

Geochemical Indicators of Weathering, Cenozoic Palaeoclimates, and Provenance from Fine-Grained Sediments in CRP-2/2A, Victoria Land Basin, Antarctica

L.A. KRISSEK^{1*} & P.R. KYLE²

¹Department of Geological Sciences and Byrd Polar Research Center, The Ohio State University, Columbus, OH 43210 - USA

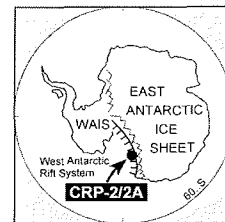
²Department of Earth & Environmental Science, New Mexico Institute of Mining and Technology (N.M. Tech), Socorro, N.M. 87801-4796 - USA

*Corresponding author (krissek@mps.ohio-state.edu)

Received 9 July 1999; accepted in revised form 15 October 1999

Abstract - The CRP-2/2A core, drilled in western McMurdo Sound in October and November 1998, penetrated 624 m of Quaternary, Pliocene, lower Miocene, and Oligocene glacial sediments. The palaeoclimatic record of CRP-2/2A is examined using major element analyses of bulk core samples of fine grained sediments (mudstones and siltstones) and the Chemical Index of Alteration (CIA) of Nesbitt & Young (1982). The CIA is calculated from the relative abundances of Al, K, Ca, and Na oxides, and its magnitude increases as the effects of chemical weathering increase. However, changes in sediment provenance can also affect the CIA, and provenance changes are recorded by shifts in the Al_2O_3/TiO_2 ratios and the Nb contents of these CRP-2/2A mudstones.

Relatively low CIA values (40-50) occur throughout the CRP-2/2A sequence, whereas the Al_2O_3/TiO_2 ratio decreases upsection. The major provenance change is an abrupt onset of McMurdo Volcanic Group detritus at ~300 mbsf and is best characterized by a rapid increase in Nb content in the sediments. This provenance shift is not evident in the CIA record, suggesting that a contribution from the Ferrar Dolerite to the older sediments was replaced by an input of McMurdo Volcanic Group material in the younger sediments. If this is true, then the relatively uniform CIA values indicate relatively consistent palaeoweathering intensities throughout the Oligocene and early Miocene in the areas that supplied sediment to CRP-2/2A.



INTRODUCTION

The Cape Roberts Project is a multinational cooperative drilling project, designed to use sediment cores as the basis for reconstructing the tectonic and climatic histories of the western side of McMurdo Sound and the adjacent portion of East Antarctica for the period from 30 Ma to approximately 100 Ma. The scientific rationale for this work, as well as the technical and logistical details of the project, have been presented by Barrett & Davey (1992), International Steering Committee (1994), Barrett (1997), and Cape Roberts Science Team (1999).

One goal of the Cape Roberts Project is to reconstruct the palaeoclimatic history of the western Ross Sea region, so biological and inorganic indicators of palaeoclimate are being examined by a number of the post-drilling studies discussed in this volume. The objective of this paper is to discuss the record provided by one such indicator, the Chemical Index of Alteration (CIA) of Nesbitt & Young (1982). The CIA is calculated from the major element geochemistry of bulk sediment samples, and was originally proposed as a means to quantify the extent to which sediments have experienced chemical weathering. Because the CIA can be affected by changes in the provenance of the sediment, independent of changes in weathering intensity, the Al_2O_3/TiO_2 ratio and the Nb content are also

considered as independent records of sediment provenance. A similar approach was used by Krissek & Kyle (1998, 1999) to examine the records of palaeoweathering and sediment provenance at CRP-1 and CIROS-1.

In this paper we present an extensive set of major and trace element analyses of over 100 bulk core samples of mudstones and siltstones. The major element analyses are used to examine the stratigraphic record of CIA values in samples from CRP-2/2A. Only minor reference is made to the trace element analyses to examine the sediment provenance and detailed examination of these data will be made in subsequent publications. The CIA values suggest that chemical weathering effects were significantly and consistently low during the Oligocene and early Miocene, as would be expected in a glacially dominated environment. However, the sediment provenance during this time also affected the major element geochemistry and, therefore, the CIAs of these sediments. In particular, sediment supply from McMurdo Volcanic Group introduced material whose unweathered composition produces anomalously low CIAs. As a result, more definitive interpretations of the palaeoweathering history contained in CRP-2/2A will be available only after detailed mixing model studies have been performed to remove the effects of changing sediment provenance.

