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Smectite Content and Crystallinity in Sediments from CRP-2/2A, Victoria Land Basin, Antarctica

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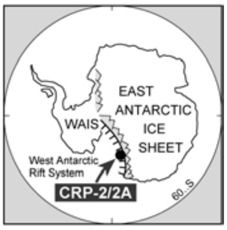
Abstract - Sediments of the CRP-2/2A drill core from the continental shelf of McMurdo Sound in Ross Sea, Pacific sector of the Southern Ocean, have been investigated for their clay mineral assemblages, especially for the smectite contents and smectite crystallinities. Highest smectite amounts and best crystallinities occur in three intervals below 485 mbsf in CRP-2/2A. They indicate deposition of sediments during a time when chemical weathering was active on large ice-free areas on the nearby Antarctic continent. In the upper part of the core, smectite contents are much lower and crystallinities are worse. This clay mineral composition indicates deposition of sediments during a time when physical weathering prevailed on an ice-covered continent. At deep-sea sites around Antarctica the shift from smectite-dominated to smectite-poor and illite-rich assemblages is well dated as earliest Oligocene, 33.9-33.1 Ma, and documents the onset of continental glaciation in East Antarctica. At CIROS-1 a corresponding shift in the clay mineralogy was observed



INTRODUCTION

One of the main objectives for drilling CRP-2/2A on the McMurdo Sound continental shelf of the Ross Sea, Pacific sector of the Southern Ocean (Fig. 1), was to reconstruct in detail the Cenozoic Antarctic climatic and glacial history. It is generally accepted that the onset of East Antarctic continental glaciation occurred in earliest Oligocene time (*e.g.* Hambrey et al., 1991; Wise et al., 1991; Ehrmann & Mackensen, 1992; Salamy & Zachos, 1999). However, very little is known on the Antarctic ice coverage and volume during the time preceeding this major event. A target of CRP-2/2A, therefore, was to penetrate into Eocene and older sediments in order to better date and reconstruct the transition from an initially ice-free Antarctic continent via a continent with local mountain glaciers and a continent with regional ice caps to, finally, a continent almost completely covered by ice (Cape Roberts Science Team, 1999).

The initial biostratigraphic investigations of the lowermost sediments of the core did not provide a precise and unequivocal age. They suggest an earliest Oligocene age, but do not discount the slight possibility of a latest Eocene age. The CRP-2/2A sediments show a strong glacial influence throughout the core and document numerous episodes of ice advance across the continental shelf and subsequent retreat of the ice to a position close to the present-day coast line. However, no major change in the ice coverage of the Antarctic continent could be reconstructed so far from the glacial facies (Cape Roberts Science Team, 1999).

The onset of East Antarctic continental glaciation in the earliest Oligocene is accompanied by a major change in the clay mineral assemblages (Ehrmann & Mackensen, 1992; Ehrmann et al., 1992). This change is well documented in pelagic sedimentary sequences drilled on Maud Rise and on Kerguelen Ridge in the Southern Ocean. The clay minerals there record a change from high smectite and low illite concentrations in the Cretaceous, Paleocene and Eocene to low smectite and high illite concentrations in the Oligocene and Neogene. It reflects the shift from chemical Antarctic weathering conditions under a relatively warm and humid climate with high smectite concentrations to physical weathering under a cool and dry climate with high illite concentrations. It thus documents probably the

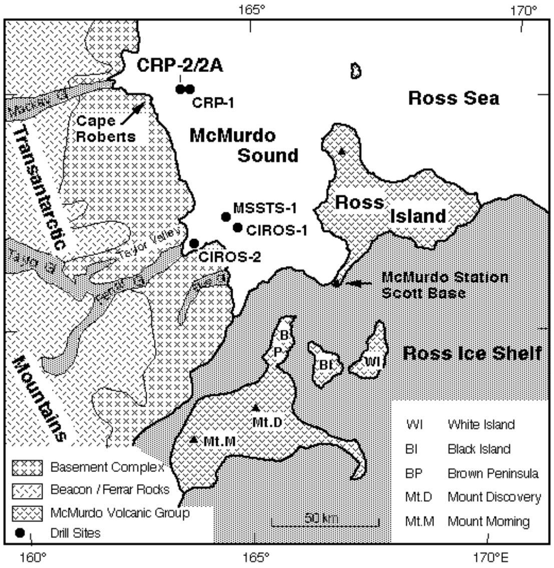


Fig. 1 - Location map of the drill site CRP-2/2A on the continental shelf of McMurdo Sound in Ross Sea, Pacific sector of the Southern Ocean. The positions of the drill sites CRP-1, CIROS-1, CIROS-2 and MSSTS-1 mentioned in the text are also indicated. Bedrock geology is from Warren (1969).

