05	0.07	0.23
16	793.72	3.51	0.49	0.88	0.67	0.67	0.00	0.16	0.04	0.13
17	815.86	3.44	0.56	0.17	0.95	1.18	0.00	0.05	0.12	0.15
18	901.20	3.44	0.56	1.51	0.17	0.39	0.00	0.10	0.05	0.17
19	918.53	3.51	0.49	1.67	0.07	0.28	0.00	0.13	0.05	0.12
20	919.06	3.54	0.46	1.55	0.12	0.38	0.00	0.14	0.05	0.10

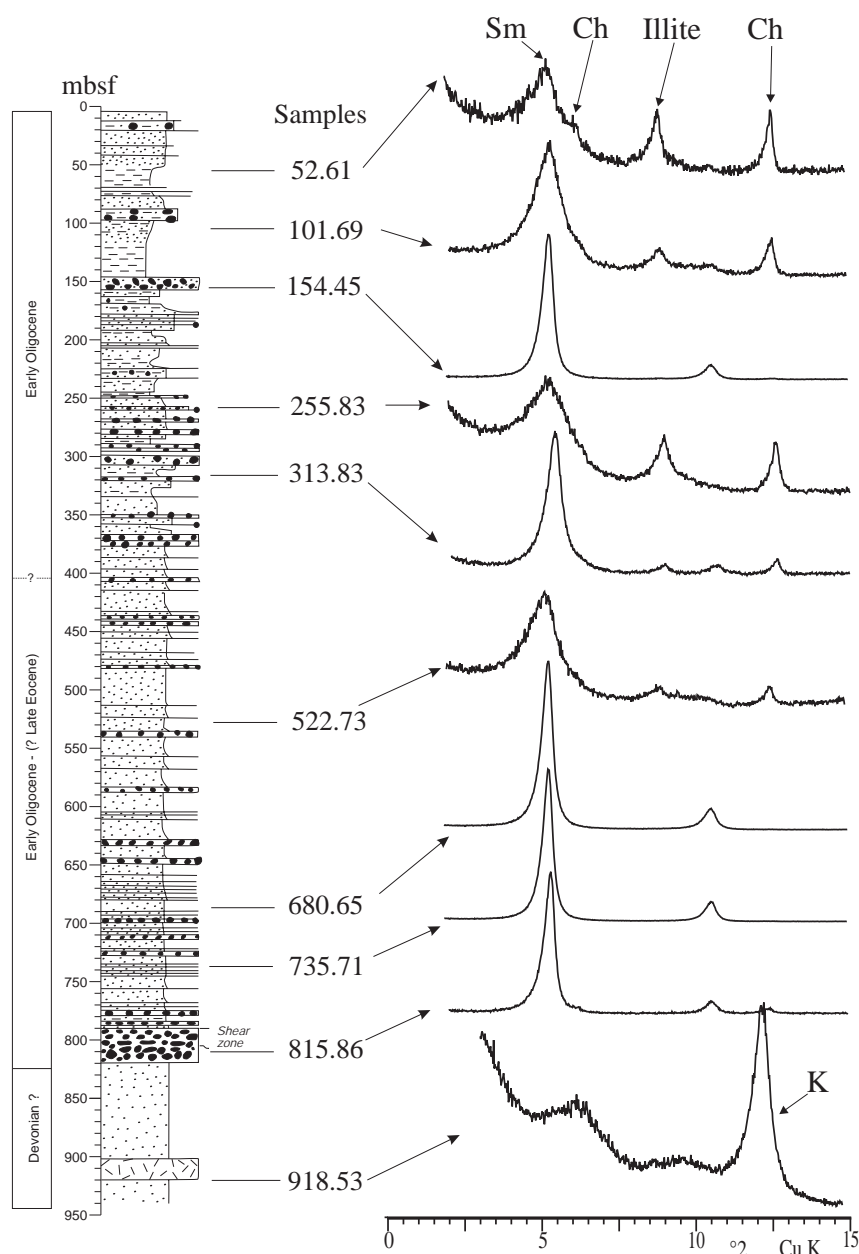


Fig. 1 - Lithostratigraphic column of the CRP-3 core with some typical XRD patterns (glycolated samples) of the clay fraction of the sediments. Sm = Smectite, Ch = Chlorite, K = Kaolinite

increasing smectite content, and attains 1 in the most smectite-rich samples. Conversely, the mixed-layer clays of the intrusive body show very low crystallinity index values (see also Fig. 1).

