Lower Miocene and Quaternary Clay Mineral Assemblages from CRP-1

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Abstract - Clay mineral assemblages in lower Miocene and Quaternary sediments recovered at the CRP-1 drillsite, McMurdo Sound shelf, Antarctica, were analysed in order to reconstruct source areas of the sediments and late Cenozoic Antarctic ice dynamics. The assemblages are dominated by smectite, illite and chlorite. Kaolinite occurs in trace amounts only. The lower part of the drillcore, below c. 70 mbsf, is characterised by high illite and chlorite, but low smectite concentrations. This assemblage is typical of a source consisting mainly of granitic and metamorphic rocks, such as are widespread in the Transantarctic Mountains and on the East Antarctic craton. In contrast, the upper c. 70 m of the core is characterised by three intervals with high smectite, but low illite and chlorite concentrations at around 59, 45 and 33 mbsf. The smectite-rich assemblage is typical of a hinterland composed of volcanic rocks, such as are found in the region of the present-day Ross Ice Shelf. The clay minerals are mainly detrital and therefore document the changing influence of different source areas through time. Correlation of the clay mineral record of CRP-1 with that of the CIROS-1 and MSSTS-1 cores implies that the oldest sediments at CRP-1 are younger than 21.8 Ma, and that there is no overlap between CRP-1 and the other cores.

INTRODUCTION

Clay minerals in sediments from the Antarctic Ocean are predominantly of detrital origin (e.g. Piper & Pe, 1977; Barker et al., 1988; Setti et al., 1997; Setti et al., this volume). Recent studies of sediment cores from the Antarctic continental margin have therefore been able to demonstrate the value of clay mineral assemblages in deciphering sediment provenance (e.g. Ehrmann et al., 1992; Petschick et al., 1996; Ehrmann, 1998). Because the composition of the clay mineral assemblages is also strongly controlled by weathering processes, i.e. physical versus chemical weathering, the clay mineral types and the proportions of the individual clay minerals have therefore been used to reconstruct the palaeoclimate and glacial history of Antarctica. Within the Antarctic Ocean clay mineral assemblages are good tracers for reconstructing the palaeoceanography (e.g. Robert & Mailiot, 1990; Hambrey et al., 1991; Ehrmann & Mackensen, 1992; Ehrmann et al., 1992; Diekmann et al., 1996; Ehrmann, 1998). Furthermore, it has been shown that downcore fluctuations in the abundance of individual clay minerals can be used for correlating sediment cores (Ehrmann, 1997, 1998).

METHODS

Bulk-sediment samples of c. 10 cm³ size were taken at about 1 m intervals in the upper c. 65 m and at about 2 m intervals in the lower part of CRP-1. The samples were
crushed, then oxidized and disaggregated by means of a 3-5% H$_2$O$_2$ solution. After sieving the samples through a 63 µm mesh, the clay fraction was isolated from the silt fraction in settling tubes. 40 mg of clay were dispersed in an ultrasonic bath and mixed with 1 ml of an internal standard consisting of a 1% MoS$_2$ suspension (0.3 µm grain-diameter). The samples were mounted as texturally oriented aggregates by rapidly filtering the suspension through a membrane filter of 0.15 µm pore width. The filter cakes were dried at 60°C and mounted on aluminium tiles. They were solvated with ethylene-glycol vapor at a temperature of 60°C for about 18 hrs immediately before X-ray analyses.

X-ray analyses were conducted using an automated powder diffractometer system Philips PW 1700 with CoKα radiation (40 kV, 40 mA). The samples were X-rayed in the range 2-40° 2θ with a speed of 0.02° 2θ per second. Additionally, the range 28-30.5° 2θ was measured with a step size of 0.005° 2θ in order to better resolve the d(002) peak of kaolinite and the d(004) peak of chlorite. X-ray diffractograms were evaluated on an Apple Macintosh Personal Computer using the "MacDiff" software (Petschick, unpublished freeware). Individual clay minerals were identified by their basal reflections at d=17 Å (smectite), 10 and 5 Å (illite), 14.2, 7, 4.72 and 3.54 Å (chlorite), and 3.57 Å (kaolinite). Semi-quantitative evaluations of the mineral assemblages were made on the integrated peak areas. The relative percentage of each clay mineral was determined using empirically estimated weighting factors (Biscaye, 1964, 1965; Brindley & Brown, 1980).