transition from a mainly ice-free Antarctic continent to a mainly ice-covered Antarctic continent. This change is well dated as earliest Oligocene, 33.9-33.1 Ma (time scale of Berggren et al., 1995). A similar change in clay mineral assemblages was found in sediments of the CIROS-1 drill core, some 75 km south of CRP-2/2A (Ehrmann, 1997, 1998a).

This paper presents preliminary results of clay mineral investigations carried out on sediments from CRP-2/2A. It concentrates on the downcore distribution of smectite abundances and smectite crystallinities. The main objectives are to reconstruct the source areas for the sediments and the paleoclimatic conditions on the Antarctic continent during deposition of the CRP-2/2A sediments. Special attention is given to the position of the Eocene/Oligocene boundary and to a correlation with the CIROS-1 core and deep-sea cores.

METHODS

For this study, 74 bulk-sediment samples were crushed, then oxidized and disaggregated by means of a 5-10% H_2O_2 solution. After washing the samples through a 63 μm sieve, the clay fraction was isolated from the silt fraction in settling tubes. Forty milligram of clay were dispersed in an ultrasonic bath and mixed with 1 ml of an internal standard consisting of a 1% MoS_2 suspension. The samples were mounted as texturally oriented aggregates by rapidly filtering the suspension through a membrane filter. The filter cakes were dried at 60°C, mounted on aluminium tiles and exposed to ethylene-glycol vapour at a temperature of 60°C before the X-ray analyses. The measurements were conducted on an automated powder diffractometer system Philips PW 1700 with CoKα radiation (40 kV, 40 mA). The samples were X-rayed with a speed of 0.02° 2θ per second. For more details of the sample preparation, see Ehrmann et al. (1992).

The X-ray diffractograms were evaluated on an Apple Macintosh Personal Computer using the "MacDiff" software (Petschick, freeware). Peak areas were calculated for MoS_2 at 6.15 Å and for smectite at 17 Å, after graphical removal of the chlorite 14 Å peak (Fig. 2). In order to get distribution patterns of smectite not influenced by dilution with other clay minerals, smectite/standard ratios were calculated. As a measure of the crystallinity of smectite, the integral breadth (Δ° 2θ) was computed. The integral breadth is the width of the rectangle which has the same height and the same area as the measured peak (Klug & Alexander, 1974: 661 ff.; Fig. 2). High values indicate poor crystallinities, low values indicate good crystallinities.

All raw data are lodged in the data bank of the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany (available via www.pangaea.de).

RESULTS

The clay content of the CRP-2/2A sediments ranges between 0% and 25% (Fig. 3). The downcore distribution curve reflects mainly the lithological log of the core. Some minor discrepancies occur, however, because the visual core description was based mainly on medium and maximum grain sizes.