### SMECTITE COMPOSITION

Smectites of CRP-3 core consist of populations of particles having variable compositions. The average composition of smectites at each level are characterised by the presence of Al in both the tetrahedral and octahedral positions and by partial substitution of  $\text{Fe}^{3+}$  and Mg for octahedral Al (see Tab. 1). In contrast to the average smectite composition in other sequences from the Ross Sea (López-Galindo et al., 1998; Setti et al., 1997, 1998,

2000), smectites at some levels of the CRP-3 core are characterised by very low Al and high Mg in the octahedral position.

Figure 2A plots the octahedral composition of individual smectite microparticles, in terms of  $(\text{Al}^{3+} + \text{Fe}^{3+})^{\text{VI}}$  vs.  $\text{Mg}^{\text{VI}}$  (Paquet et al., 1987; Weaver & Pollard, 1973). The diagram shows the compositional fields of dioctahedral (nontronite and beidellite-montmorillonite), trioctahedral (saponite, stevensite, hectorite) and intermediate smectites. The limits of the dioctahedral domain are  $(\text{Al}^{3+} + \text{Fe}^{3+}) > 1.3$  and  $\text{Mg}^{\text{VI}} < 1.83$  atoms per half unit cell. The existence of an intermediate domain between di- and trioctahedral smectites has been demonstrated experimentally by Grauby et al. (1993). Compositions of smectite microparticles of the CRP-3 core fall into both the dioctahedral and the intermediate fields, and

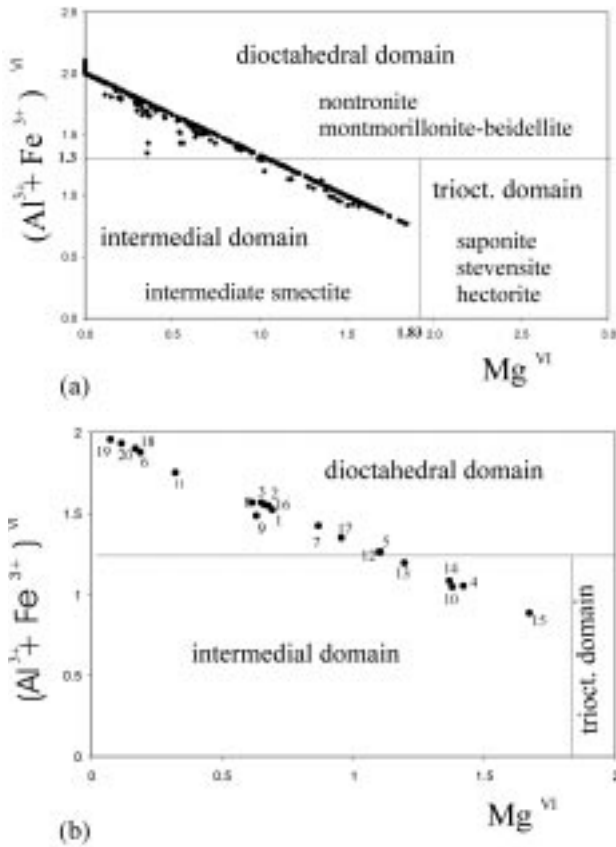


Fig. 2 - a) Octahedral composition of individual smectite particles: (Al<sup>3+</sup>+Fe<sup>3+</sup>)<sup>VI</sup> vs. Mg<sup>VI</sup>, the compositional fields of dioctahedral, intermediate and trioctahedral domains from the literature (see text); b) plots of average chemical composition of smectites from each level.

some plot close to the limit of those with trioctahedral characteristics. The number of smectite microparticles with compositions that plot in the intermediate field is higher in the CRP-3 core than in