In order to determine distribution patterns of each individual clay mineral not influenced by dilution with other minerals, the calculated peak areas were set in relation to the peak area of the MoS$_2$ standard at 6.15 Å (Ehrmann et al., 1992).

The crystallinity, a measure of the lattice ordering and crystallite size, is expressed as the integral breadth (Δ2θ) of the smectite 17 Å and illite 10 Å peaks. 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.). High values indicate poor crystallinities, low values indicate good crystallinities. Integral breadths are more sensitive for peak-tail variations than the usually applied half width. The following crystallinity categories (ranges of values) can be used for smectite: well crystalline (<1.5), moderately crystalline (1.5-2.0), poorly crystalline (>2.0). Categories for illite crystallinities are: very well crystalline (<0.4), well crystalline (0.4-0.6), moderately crystalline (0.6-0.8), poorly crystalline (>0.8) (Diekmann et al., 1996).

Illite chemistry was inferred from the 5/10 Å peak area ratio. According to Esquevin (1969), values >0.4 correspond to Al-rich illites (muscovite). The ratio decreases with Mg and Fe substituting for octahedral Al. Mg- and Fe-rich illites (biotite) therefore have values <0.15.

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

RESULTS

Results of the clay mineral investigations are presented in figures 2, 3 and 4. The description given in this chapter of the paper therefore concentrates on the main features only.

The clay content of the CRP-1 sediments ranges from 0 to 25% (Fig. 2). The down-core distribution curve reflects only in parts the lithological log of the core, because core description was based mainly on medium and maximum grain sizes. Clay contents are relatively low at 141-103 mbsf (metres below sea floor) and in the upper c. 54 m. They are generally relatively high below 141 mbsf and in the interval 103-54 mbsf. In the latter interval, however, the clay content shows major fluctuations between minimum values of 0% and maximum values of 25%.

Clay mineral assemblages in the CRP-1 core are dominated by illite, smectite and chlorite (Fig. 3). Kaolinite occurs in trace amounts only. Other minerals in the clay fraction, which are present in all samples in high amounts, are quartz, plagioclase feldspars and K-feldspar. However, they have not been quantified.

Fig. 2: Lithological log of the drillcore CRP-1 (simplified after Cape Roberts Science Team, 1998) and clay content (%) in the sediments.
Clay mineral percentage curves have been graphically compared with mineral/internal standard curves (not reproduced in this paper) in order to detect possible dilution effects in the samples investigated for this study. In general, the visual correlation was convincing and indicates that dilution plays only a very minor role in the clay mineral distribution patterns of the CRP-1 sediments. The correlation coefficient (r) between percentages and the mineral/standard ratios was 0.90 in the case of smectite, and 0.76 in the case of illite.

Concentration patterns of individual clay minerals allow a threefold subdivision of the sedimentary sequence of CRP-1 (Fig. 3). The lower part of the core, up to 103 mbsf is characterized by relatively constant concentrations of all clay minerals. The smectite concentrations range from 15 to 30%, the illite contents from 50 to 60% and the chlorite contents from 15 to 25%. Also, the interval 103-70 mbsf is characterised by only minor fluctuations in the concentrations of all individual clay minerals, but by slightly lower smectite concentrations (10-25%) and slightly higher illite concentrations (60-70%). Chlorite concentrations, in contrast, do not differ from those of the lower part of the core. The uppermost core interval, above 70-65 mbsf, shows major fluctuations in the concentrations of smectite, illite and chlorite. Thus, smectite varies from 25% to 90%, with distinct maxima around 59, 45 and 33 mbsf. Illite exhibits a down-core distribution pattern that is strongly opposite to that of smectite, and concentrations from 5% to 55%. Also, the chlorites are strongly fluctuating, and their pattern is also roughly opposite to that of smectite. The kaolinite distribution is relatively invariable throughout the core, with concentrations ranging from 0% to 4% (Fig. 3).