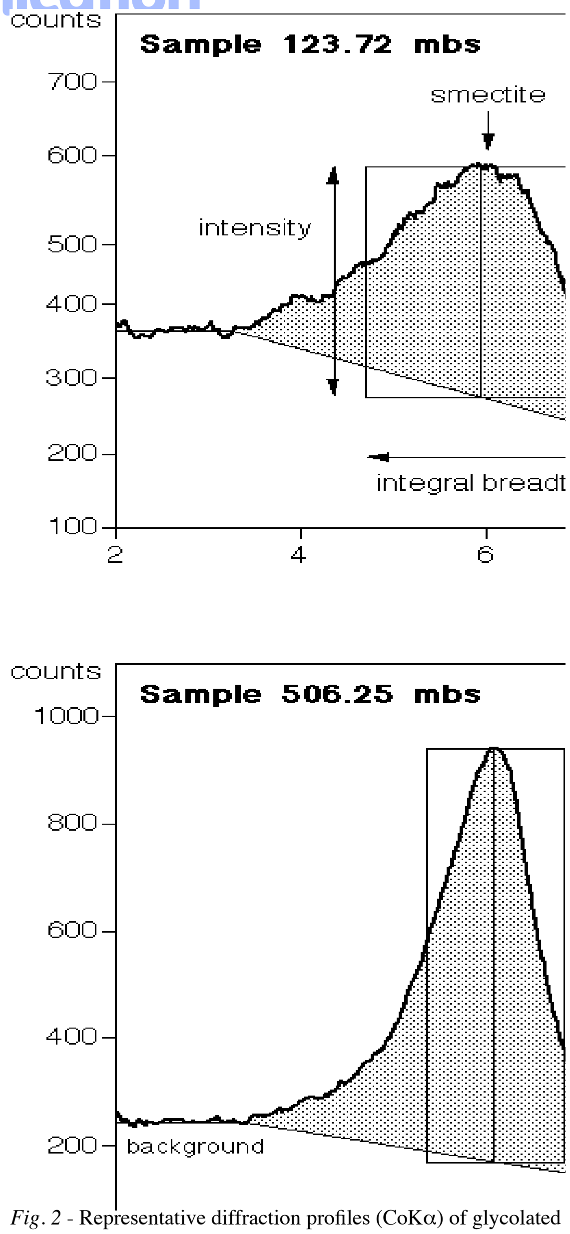


Fig. 2 - Representative diffraction profiles (CoKα) of glycolated samples from the CRP-2/2A drillhole. Note the low smectite content and poor crystallinity in the upper sample and the high smectite content and relatively good crystallinity in the lower sample.

The sediments above *c.* 485 mbsf (metres below sea floor) have smectite/standard ratios showing relatively minor fluctuations and low values between 0.5 and 3. This upper part of the core can be subdivided into 4 intervals: an uppermost interval 0-110 mbsf with mean ratios of 0.90, an interval 110-270 mbsf with mean ratios of 1.27, an interval 270-440 mbsf with mean ratios of 1.82, and an interval 440-485 mbsf with mean smectite/standard ratios of 1.20 (Fig. 3). In contrast, highest smectite contents with smectite/standard ratios of up to 7.5 occur in the lower part of core CRP-2/2A, below *c.* 485 mbsf. A characteristic feature of this interval are strongly fluctuating ratios resulting in several maxima and minima.

The smectite crystallinity fluctuates generally between 1.8 and 2.4 Δ° 2θ in the upper *c.* 485 m of core CRP-2/2A.

In the lower part of the core, several intervals with much better crystallinities occur and coincide with high smectite abundances. In these intervals, integral breadth values reach up to 1.4 Δ° 2θ (Fig. 3).

DISCUSSION

The patterns of smectite abundance as expressed by smectite/standard ratios are not related to facies changes and also do not reflect the proximity of the ice. They also show no correlation to the clay content of the sediments (Fig. 3). It thus seems that they are not influenced by transport, sedimentation or reworking processes. The smectite concentrations are therefore controlled probably only by source lithology and climate-dependent weathering conditions.

The origin of smectite in marine sediments is still under debate. It may be derived from submarine weathering of volcanic material. Although some volcanic debris has been recognised in the CRP-2/2A core (Cape Roberts Science Team, 1999; Smellie, this volume), no correlation is evident between the smectite content and the volcanic-derived sand and gravel. Furthermore, there are no differences between the clay mineral assemblages of lodgement tills and of glaciomarine sediments, suggesting that the clay minerals are derived from land. A detrital origin of the smectites is also supported by microanalytical investigations (Setti et al., this volume).