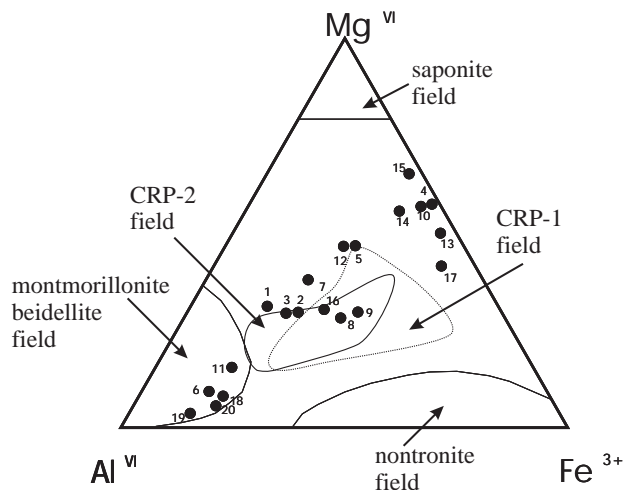


Fig. 3 - Ternary Al-Fe-Mg plot of average octahedral site composition of smectites from the CRP-3 core; smectite compositional fields of cores CRP-1 and CRP-2 core are also shown. Montmorillonite-beidellite field normally contains detrital smectites, saponite and nontronite fields normally comprise authigenic smectites.

the other sequences, *e.g.* CRP-1, CRP-2, CIROS-1, DSDP 270 and 274, from the Ross Sea (López-Galindo et al., 1998; Setti et al., 1997, 1998; 2000).

A plot of the average chemical composition of smectites from each level (Fig. 2B) highlights those with an intermediate composition that are concentrated at certain horizons within the core.

Al-Fe-Mg variation in the octahedral site of the smectites (*e.g.* Weaver & Pollard, 1973), together with compositional fields of smectites from CRP-1 and CRP-2 cores (Setti et al., 1998, 2000) are plotted in figure 3. The plot shows that the CRP-3 smectites have a more variable composition than those of CRP-1 and CRP-2. In particular, one group of smectite compositions occupy the central part of the diagram and overlaps the compositional fields of CRP-1 and CRP-2 smectites (Setti et al., 1998, 2000). A second group of smectites is characterised by higher Mg and are intermediate di-trioctahedral types. Conversely, a third group of smectites, which also includes those from the altered intrusive rocks, is close to the Al<sup>VI</sup> corner.

These compositional characteristics are confirmed by figure 4 (after McMurtry et al. 1983) where Al, Fe

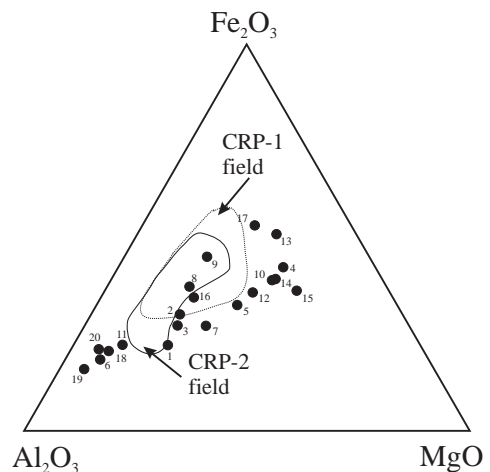


Fig. 4 - Ternary Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-MgO plot of smectite compositions from the CRP-3 core, together with the compositional fields of the smectites from CRP-1 and CRP-2 cores.

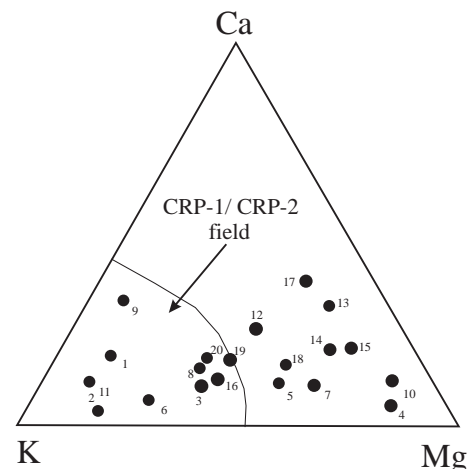


Fig. 5 - Ternary plot K-Ca-Mg of the smectite interlayer site compositions.

and Mg, expressed as oxides, also reflect the octahedral site distribution.

In figure 5, the interlayer composition (Ca, Mg, K; Tab. 1) of smectites from each level is plotted with respect to depth. Smectites in the three upper levels, in some levels in the central part of the section and in the lower intrusive body plot in the fields of CRP-1 and CRP-2 smectites, with K being the most abundant cation. Smectites at lower levels, and in some levels of the central part of the core are characterised by higher Mg and lower K contents.

### MORPHOLOGIC FEATURES OF CLAY PARTICLES

TEM observations on the clay fraction allow smectite and other minerals to be distinguished by their morphologies.

