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Terra Antartica
2001, 8(3), 275-280

Weathering Rinds as Palaeoenvironmental Indicators: Evidence from the Cape Roberts Drill Core (CRP-3), Victoria Land Basin, Antarctica

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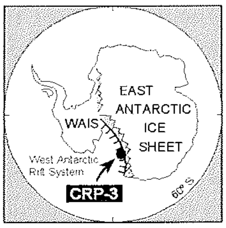
Received 26 October 2000; *accepted in revised form* 10 October 2001

Abstract - XRD analysis of weathering rinds on ocean-deposited ice rafted clasts provide a snapshot of palaeo-terrestrial conditions prevailing at the time of rind formation. Investigation of weathering rinds found on some CRP-3 clasts indicate environmental conditions conducive to the formation of expanding clays, mostly smectites. Although sampling for clasts with weathering rinds was limited, those obtained for the 272 to 300 and 480 to 561 mbsf (metres below sea level) regions show rinds commensurate with relatively wet and warm terrestrial conditions that would have been conducive to enhanced chemical weathering. The occurrence of clasts with weathering rinds within those parts of the core substantiate the palaeoenvironmental reconstructions of other investigators in the Cape Roberts Project.



INTRODUCTION

A pilot study undertaken on the CIROS-1 (Cenozoic Investigations of the Ross Sea) drillcore examined the feasibility of using X-ray diffraction (XRD) analysis of weathering rinds on ice rafted debris (IRD) as a proxy for former terrestrial environmental conditions (Hall and Bühmann, 1989). Rind analysis is based upon the premise that the clay mineralogy/chemistry of the weathering rind is developed under the terrestrial weathering regime and then preserved during subsequent glacial transport and off-shore deposition, it provides a proxy "snapshot" of environmental conditions during the time of rind development. Results from the initial study (Hall and Bühmann, 1989) were able to demonstrate the viability of this approach with, for CIROS-1, the identification of cold, wet subaerial periods with podsolized soils forming under forest or scrubland. An adjunct to the weathering rind analysis used on CIROS-1, but not undertaken on CRP-3, was that of recording clast weathering fluctuations through the core coupled with how those varied as a function of clast lithology. Based upon both the degree of clast weathering and weathering rind analysis, the CIROS-1 data were able to show that rind alteration did not occur after deposition, and the same assumption is used in the interpretation of the CRP-3 rinds.

Weathering features have, for a long time, been used to date Quaternary deposits (see Brookes, 1995 for a discussion), but these have generally been simple visual observations or field techniques. Weathering rind development has also been used to help date Quaternary deposits and, in so doing, have produced indirect evidence of environmental conditions (*e.g.* Colman and Pierce, 1981; Chinn, 1981). The technique, as applied here is, though, a new one. Nevertheless, it has a good scientific foundation. Essentially it applies the same premise as the use of palaeosols for the determination of palaeo-environments (*e.g.* the use of palaeopodsols to prove the presence of former forests by Bryson, et al., 1965); the initiation of present-day pedogenesis in Antarctica as evidenced by chemical weathering (*e.g.* Balke, 1988) uses this same basic foundation. Elsewhere, particularly in hot desert studies, crusts and varnishes are used to determine palaeoenvironmental conditions (*e.g.* Watson and Nash, 1997). Thus, despite the new approach, the principles are founded on those applied elsewhere, particularly with respect to the use of palaeosols.

Analysis of IRD weathering rinds, where no post-depositional change has taken place, should have every expectation of offering indications of former terrestrial environments. What is unknown is time: time *for* formation (a reflection of the degree of warmth and/or moisture) or the actual time *of* formation (as the IRD may be subject to a substantial transport period). Despite these limitations, conditions are otherwise relatively "ideal". Clast transport by glaciers, largely in a subsurface situation when clasts are passively received by the glacier within the accumulation zone, means that ambient temperature and moisture conditions severely limited any alteration or rind formation - chemical weathering being extremely limited if at all active in the

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englacial situation. Thus, the character of the weathering rind must reflect the nature of the terrestrial environment *prior* to its incorporation within the glacier that transported it to its oceanic depositional situation. In the case here, large components of the glacier, if not the whole glacier, are presumed to be cold-based. With the clear foundation that chemical alteration of the clast is going to be limited by availability of water and the presence of positive temperatures, any englacial or subglacial transport is going to be severely inhibiting with respect to possible chemical weathering. Even with a warm-based glacier, englacial temperatures will still inhibit chemical weathering. In this latter case, certainly the potential arises for chemical weathering at the glacier base but this must be very slow due, again, to subglacial temperatures. While supraglacial debris *could* be subject to chemical weathering as rock thermal conditions may be conducive for part of the summer, nevertheless, water would still help limit this and rates would, of necessity be very slow. Thus, although in-transport weathering has to be considered, attributes would suggest that here it is not a significant factor and may play no role whatsoever.