On the continents smectite generally forms by hydrolysis under humid and relatively warm climatic conditions. In Antarctica such conditions are thought to have prevailed before the onset of continental glaciation, in Eocene and older times (Robert & Maillot, 1990;

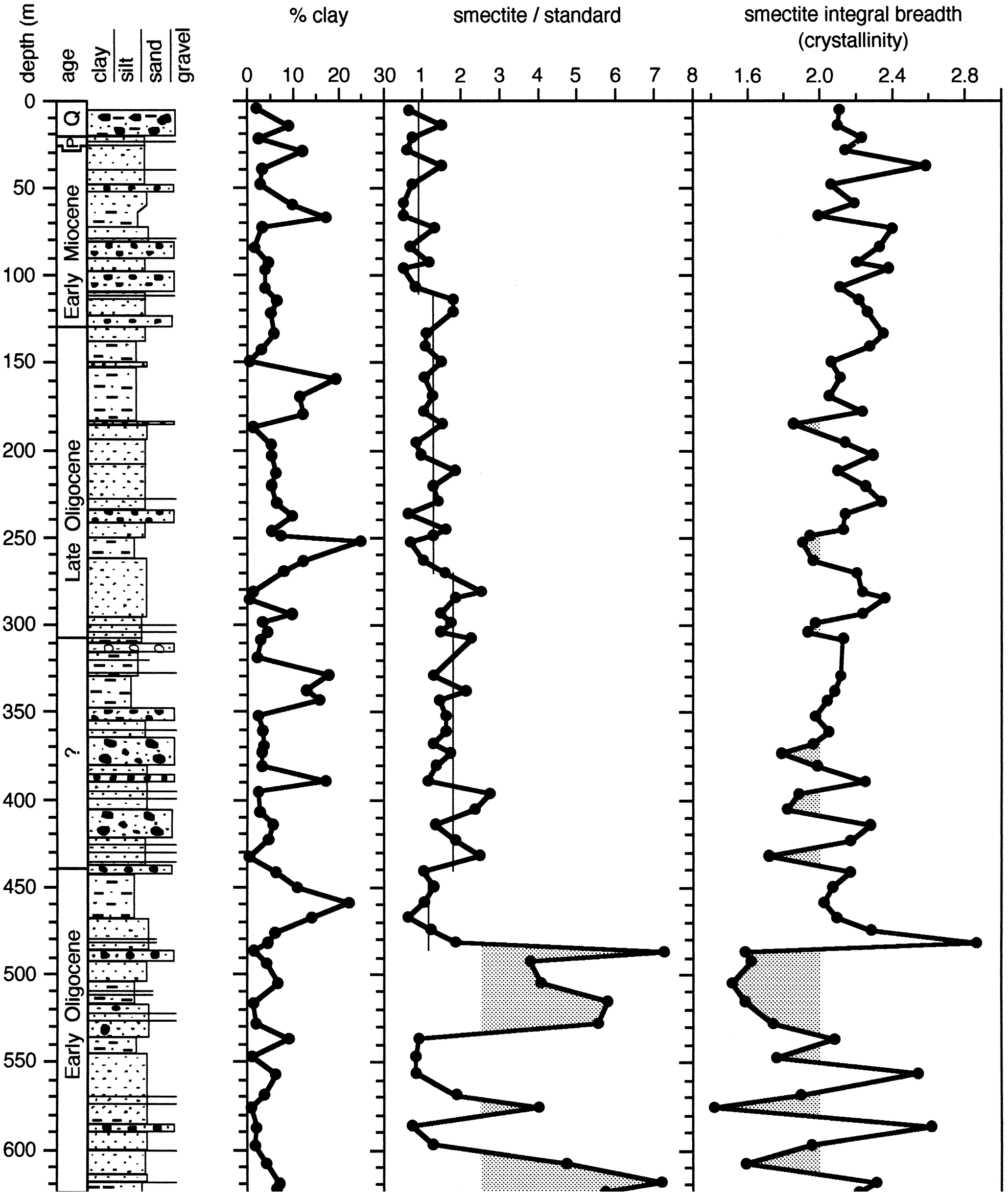


Fig. 3 - Lithological log of the drill core CRP-2/2A (Cape Roberts Science Team, 1999), clay content (%), smectite/standard ratio and smectite crystallinity (Δ° 2θ) in sediments of core CRP-2/2A.

Ehrmann & Mackensen, 1992; Ehrmann et al., 1992). Evidence of smectite formation under a polar climate has been reported from a few soils and tills in Antarctica (Campbell & Claridge, 1987: 130 ff.; Chamley, 1989: 26 ff.). In general, smectite formation in the recent Antarctic environment is only a subordinate process. However, high smectite concentrations have been reported from glaciomarine sediments in areas with basalts in the hinterland (Ehrmann et al., 1992; Ehrmann, 1998a, b), showing that basalts can provide considerable amounts of smectite under a polar climate.