Figure 6 shows authigenic Mg-rich smectites from level 710.81 mbsf. The smectite particles are large and very abundant, and display curled edges typical of authigenic phases. Figure 7 shows the detail of a curled edge of a Mg-rich smectite from level

680.65 mbsf, while figure 8 illustrates a Fe-Mg rich smectite particle from level 815.88 mbsf.

Figures 9-12 show clay assemblages of the altered intrusive rocks in the lowermost part of the core. In particular, of figures 9 and 10 (level 901.2 mbsf) show a heterogeneous assemblage composed of several similar particles of Al-rich smectites together with Fe-oxides with acicular morphology. In figure 10 apatite, feldspars, kaolinite and halite particles are also present. Similarly, the clay assemblage from level 919.06 mbsf (Fig. 11) is mainly composed of Al-smectites and acicular Fe-oxides, and from level 918.53 mbsf (Fig. 12) aluminous smectites are accompanied by some kaolinite.

### DISCUSSION

Considering the variations of smectite composition within the core, those in the lower part (between 602.05 and 815.86 mbsf) are Mg-rich and can be classified as intermediate types of the beidellite-saponite series. These smectites also have lower K and their average composition is similar to that of

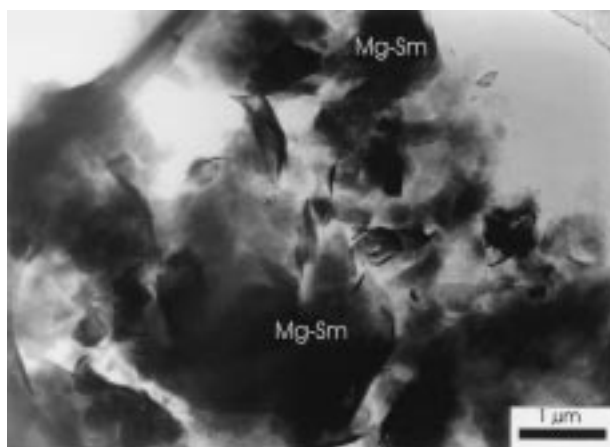


Fig. 6 - Core level 710.81 mbsf, TEM image showing authigenic Mg-rich smectite particles.



Fig. 8 - Core level 815.88 mbsf, TEM image showing authigenic Fe-Mg rich smectite particle.

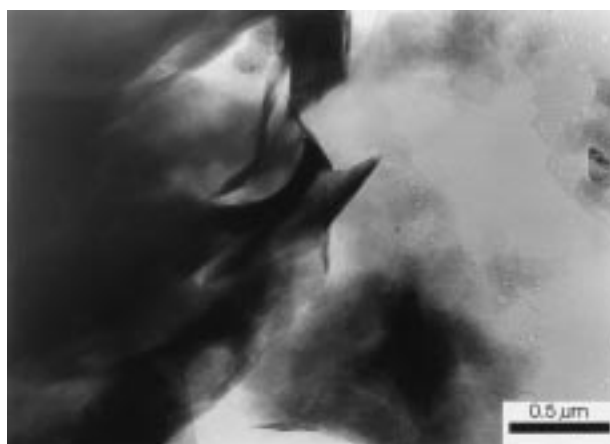


Fig. 7 - Core level 680.65 mbsf, TEM image showing detail of curled edge of authigenic Mg-smectite particle.

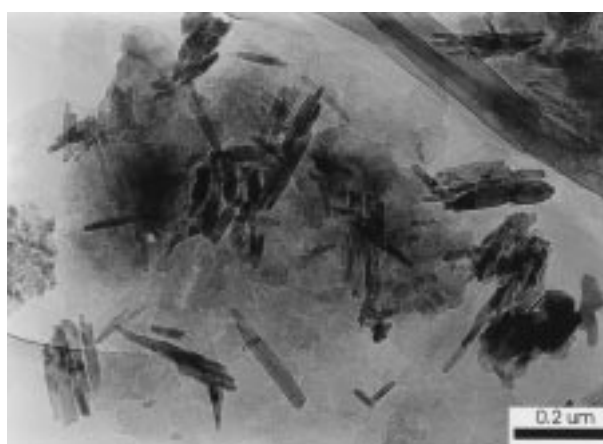


Fig. 9 - Core level 901.2 mbsf, TEM image showing smectite and Fe-oxides.



Fig. 10 - Core level 901.2 mbsf, TEM image showing an assemblage with apatite, smectite, feldspars, kaolinite and halite.