The possibility of *post*-depositional weathering must be considered. However, the argument applied here is the same as that in Hall and Bühmann (1989), for which more material were available, namely the absence of weathering rinds on all clasts. If post-depositional weathering occurred then it should be expected that all clasts would show some sign of weathering. This was not the case in the CIROS core and appears not to be the case in the CRP-3 core. That not all transported clasts should show weathering *is* to be expected as they will comprise a mix of surficial weathered debris mixed with sub-surface (eroded) non-weathered debris. This argument also helps further justify that in-transport weathering was negligible.

Although smectite was recognised in CRP-2/2A (Cape Roberts Science Team, 1999, p. 95) and identified as being representative of "...hydrolysis under climatic conditions between warm-humid and cold-dry, in environments characterized by very slow movement of water.." the interpretation of the results (Cape Roberts Science Team, 1999, p. 96) lacks consideration of the *in situ* weathering rinds on clasts within the core and the information that it could provide regarding terrestrial conditions. This argument can be justified by consideration of the core matrix clay mineralogy (Cape Roberts Science Team, 1999) that states smectite concentrations in CIROS-1 at *c*.290-320 mbsf (unit 12) may be a result of several causes, one of which may be "..warmer and more humid conditions...resulting in more intense chemical weathering..". This is exactly the region (unit 12) where Hall and Bühmann (1989) recorded smectite concentrations in the weathering rinds of IRD (also for unit 22 where the fine fraction analysis also showed a transition from smectite-rich to illite-rich conditions). Unfortunately, the evaluation of the smectite in the core fine fraction of CIROS-1 reported in the review by Cape Roberts Science Team (1999, p. 96) takes no cognizance of the findings by Hall and Bühmann (1989), which argued for the warmer, moister conditions, and how those data may have helped resolve the clay mineralogy for the fine fraction.

In the clay mineral analysis of the CRP-1 core (Ehrmann, 1998, p. 617), it is argued that although smectite is often a result of chemical weathering under warm, more humid conditions, because of the "... 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". This does not have to be the case. The presence of glaciers or ice caps within an area is not an inhibitor (unless of course all the rock is covered) for, as is the case in the present-day Alaska pan handle, there is a substantial ice cover coupled with extensive forest growth and yet, within the surrounding ice-free areas, the *in situ* development of clay minerals occurs. Despite the cold air temperatures within the Antarctic, rock temperatures are substantially above zero and do not, in the summer, prove a limitation on the potential for chemical weathering. Rather, as Balke et al. (1991) have shown for the Antarctic, the main limitation on chemical weathering is not temperature but rather the availability of moisture. As the units for which smectite is identified appear (from the core interpretations) to be ones with enhanced moisture availability, there is no reason why clay minerals could not be produced, given sufficient time, in weathering rinds on rock exposures (later to be ground down by glacial action to help provide the fines). Certainly research has shown that given moisture then Antarctic summer *rock* temperatures (*i.e.* as opposed to air temperatures)are conducive to chemical weathering (see Meiklejohn and Hall, 1997 for a brief review). Thus, the principle that weathering rinds on IRD surviving glacial transport and deposition in off-shore sediments can, particularly in conjunction with the clay mineral analysis of the fine fraction, offers a valuable insight into palaeo-terrestrial conditions.

In summary, there appears to be justification for the analysis and interpretation of weathering rinds and that these data, if integrated with those for the clay mineralogy of the fine fraction, would be a valuable adjunct in the understanding of former terrestrial conditions. Thus, with this premise the preliminary findings are reported here. Once the clay mineralogy for the core and the palaeoenvironmental reconstructions based on the sedimentological studies are available, the rind information may be refined.

SITE

Cape Roberts Project drill core 3 (CRP-3) was obtained from a sea-floor high about 12 km off-shore from Cape Roberts at 77.0106°S, 163.6404°E in western McMurdo Sound. The core was drilled to a depth of 939 m and had a 97% recovery. Details of the core division and reconstructed depositional environments are provided by Powell et al. (this volume).