In core CRP-2/2A, highest smectite amounts occur in the lower part, below *c*. 485 mbsf (Fig. 3). The smectite/standard ratios of 0.8-7.3 correspond to about 30-95% of the main clay mineral groups smectite, illite, chlorite and kaolinite. Investigations of the sand and gravel have shown that the source area for the terrigenous components in this part of the core has to be sought in the Transantarctic Mountains (Cape Roberts Science Team, 1999; Neumann & Ehrmann, this volume; Polozek, this volume; Smellie, this volume; Talarico et al., this volume). The hinterland consists of a crystalline basement of late Precambrian and early Paleozoic granitic and metamorphic rocks. The basement rocks are overlain by quartzose sedimentary rocks of the Devonian to Triassic Beacon Supergroup. Both basement and sedimentary strata are intruded by sills and dykes of the Jurassic Ferrar Dolerite (Fig. 1).

The smectite-dominated clay mineral assemblage of several intervals in the lower part of the core is hard to explain in terms of weathering a mixed source in the Transantarctic Mountains under a polar climate. The dolerites would possibly provide smectite also under these conditions, but the sedimentary strata and the crystalline basement rocks would provide mainly illite and chlorite, which then would dilute the smectite. Thus, samples of recent glacial debris taken from the Taylor Glacier and the Mackay Glacier during the Cape Roberts drilling campaign do not contain any smectite. By chemical weathering under a humid and relatively warm climate, in contrast, the source rocks in the Transantarctic Mountains would provide abundant smectite.

The strong fluctuations in the smectite abundances in the lower part of core CRP-2/2A can hardly be formed in front of a fully glaciated area, where physical wheathering conditions should prevail and where glacier paths and source areas should be rather constant according to the given morphology. However, in a periglacial environment the fluctuations can be explained by rapid changes in local weathering regime and/or source area, due to varying proximity of the glaciers and due to glaciofluvial sediment supply.

The intervals of high smectite abundances thus probably indicate times with chemical weathering conditions under a relatively warm and humid climate on the nearby continent. The distinct decrease between 485 and 469 mbsf (Fig. 3) is best interpreted as the transition from a mainly ice-free continent with chemical weathering and smectite formation to a glaciated continent with cooler climate, physical weathering and consequently less smectite production.

A very distinct shift in the clay mineralogy from a smectite-dominated assemblage to a smectite-poor assemblage is also documented in other sites in the Southern Ocean, for example, on Maud Rise and on Kerguelen Plateau (Ehrmann & Mackensen, 1992; Ehrmann et al., 1992). There, the shift is well dated. In Eocene sediments older than 37.0 Ma the smectite contents are >90%. Between 37.0 and 33.9 Ma they range around 75%. The most distinct shift starts at 33.9 Ma with smectite concentrations decreasing to minimum values of 15% at 33.1 Ma. In the remaining Oligocene and Neogene sediments smectite concentrations range around 30-40%.

A very similar pattern of smectite distribution as in CRP-2/2A was reported from the CIROS-1 drill core, situated some 75 km to the south of CRP-2/2A (Fig. 1). Also in CIROS-1 highest smectite contents with smectite/standard ratios of 2-10 occur in the lower part of the core, below *c*. 425 mbsf (Fig. 4; Ehrmann, 1997). Just as in CRP-2/2A, the ratios are strongly fluctuating. In contrast, the core above 425 mbsf has smectite/standard ratios with relatively constant values of 1-3. The change in clay mineral assemblages combined with biostratigraphic data was used to constrain the age of the sediments in the lower part of the core and to place the Eocene/Oligocene boundary at 455-468 mbsf (Ehrmann, 1997, 1998a; Hannah et al., 1997).

By comparison with other drill sites from the Southern Ocean, the CRP-2/2A sediments at 469 mbsf with minimum smectite abundance are likely to have an age of 33.1 Ma. The Eocene/Oligocene boundary (33.70 Ma according to Berggren et al., 1995) could be expected at 485 mbsf. However, this estimate is very uncertain, because there is no control at all on the sedimentation rates.