The smectites in the sediments of CRP-1 are moderately to poorly crystalline (Fig. 4). No distinct change in crystallinity is obvious from the downcore distribution of
the integral breadth values. However, there is a slight trend to lower values (better crystallinities) in the lower part of the core. Thus, the values fluctuate around 2 Å⁻2 below 70 mbsf and between 2 and 2.5 Å⁻2 above 70 mbsf. The illites are strongly to moderately crystalline, with a tendency to slightly less crystallinity below 70 mbsf (values around 0.6 Å⁻2), and to slightly better crystallinities in the uppermost 70 m of the core (values 0.5-0.6 Å⁻2).

The illites below 70 mbsf have 5/10 Å ratios <0.2, indicating an Mg- and Fe-rich composition close to that of biotite. Above 70 mbsf, the ratios are around 0.2 or higher. In some samples, the ratio increases to >0.4, indicating an Al-rich composition close to that of muscovite (Fig. 4). The d-values of the illites generally range from 9.98 Å to 10.09 Å, with the tendency to slightly higher and more constant values below 70 mbsf.

**DISCUSSION**

The percentage distributions of the individual clay minerals, their crystallinities and chemical compositions (Figs. 3 & 4) are not related to sediment facies changes or to the clay content of the sediments (Fig. 2), and also do not reflect the proximity of the ice. In particular, there are no major or systematic differences between the clay mineral assemblages of proximal and distal glacilamnic sediments, nor between coarse-grained and fine-grained sediments, suggesting that the assemblages are not influenced by transport, sedimentation or reworking processes. This also implies that the clay minerals are probably not the result of diagenetic alteration of appropriate detrital minerals. The main controls on the composition of the clay fraction, therefore, have to be climate and source area.

The lower part of the core, below 70 mbsf, is characterised by high illite concentrations of >50%, relatively high chlorite concentrations of >15%, but relatively low smectite concentrations of <30%. A similar assemblage also dominates the Oligocene to Lower Miocene sediments of the drillcores CIROS-1 and MSSTS-1, some 70 km further south in McMurdo Sound (Ehrmann, 1997, 1998).

There is no evidence that illite can form in situ in the marine environment, and chlorite can form in the marine environment only under rather restricted conditions (Griffin et al., 1968; Windom, 1976). Thus, illite and chlorite are detrital clay minerals, products of physical weathering and glacial scour, and are typical of the recent high latitudes. They are derived particularly from crystalline rocks, such as those that are widespread on the East Antarctic craton and in the Transantarctic Mountains (Fig. 1). Chlorite is a characteristic mineral for low grade, chlorite-bearing metamorphic and basic source rocks, but is not resistant against chemical weathering and transport. Illite tends to be derived from more acidic rocks and is relatively resistant (Biscaye, 1965; Griffin et al., 1968; Windom, 1976). Both clay minerals can also be derived from the sediments of the Beacon Supergroup (La Prade, 1982), which overlie the basement in the western part of the Transantarctic Mountains (Fig. 1).

The 5/10 Å illite peak area ratios show typical values of 0.10-0.22 in the sediments of the lower part of the core, below 70 mbsf (Fig. 4). The illites are therefore assumed to contain relatively low amounts of Al, but higher amounts of Mg and Fe, and thus have a more biotite-like nature. The biotite-like nature is also indicated by relatively high d-spacings, mainly of 10.05 Å, but also up to 10.09 Å. Biotite-bearing granitic and high-grade metamorphic rocks crop out in the Transantarctic Mountains. Under non-glacial conditions such micas normally suffer a complete degradation and rapid transformation to other clay minerals (Heim, 1990). In glacial regimes, in contrast, physical degradation such as grain diminution predominates, and biotite-like illites may preserve their chemical and structural properties.