TECHNIQUE

Clasts that appeared to show signs of weathering to be used in XRD analysis were collected from the core. Samples of rock were removed from the centre of each clast (here considered to be "unweathered") and from the edges where the rinds occurred (the "weathered" component) using a 0.5 mm drill bit operated at 20,000 rpm. Each sample was then ground to <50 :m in diameter for XRD analysis. This was conducted on the samples mounted on glass-slides using acetone. The powder mount was scanned from 2 to 65° at ambient conditions at a step size of 0.02° and a collection period of 5 - 10 seconds per step. Samples were also solvated with glycerol to determine the presence of expanding clay minerals. Identification of the minerals in the samples was based on the following criteria: (1) quartz - 0.425, 0.334, 0.245, 0.228 and 0.182 nm reflections, (2) feldspars - 0.635, 0.404-0.420, 0.315-0.325 nm reflections, (3) amphiboles - 0.826, 0.324, 0.304 and 0.270 nm reflections. Identification of clay minerals was based on the following: Kaolinite and chlorite were recognised by the reflections at 0.71 nm and 1.4 nm respectively (Barnhisel and Bertsch, 1989) while mica was identified from the 1.0 nm reflection. Expanding 2:1 type of clays were recognised by the reflection at around 1.7 nm in glycerol-solvated samples.

RESULTS AND DISCUSSION

The absence of striations on the tested clasts suggests that they were either not under a temperate glacier or were not in a subglacial position. Rates of chemical weathering of clasts (*e.g.* Colman and Pierce, 1981) indicate the observed rind thicknesses (*c.* 0.2 to 2.0 mm) would, under relatively wet and warm conditions (see Colman and Pierce, 1981 and Cernohouz and Solc, 1966) take between 30 000 and 180 000 years to form. Here conditions may not have been quite as wet as those used in the derivation of the above weathering rates and so such time spans would argue well for development under terrestrial weathering conditions. Thus, even if clasts with striations were found in the vicinity of those used here, the required time spans would argue against any significant in-transport weathering.

Clay mineralogy of the fine fraction from the cores was undertaken in CRP-1 and CRP-2/2A (Ehrmann, 1998; Cape Roberts Science Team, 1999, p. 94) and CRP-3 (Marinoni and Setti, this volume) with the aim of this information providing some palaeoenvironmental reconstructive evidence. However, the relationship between those studies and the detail that would be available from the weathered clasts remains unclear, partly because the interpretation of the fine fraction mineralogy lacks any obvious terrestrial point of reference to help validate the explanation. The smectite may be due to a period of increased terrestrial chemical weathering or it may reflect a change in source area for the sediments (and hence the chemistry).

Figure 1 shows the preliminary results. In figure 1, clasts are identified by the depths (mbsf) at which they were collected. Note, of the samples available not all show weathering rinds. In terms of mineral composition of the core, clasts could be classified into two groups of samples (Fig. 1):

Group 1 = clasts at depths 272.11-272.15 (our sample #2), 290.21-290.27 (#3), 297.79-297.83 (#4), 300.0-300.05 (#5), 480.69-480.74 (#11), 537.51-537.54 (#13), and 561.75-561.80 (#14).

Group 2 = clasts at depths 305.71-305.72 (#6), 306.55-306.57 (#7) and 478.68-478.70 (#9).

In Group 1 the samples from the centre of the clasts contain a high amount of weatherable minerals such as feldspars and amphiboles as well as quartz and clay minerals (Figs. 1A, C, E, F, G, H and J). In clast no. 5 (Fig. 1G), albite (Na-rich) is estimated to be > 90% using the separation of –132 and 131 x-ray reflections (Smith 1956 in Huang, 1986). Unweathered clasts in Group 1 show the presence of 1.2 nm reflection indicating the occurrence of 2:1 expanding clays in the presence of micacaeous minerals. The x-ray reflection for expanding clays is dependent upon cation saturation, organic solvent solvation and relative humidity such that x-ray reflections could vary 1.2 to >1.5 nm (Douglas, 1986). The samples shown in figure 2 are not saturated with specific cation but are solvated only with glycerol. Thus, depending on which species is present (*e.g.* montmorillonite, beidellite or nontronite), smectite expands at glycerol solvation from 1.5 to 1.8 nm. Vermiculite normally does not expand beyond 1.4 nm upon glycerol solvation but does expand to 1.6 nm upon ethylene glycol solvation. Also, in terms of surface charge, vermiculite has a higher charge (>0.65 charge per formula unit) than smectite (<0.65 charge per formula unit).