The smectite crystallinity fluctuates between 1.8 and 2.4 $\Delta° 2\theta$ in the upper 485 m of core CRP-2/2A (Fig. 3). These values seem to be typical for weathering processes in a glacial regime, because such values were also found in Oligocene and younger sediments from cores CIROS-1, CIROS-2, MSSTS-1 and CRP-1 (Ehrmann, 1997, 1998a, b), which were all drilled in McMurdo Sound (Fig. 1).

Below *c*. 485 mbsf in the CRP-2/2A core, in contrast, better crystallinity with values mainly 1.4-2.0 $\Delta° 2\theta$ occurs in several intervals. One possible explanation would be that these smectites have not been formed by glacial but by chemical weathering. This view is supported by the partial correlation between smectite crystallinity and abundance in the lower part of the core (Fig. 3). Best crystallinity values correspond to highest smectite amounts and could reflect maxima in the intensity of chemical weathering. However, with chemical weathering one normally would expect more intense degradation processes and therewith a tendency to poorer crystallinities than with physical weathering under a glacial climate. Another cause for the change in crystallinities could be sought in the grain sizes, with larger smectites resulting in a better crystallinity occurring in the lower part of the core. In the upper part, with the onset of intense glacial scour on the Antarctic continent, smaller and poorer crystalline smectites could be expected. However, no grain size investigations of the clay fraction have been carried out. The changes in crystallinity also could be due to different mineralogical compositions of the smectites. In fact, the average composition of smectite shows a downcore trend to more alluminiferous terms, which could reflect the increase of the chemical weathering processes (Setti et al., this volume).

Also in the case of crystallinities there is a distinct similarity between CRP-2/2A and CIROS-1. In the upper 445 m of core CIROS-1, the smectite crystallinity fluctuates generally between 2 and 2.8 Δ° 2θ. In the lower part of the core, the smectites have better crystallinities with values between 1 and 2.2 Δ° 2θ (Fig. 4).

Thus, smectite crystallinities, even if not totally understood, and smectite contents indicate a major environmental shift at 485-469 mbsf in CRP-2/2A. This shift by comparison with other deep-sea cores around Antarctica can be correlated with the transition from a mainly ice-free to a mainly ice-covered Antarctic continent, which occurred in the earliest Oligocene. Thus, the glaciomarine sediments in the lower part of CRP-2/2A probably reflect a regional ice cover with glaciers calving into the sea.

CONCLUSIONS

The most prominent change in the clay mineralogy occurs at 485-469 mbsf in CRP-2/2A and obviously correlates with the clay mineral shift at 445-425 mbsf in CIROS-1. Such a shift in the clay mineralogy was also detected in deep-sea drill cores from the Southern Ocean (*e.g*., Ehrmann & Mackensen, 1992; Ehrmann et al., 1992; Ehrmann, 1997, 1998a), and there was well dated as earliest Oligocene, 33.9-33.1 Ma.

The most likely explanation for the high smectite content and the good smectite crystallinity recorded in the glaciomarine sediments below *c*. 485 mbsf in core CRP-2/2A is that these sediments were deposited during a time when large parts of the Antarctic continent were ice-free and chemical weathering was active in these areas. Humid and possibly temperate conditions allowed the formation of smectite. The sediments thus reflect a regional ice cover