The small amounts of smectite in the lower part of the core could come either from soils in the Transantarctic Mountains or from the weathering of volcanic rocks in the southern McMurdo Sound, in the region of the present-day Ross Ice Shelf. The chemical composition of the smectites suggests a volcanic source (Setti et al., this volume).

From the clay mineral record alone, however, it is hard to tell where the source area for the CRP-1 sediments has to be sought. It is most likely that the ice, during the deposition of the lower part of the core, came from the west, and that glaciers breaching the Transantarctic Mountains transported debris derived from a granitic or metamorphic basement and from sedimentary rocks. Thus, not only the illite, chlorite, quartz and K-feldspar of the clay-size fraction, but also all the gravel fraction (Cape Roberts Science Team, 1998; Talarico & Sandroni, this volume) and most of the sand fraction of the sediments (Smellie, this volume) is derived from these rock types. The discharge system then would be a precursor to that of the present-day Mackay Glacier (Fig. 1).

It is also theoretically possible that the ice came from the south, although in the region of the present-day Ross Ice Shelf, large areas are occupied by basaltic, trachytic and phonolitic rocks of the McMurdo Volcanic Group (Fig. 1) that would supply smectite rather than illite. The oldest volcanic surface samples of this region are 19 Ma old (Kyle, 1990). Because the sediments below 70 mbsf are older than 18.5 Ma (Cape Roberts Science Team, 1998), one could argue that the McMurdo Volcanic Group did not exist or that it covered a much smaller area during the time of deposition of the smectite-poor sediments at CRP-1. Ice coming from the south then would have been characterised by debris that included illite and chlorite, derived from basement areas in the hinterland of the present-day Ross Ice Shelf.

However, magnetic surveys indicate that many more volcanic centres of similar size as the present-day outcrops exist beneath the Ross Sea continental shelf, the Ross Ice Shelf and the West Antarctic ice sheet (Behrendt et al., 1994, 1995). Although the age of these centres is not known, they seem to be much older than the age of the outcrops. Thus, in the CIROS-1 and MSSTS-1 cores, high smectite contents (Ehrmann, 1998) and volcanic components in the sand and gravel fractions (Barrett et al., 1986; George, 1989) indicate that volcanic rocks in the
south already existed in late Oligocene time and acted as a periodic source. One would therefore expect that Miocene ice coming from the south would also bring in higher smectite concentrations. Furthermore, in a setting with ice coming from the south, but with no McMurdo Volcanic Group existing, one would expect that the ice carried debris from the hinterland of the present-day Ross Ice Shelf. This hinterland comprises large areas of characteristic metamorphic rocks of the Skelton Group. Such rocks, however, were not found as clasts in the CRP-1 core (F. Talarico, pers. comm.; Talarico & Sandroni, this volume). Thus, ice masses discharging from the south and depositing the CRP-1 sediments below 70 mbsf are unlikely.

The CRP-1 core below 70 mbsf is characterized by only minor fluctuations in the concentrations of the individual clay minerals (Fig. 3), although several major changes in lithology and in the clay abundance (Fig. 2) are documented in the core. The influence of different source rocks in the hinterland appears to have been constant during deposition of the sediments below 70 mbsf. The only change documented in the core occurs at 103 mbsf. At that level, which is dated to about 20 Ma (Cape Roberts Science Team, 1998), a slight increase of 10% occurs in the illite concentration, and there is a slight decrease of 10% in the smectite concentration. This shift could indicate a stronger influence of granitic basement rocks.

In contrast to the lower part of the core, the upper c. 70 m are characterized by strongly fluctuating smectite concentrations reaching up to 60-90% at around 59, 45 and 33 mbsf (Fig. 3). The smectite maxima occur within sandstones, siltstones and biogenic calcareous sands, and show no correlation with distinct sediment facies.