Figure 1 shows the minimal differences between the unweathered core and the weathered rind. For example, figure 1E shows similar XRD patterns between the unweathered core and the weathered margin of clast no. 4. However, after glycerol solvation, the presence of higher amounts of 2:1 expanding clays (probably vermiculite and smectite) in weathered rind is evident from the shift of the diffraction peak from 1.2 nm to 1.42 and even 1.85 nm regions (Fig. 2A). Clast no. 5 (300.00-300-05 mbsf) also shows XRD patterns very similar to clast no. 4. In figure 1A, untreated clast no. 2 shows

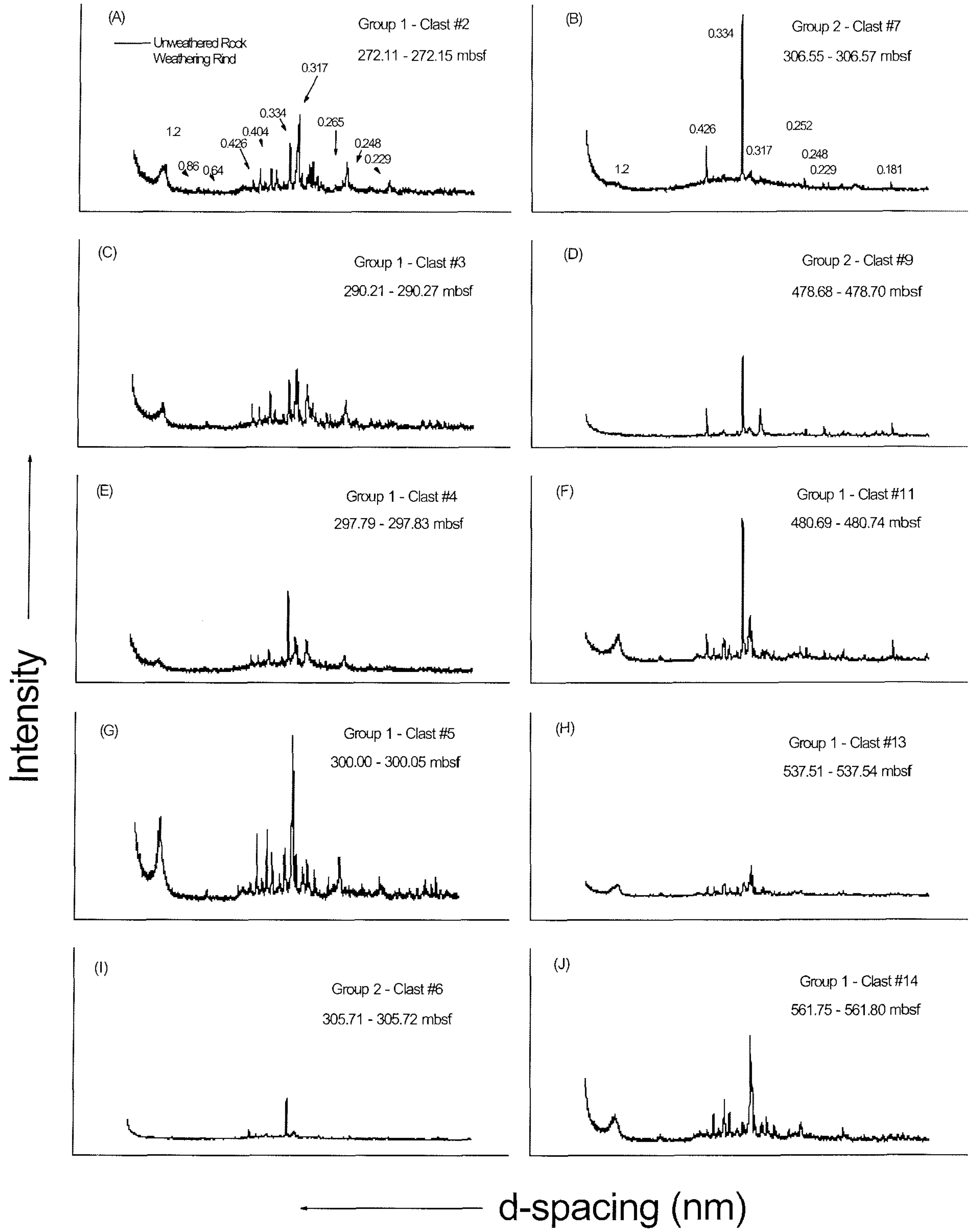

Fig. 1 - Diffractograms for the 10 clasts analyzed using x-ray diffraction. Group 1 - Clast Nos. 2 (A), 3 (C), 4 (E), 5 (G), 11 (F), 13 (H), 14 (J); Group 2 - Clast Nos. 7 (B), 9 (D), 6 (I).

similar XRD patterns to untreated clast no. 4 (Fig. 1E) indicating similarity in mineralogy. However, figure 2B does not have the reflections at higher d-spacings at 1.42 and 1.85 nm that are present in clast no. 4 probably indicative of the differences in weathering environments of formation.