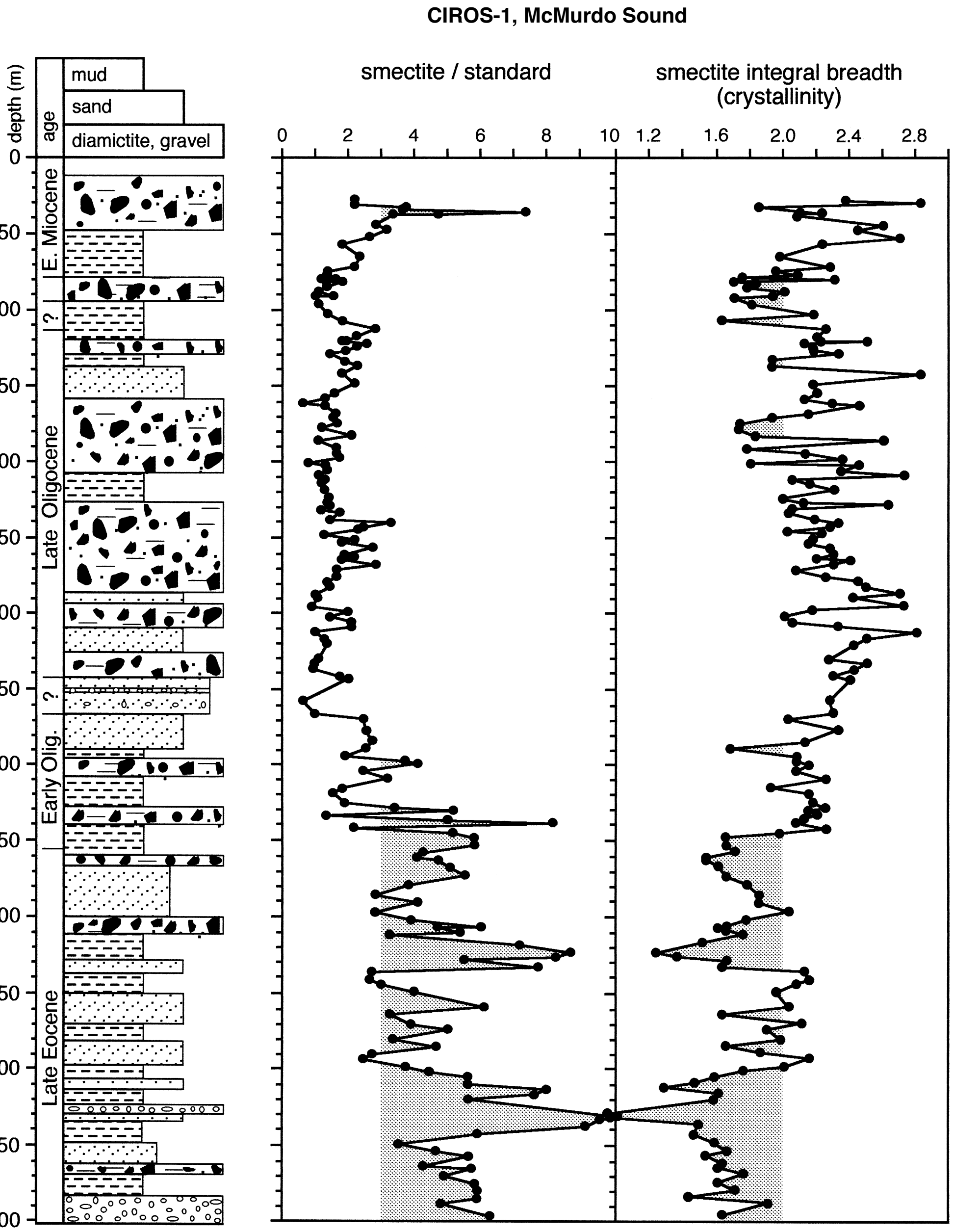


Fig. 4 - Smectite/standard ratio and smectite crystallinity (Δ° 2θ) in sediments of core CIROS-1 (after Ehrmann, 1997). Stratigraphy mainly follows Harwood et al. (1989) and Hannah et al. (1997). Oligocene/Miocene boundary adjusted to Berggren et al. (1995).

of the Transantarctic Mountains with mountain glaciers calving into the sea and the grounding line of a glacier approaching the position of CRP-2/2A several times, as indicated by the coarse fraction of the sediments.

The smectite record in the lowermost part of the sequence shows an obviously cyclic pattern (Fig. 3). Three climatic optima with enhanced formation of well crystallized smectites are documented. They are interrupted by intervals characterized by less intense formation of poorly crystallized smectite. Similar patterns can be seen in the lowermost part of core CIROS-1. However, a detailed correlation of the patterns between the two cores needs confirmation by further investigations.

In the sediments above 485 mbsf, smectite abundances are relatively uniform and low, but illite contents are relatively high (not shown in this paper). These sediments probably were deposited during a time, when full glacial conditions prevailed on the Antarctic continent. Physical weathering of both basement and sedimentary rocks provided mainly illite and much less smectite. A similar composition of the clay fraction was described from core CRP-1 (Ehrmann, 1998b).

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