High smectite concentrations are mostly a product of chemical weathering and normally form by hydrolysis under climatic conditions ranging from warm-humid to cold-dry, in environments characterized by very slow movement of water (Chamley, 1989). In general, smectite formation in the recent Antarctic environment is only a subordinate process. Smectite formation has been reported from a few soils in Antarctica (Claridge, 1965; Ugolini & Jackson, 1982; Claridge & Campbell, 1984, 1989; Campbell & Claridge, 1987; Chamley, 1989). Some Antarctic tills also contain smectite (Bardin et al., 1979; Bardin, 1982). High smectite concentrations have been reported from glaciomarine sediments in areas with Mesozoic basaltic in the hinterland (Ehrmann et al., 1992), showing that basalts can provide considerable amounts of smectite under a polar climate.

Because the host sediments in CRP-1 show evidence of ice being present on the nearby Antarctic continent throughout the time represented by the core, chemical weathering on land is not a likely source of the high smectite content. Weathering of Ferrar Dolerite or any other volcanic rock possibly present in the Transantarctic Mountains or on the East Antarctic craton is also not a likely explanation for the high smectite concentrations, because illite and chlorite derived from basement rocks, or from the Beacon Supergroup occurring in the same area, would probably strongly dilute the smectite. The smectite rather indicates a source that is characterised by volcanic rocks, such as those which occur in the McMurdo Volcanic Group. Rocks of this unit occur in the region of Ross Island, White Island, Black Island, Brown Peninsula, Mt. Discovery and Mt. Morning (Fig. 1; Cole & Ewart, 1968; Kyle, 1981, 1990; LeMasurier & Thomson, 1990). A volcanic source area is also suggested by the chemical composition of the smectites (Setti et al., this volume), and by the presence of high concentrations of volcanic glass and volcanic debris in smear slides, and in the sand fraction in the uppermost c. 65 m of the core (Cape Roberts Science Team, 1998; Smellie, this volume).

All smectites in the CRP-1 core are relatively poorly crystalline with integral breadth values mainly >1.8°. Poor smectite crystallinities with values of 2.2-2.8° have been observed also in the Oligocene and lower Miocene sediments of the nearby drillcores CIROS-1 and MSSTS-1, as well as in the Pliocene to Quaternary sediments of CIROS-2 (Ehrmann, 1997, 1998). Although crystallinities are difficult to interpret, the poor smectite crystallinity seems to be characteristic of Oligocene to recent sediments in McMurdo Sound.

Poor crystallinity is often associated with chemical weathering and intense degradation processes, whereas physical weathering under a glacial climate tends to produce better crystallinities (e.g. Petschick et al., 1996). Because the Miocene and Quaternary sediments of the CRP-1 core show evidence of a glacial climate with physical weathering throughout, the poor crystallinity cannot be the result of chemical weathering on land. Possibly, the intense alteration processes and smectite formation, enhanced in hydrovolcanic rocks erupted subaerially and beneath the ice or in the sea (Jakobsson, 1978; Wohletz & Sheridan, 1983; Smellie & Skilling, 1994), could be an explanation for both the high smectite concentrations and the poor crystallinities. Hydrovolcanic eruptions were also suggested as a source of the blocky, non- or poorly-vesicular glass shards in the CRP-1 sediments (Smellie, this volume). Another cause for the poor crystallinities could be grain size. Generally, larger smectites have a better crystallinity than smaller smectites. With intense glacial scour on the Antarctic continent resulting in diamictons with abundant silt and clay, smaller and poorer crystalline smectites would be expected.

Glacial transport of sediment to the drillsite was not restricted to volcanic debris. Thus, the illite and chlorite accompanying the smectite at all levels indicate the persistent influence of basement or sedimentary rocks, as is also indicated by clast compositions. Thus, gravel clasts derived from the granitic basement in the Transantarctic Mountains are distributed throughout the upper part of the core. The same is valid for quartz, feldspar and a distinct heavy mineral association, which all indicate a source in the basement or in the Beacon Supergroup (Cape Roberts Science Team, 1998; Ehrmann, this volume; Polozek & Ehrmann, this volume; Smellie, this volume; Talarico & Sandroni, this volume).