Generally, smectite does not exist in sediments buried deeper than 4 km because Mg, Fe, Al and/or Mg are incorporated in smectite to form mica or chlorite (Borchardt 1986). In terrestrial environment, one of the general pathways related to the origin of 2:1 expanding clays is the removal of potassium from

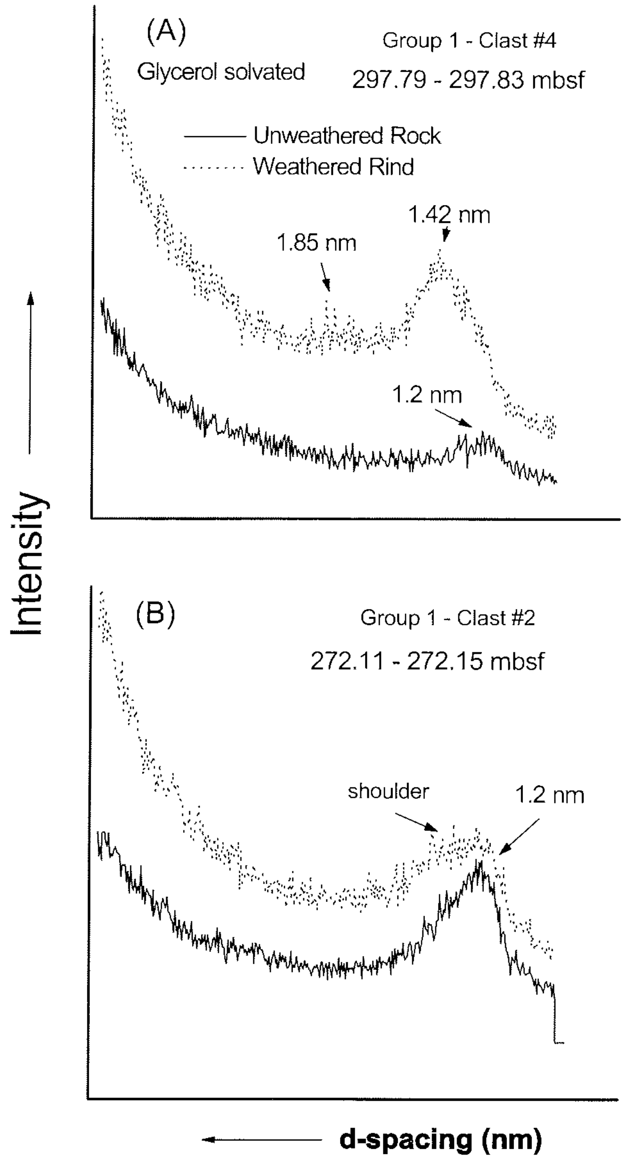

Fig. 2 - XRD diffractograms of glycerol solvated samples of (A) Group 1 - Clast no. 4 and (B) Group 1 - Clast no. 2. XRD reflections at 1.42 to 1.85 nm show the presence of 2:1 expanding clays in the weathering rind of clast no. 4.

mica or Mg from chlorite in leaching (or humid) environment (Borchardt, 1986; Douglas, 1986). Because our samples were collected from sediments shallower than 4 km, it would appear that the presence of vermiculite and smectite in the clasts of Group 1, were probably formed as a result of terrestrial weathering processes in moist (or humid) environment. The lower intensity of the x-ray reflections at 1.42 and 1.85 nm for some clasts in Group 1 may indicate source areas of less humid environment. In other words, water is less available to remove K from mica or chlorite. Caution must be observed in interpreting the relationships of smectite and moisture conditions because, under restricted environment, smectites may precipitate from soil solution in almost any parent material (Borchardt 1986).