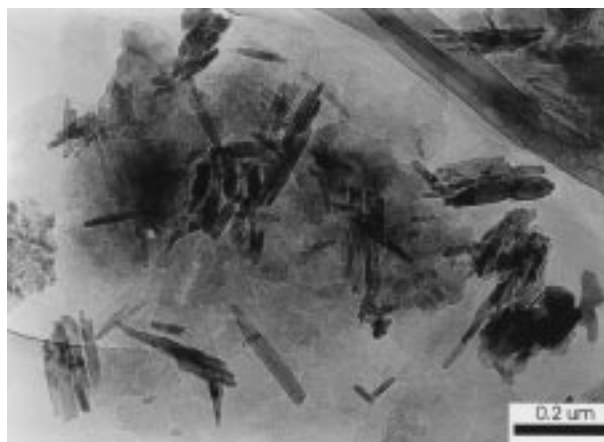


Fig. 12 - Core level 918.53 mbsf, TEM image showing aluminous smectites and kaolinites.

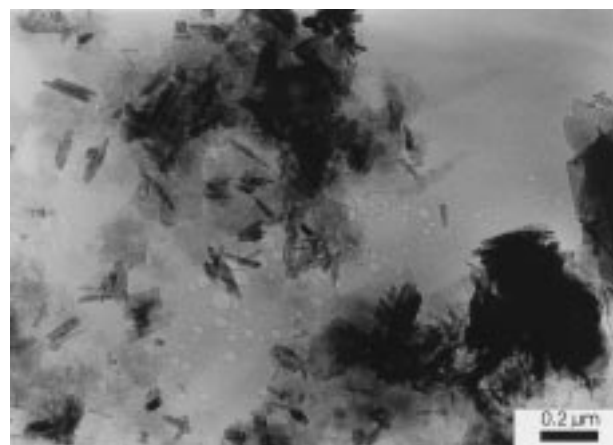


Fig. 11 - Core level 919.06 mbsf, TEM image showing aluminous smectites and Fe-oxydes.

authigenic smectites described in the literature (Chamley, 1989; Cole & Shaw, 1983; Desprairies et al., 1989; Hillier, 1995). The clay fraction at these levels is almost exclusively made up of very well crystallised smectite while typical detrital clay minerals such as chlorite and illite are virtually absent. Smectite is also very abundant in the bulk sediments (Neumann & Ehrmann, this volume).

In general, detrital smectites formed through chemical weathering processes on the continent are accompanied by other clay phases and have a lower crystallinity index. Consequently, a large part of smectites from the lower part of the CPR-3 core would mainly appear to be authigenic. The presence of abundant authigenic smectites in this part of the core is also supported by the investigations of Ehrmann (this volume), Wise et al. (this volume) and Aghib F.S. (pers. comm.).

Smectites in the upper part of the CRP-3 core (above 101.69 mbsf) are dioctahedral types and can be classified as Al-Fe beidellites. Their interlayer and octahedral composition is similar to that of smectites

in CIROS-1, CRP-1 and CRP-2 cores that are considered to be of detrital origin (López-Galindo et al., 1998; Setti et al., 1997, 1998, 2000). Similar Al-Fe beidellites also occur in some soils of Antarctica formed on tills derived from dolerites (Campbell & Claridge, 1989), and detrital smectites frequently contain significant amounts of K (Drief & Nieto, 2000). In clay fractions of the upper part of the CRP-3 core, illite and chlorite are also present in relevant amounts, and smectites have a lower crystallinity index. Bulk sediments are largely composed of detrital minerals such as quartz and feldspars (Neumann & Ehrmann, this volume). These characters suggest the smectites in the upper part of the core are detrital.

Smectites in the central part of the core (levels between 154.45 and 522.73 mbsf) show a large compositional variability that does not appear to be related to the textural or sedimentological features of the sequence. In particular, smectites at levels 255.83 and 522.73 mbsf are the most Al-rich, Mg-rich smectites are also present (levels 154.45 and 435.34 mbsf) as well as Fe-Al beidellites (levels 341.46 and 406.34 mbsf).

Smectites in the altered igneous body (levels 901.20, 918.53 and 919.06 mbsf) are homogeneous and can be classified as Al-rich beidellite-montmorillonite. The clay fraction is mostly composed of kaolinite with mixed-layers smectite-illite (or kaolinite-smectite). Preliminary chemical analyses confirm that the clay fraction of the igneous body is mainly composed of Al-rich phases (Marinoni & Setti, 2001).