One possible explanation for the mixed composition of the clay fraction is that the ice masses depositing the upper sediments at the CRP-1 site originated in the far south. They incorporated illite and chlorite in the Transantarctic Mountains, south or southwest of the
been dated to Miocene intervals there is characterized by relatively low smectite concentrations, whereas the upper part in each part of the core, and this could represent the background level of smectite transport by suspension. At certain time intervals within the late Early Miocene and the Quaternary, smectite concentrations increased dramatically to 90%, possibly because of enhanced volcanic activity in the south. One problem is that at least two of the smectite maxima correlate with an enhanced input of sand-sized volcanic debris (Smellie, this volume), which probably was not transported by icebergs but by ocean currents coming from the south. During deposition of the upper part of the core, icebergs came mainly from the south. In this scenario, one would expect a close correlation between the clay mineral distribution and other sediment components, such as the heavy minerals, which is not evident (Polozek & Ehrmann, this volume).

A third possibility is that sedimentation at CRP-1 was not controlled by grounded or floating ice masses, but by icebergs of various origin drifting over the site. During deposition of the lower part of the core, icebergs mainly calved from mountain glaciers in the west, but some icebergs came from the south. During deposition of the upper part of the core, icebergs came mainly from the south, but some icebergs originated in the west. However, also in this case one would expect a correlation between the distribution patterns of diagnostic clay and heavy mineral assemblages: this, too, is not evident.

Yet another possibility is that smectite has not been transported by ice but by ocean currents coming from the south. This scenario would allow a permanent ice discharge through the Transantarctic Mountains, which is also indicated by the homogeneous composition of the gravel clasts (Talarico & Sandroni, this volume). Smectite concentrations of around 20% are dominant in the lower part of the core, and this could represent the background level of smectite transport by suspension. At certain time intervals within the late Early Miocene and the Quaternary, smectite concentrations increased dramatically to 60-90%, possibly because of enhanced transport, or because of enhanced volcanic activity in the south. One problem is that at least two of the smectite maxima correlate with an enhanced input of sand-sized volcanic debris (Smellie, this volume), which probably was not transported by currents but by ice, or which represents volcanic airfalls.

Lower Miocene sediments have been drilled not only at CRP-1, but also at CIROS-1 and MSSTS-1 in the southern McMurdo Sound (Fig. 1). About 35 m have been recovered at each of those sites, and the sediments had an age of c. 23.8-21.8 Ma. CIROS-1 and MSSTS-1 have been correlated on the basis of the percentage distribution of smectite (Ehrmann, 1998). The lower part of the Miocene intervals there is characterized by relatively low smectite concentrations, whereas the upper part in each case contains c. 70-80% smectite. The concentration change occurred at c. 23.3 Ma. The Miocene of the CRP-1 core has been dated to c. 17.5-22.5 Ma (Cape Roberts Science Team, 1998). Dating of the lowermost sediments is uncertain. Because the lower CRP-1 sediments have low smectite concentrations, these sediments are probably younger than the Miocene sediments of CIROS-1 and MSSTS-1, i.e. younger than c. 21.8 Ma.

CONCLUSIONS

The study of clay mineral assemblages in the CRP-1 drillcore has demonstrated the significance of clay mineral assemblages for reconstructing the source areas of the sediments deposited off Cape Roberts. In the lower part of the core, the dominance of illite and chlorite over smectite clearly indicates that the principal source was in the Transantarctic Mountains or on the East Antarctic craton beyond the Transantarctic Mountains. The assemblage is quite uniform from the bottom of the hole up to c. 70 mbsf, indicating relatively stable conditions in the hinterland and relatively constant erosion and transport of debris by glaciers.

In contrast, the upper part of the core is characterized by strong fluctuations in the composition of the clay fraction. Three intervals with high smectite concentrations, but low illite and chlorite contents, occur at 59, 45 and 33 mbsf. During these intervals the clay fraction was provided mainly by the volcanic rocks that form the McMurdo Volcanic Group in the region of the present-day Ross Ice Shelf. Probably, hydrovolcanic eruptions were responsible for the generation of high amounts of smectite. However, the presence of illite and chlorite, as well as the composition of the gravel and sand fraction of the sediments, demand an additional source in the Transantarctic Mountains.

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