Group 2 clasts have their centres dominated by quartz (likely igneous (primary) derivation as these clasts are from tholeiitic dolerites). Amphiboles and other weatherable minerals are not apparent from x-ray diffractograms; if present, they are in minor quantities. Generally, where weathering rinds are present in this group, no expanding clays (*e.g.* smectite) are apparent. This could be due to low amounts of feldspars, amphiboles and possibly mica or chlorite as well as the moisture conditions. Removal of potassium from mica and Mg from chlorite are major sources of smectite and vermiculite formation in soils. Thus, those clasts in Group 2 may have originated from areas that are too dry to limit the neoformation of smectite or too wet where the removal of Mg is so intense preventing the formation of smectite (Borchardt 1986).

Although the clast sampling for weathering rind analysis lacks any systematic basis and is not tied directly to other observations (*e.g.* lithological changes or striated clasts) it can, nevertheless, offer some ancillary information in support of other hypotheses. For example, Atkins (this volume) suggests that clast features and fabrics, in the upper 330 mbsf of the core are consistent with the presence of nearby ice experiencing repeated advance and retreat. Powell et al. (this volume) also suggested that the upper 400 mbsf represent shallow, marine, glacially-influenced sediments deposited during several glacial fluctuations. The lithofacies interpretations indicate that a substantial amount of meltwater was present and this, taken with the high rates of sediment discharge, suggest the presence of a warmer climate than at present (Powell et al., this volume). Raine and Askin (this volume), from palynological information, suggest the presence of *Nothofagus* and podocarpus conifers and, at some sites, there may have been low scrub or closed forest and even possibly wetland vegetation. Taken together, this information suggests an environment conducive to chemical weathering in which smectite weathering rinds could occur. The limiting factor for chemical weathering in the Antarctic environment is water (Balke et al., 1991), but the conditions, glacial outwash and possible wetland vegetation, coupled with warmer conditions that would give a longer-than-present summer weathering period, would have been conducive to bedrock/clast weathering and smectite production. Thus, the occurrence of clasts with weathering rinds and the presence of smectite at 272-300 mbsf depths would be in accord with a more conducive chemical weathering environment. The corollary to all this is that it would have been surprising *not* to have found weathered clasts at these depths and so their presence supports such a palaeoenvironmental interpretation.

The finding of weathering rinds on clasts at depths of *c.* 480 and 537 to 561 mbsf also suggests conditions suitable to chemical weathering in the terrestrial environment. Analysis of depositional environments for these depths (Powell et al.,this volume) suggests deltaic conditions with, possibly, all valleys not being completely ice-filled. It could be envisaged that chemical weathering was viable within valleys having ice-free rock exposures and meltwater available. Palynological evidence for substantial vegetation is lacking although it was conceded that some may have been present (Raine and Askin,this volume). Thus, some localized weathering of rock, constrained by water availability, appears possible. Certainly the rinds observed would be consistent with a palaeoenvironmental reconstruction comprising "...cyclopels from highly sediment-charged glacial streams.." (Cape Roberts Science Team, 1999, p.66) necessitating warmer, melting conditions conducive to smectite production as found in the CIROS-1 investigation (Hall and Bühmann, 1989). Detailed information, such as "Lithology, Facets and Surface Features" for CRP-3, as were undertaken in CRP-2/2A, will, ultimately, provide adjunct information that may help tease-out more detail regarding the significance of the rind information found here.

CONCLUSION

As a technique, our work on CRP-3 samples further demonstrates the validity of using XRD examination of weathering rinds on IRD as a proxy for palaeo-terrestrial environmental conditions. However, the limited availability of clasts from CRP-3 coupled with the absence of weathering rind evaluation for the whole core limits the applicability with respect to this study. From the available information, it appears that environmental conditions suitable for the development of 2:1 expanding clays, particularly smectites, occurred in some units (*e.g.* unit 7.5) and, at that time, conditions may have been relatively mild and wet. Recognizing that the limiting condition for chemical weathering on the Antarctic continent is largely moisture (rather than temperature), the presence of such weathering rinds is indicative of warmer, and hence moister, conditions. Had clasts with weathering rinds *not* been found during the reconstructed warmer and wetter times then this would have been worrisome given the palaeoenvironmental interpretation of other CRP-3 investigations. The presence of weathering rinds helps substantiate those palaeoenvironmental reconstructions.

ACKNOWLEDGEMENTS - We are grateful to Frano Talarico for helping to collect CRP-3 clasts for this study. NSERC awards (#185756 for KH and #21027 for JMA) allowed the undertaking of this weathering study.

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