## CONCLUSIONS

Smectites in Quaternary and Cenozoic sediments in cores CRP-1, CRP-2, CIROS-1, DSDP 270 and 274 from the Ross Sea are essentially dioctahedral Fe-Al members of the nontronite-beidellite series.

Compositional and morphological features indicate that smectites in these cores are detrital and formed through chemical weathering of lithologies probably containing basic volcanic or volcanogenic material (López-Galindo et al., 1998; Setti et al., 1997, 1998, 2000).

Smectites in the CRP-3 core have highly variable compositions, suggesting authigenic and detrital origins. In particular, smectites in the lower (between 602.05 and 815.86 mbsf), and in some levels in the central part of the core (154.45 and 435.34 mbsf) are mostly intermediate members of the beidellite-saponite series, and are considered to be authigenic. In contrast, smectites in the uppermost part of the core (above 101.69 mbsf) and in some levels in the central section (levels 200.25, 255.83, 313.83, 341.46, 406.34, 522.73 mbsf) are Fe-Al beidellites that are compositionally similar to smectites from the CIROS-1, CRP-1 and CRP-2 cores and are likely to be detrital. Terrigenous smectite and other clay minerals are believed to derive from the weathering of the lithologies in the Transantarctic Mountains, under a relatively warm and humid climate (Ehrmann, this volume). The clay fraction of an igneous body (below level 901.2 mbsf) is mostly composed of kaolinite with mixed-layers smectite-illite (or kaolinite-smectite). Coexisting smectites are homogeneous (Al-rich beidellite-montmorillonite).

Processes that gave rise to the formation of the authigenic smectites in the Antarctic Cenozoic sediments are still problematical, but three main processes may have been involved (Chamley, 1989; Cole & Shaw, 1983; Hillier, 1995):

- 1) precipitation from hydrothermal fluids;
- 2) alteration of volcanic rock fragments and glass or precipitation from solutions in basalt cavities at low temperature;
- 3) low-temperature combination of iron oxyhydroxide and biogenic silica.

In addition burial diagenesis may also have induced the formation of authigenic clays (Chamley, 1989; Güven, 1988; Hillier, 1995; Singer, 1984).

The characteristics of the smectites in the CRP-3 core imply that they had a different thermal and diagenetic history from those in the CIROS-1, CRP-1 and CRP-2 cores. Fe-Ti oxides and clinopyroxenes in volcanic clasts in the CRP-3 core are largely altered to smectite, and the cryptocrystalline matrix is altered to sericite and other clay minerals (Cape Roberts Science Team, 2000). Since the weathering of clinopyroxenes and oxides generally produces trioctahedral Mg-smectites and nontronites (Banfield & Eggleton, 1990; Eggleton et al., 1991), intermediate di-trioctahedral smectites may be formed through the alteration of pyroxenes and other volcanic detritus. The prevalence of authigenic smectites in the lower core levels is possibly attributed to early diagenetic processes. Conversely, the large compositional variations of smectites in the central part of the core could relate to differences in the size, porosity and

composition of the host sediments, as all these parameters can greatly influence the alteration potential of volcanic material (Chamley, 1989).

Scanning electron microscopy investigations by Aghib F.S. (pers. comm.) and Wise et al. (this volume) indicate that smectite is often present as coatings on sand grains. Therefore, authigenic smectite might also be precipitated from fluids, whose origin (diagenetic, hydrothermal) is, at present, uncertain. Nevertheless, it is known that interstratified minerals represent intermediate products of mineral transformation as a result of increasing temperature in diagenetic and hydrothermal environments (Chamley, 1989). Diagenetic formation of interstratified minerals generally requires a burial depth > 1 km, and the occurrence of these minerals in the samples of basement rocks below 901 mbsf might also be attributed to hydrothermal activity. This hypothesis is also supported by the occurrence of breccia at about 918 mbsf, which indicates that hydrothermal alteration at a lower temperature can have accompanied, or followed, the emplacement of the igneous body (Cape Roberts Science Team, 2000). The variations in the chemical compositions of smectite, and the related differences in the origin of the mineral, are also supported by preliminary chemical analyses of major, minor, trace elements and REE on the clay fraction of the sediments of the core (Marinoni & Setti, 2001).

Since clay minerals represent reliable indicators of paleoclimate only when they are of detrital origin, the large abundance of authigenic smectites in the lower and central parts of the CRP-3 core implies that the paleoclimatic and paleoenvironmental reconstruction has to be approached with care.

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