BACKGROUND OF GEOCHEMICAL INDICATORS USED

The CIA is calculated as

$$\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

where the elemental abundances are expressed as molar proportions, and CaO* represents the CaO contained only in the silicate fraction. The CIA is generally used to provide an indication of the relative abundances of "unweathered" material and chemical weathering products; the "unweathered" materials of particular interest are the feldspars, which are common and contain relatively mobile Ca, Na, and K, whereas the chemical weathering products of particular interest are the Al-rich clays. However, the CIA of a sample can also be affected by the grain size of the sample and by the provenance of the sediment, as discussed in more detail below.

The CIA of a sediment increases as the extent of chemical weathering increases, from values of approximately 50 for "unweathered" feldspar-rich rocks to values near 100 for highly weathered, kaolinite- or gibbsite-rich sediments. CIA values for "average" shales, dominated by illite, range from 70 to 75 (Young & Nesbitt, 1998). The CIA value for a sediment also tends to increase as grain size decreases, because clay minerals are preferentially enriched in the finest grain sizes. As a result, the CIA was originally proposed for use with true shales or "lutites" (Nesbitt & Young, 1982). In a sequence where true shales are rare, such as the section cored at CRP-2/2A, care must be taken to consider the potential effect of grain size variations on stratigraphic trends in the CIA. The provenance effect is particularly important if sediment provenance changed significantly during deposition of a stratigraphic sequence, and if any of the potential sediment sources has an unusual geochemical composition. Such a provenance effect must be considered for CRP-2/2A because potential source rocks include two basic igneous units, the McMurdo Volcanic Group and the Ferrar Dolerite, whose bulk geochemistries produce CIA values lower than the CIAs of unweathered feldspar.

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of a sediment can serve as a preliminary indicator of that sediment's source rock composition (Nesbitt, 1979; Young & Nesbitt, 1998) for two reasons: 1) the ratio varies markedly in primary igneous rocks, from approximately 10 for basalts and gabbros to approximately 47 for granites (LeMaitre, 1976), and 2) Al and Ti are both considered to be relatively immobile under most weathering regimes. Trace element abundances can also serve as valuable indicators of sediment provenance because trace elements are also relatively immobile during weathering, and because trace element abundances can vary significantly between two igneous or metamorphic bodies with relatively similar major element compositions (*e.g.*, two granites can have significantly different trace element compositions). In this study, concentrations of the trace element Nb are used to identify the relative importance of input from the McMurdo Volcanic Group, a potential source rock with elevated Nb contents.

MATERIALS AND METHODS

In this study fine grained samples were analyzed for major and trace elements by x-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) (Tab. 1). Most of the analyzed samples were bulk core collected from the finest grained lithologies (mudstones and siltstones) and taken at approximately 5-m intervals from 17 to 624 msbf. Six of the samples were a split of the <63 μm size fraction remaining after foraminifera processing.

The XRF and INAA analyses were made at New Mexico Tech, using procedures similar to those described by Hallett and Kyle (1993) with some minor modifications. Major elements and S and Cl were analyzed on 104 samples using glass disks formed by fusing 1 gram of sample with 6 grams of a lithium borate flux (35.3% lithium tetraborate, 64.7% lithium metaborate) in a 95%Pt/5%Au crucible at 1100°C. Trace elements were determined on 98 samples by XRF (V, Cr, Ni, Cu, Zn, Ga, As(X), Rb, Sr, Y, Zr, Nb, Pb, Th(X), U(X)) using pressed powder samples (Norrish & Chappell, 1977) and on 63 samples by INAA (Sc, As(I), Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Ta, Th(I), U(I)). A number of elements were measured by both XRF and INAA and showed excellent agreement. For elements As, Th and U both the XRF (X) and INAA (I) are listed (Table 1), because the INAA data are more precise. However, only 63 samples were analyzed by INAA, so the XRF data are more complete. The XRF was calibrated using a wide variety of well-analyzed rock standards. Several rock standards were used to monitor the analytical precision, and proficiency tests administered by the International Association of Geoanalysts provide data on the analytical accuracy. For the INAA analyses between 120 and 250 mg of samples was sealed in polypropylene vials and irradiated for 7 to 12 hours at the Nuclear Science Center, Texas A&M University. The activated samples were counted at New Mexico Tech using two high purity Ge detectors (25% efficient, 1.85keV resolution at 1332 keV) at various intervals following an initial 5 days of decay. National Institute of Standards and Technology (NIST) fly ash standard reference material (SRM) 1633a was used to calibrate the INAA data (Hallett and Kyle, 1993). Various rock standards were run as checks on the accuracy and precision of the INAA data (these data are available on request from P. Kyle).

The primary goal of this paper is to examine the CIA index, so no attempt is made here to examine all of the major and trace element data from CRP-2/2A. All the data are listed in Table 1 so as to be useful to other investigators. The Al_2O_3 , TiO_2 and Nb analyses are used here in a preliminary effort to evaluate the effect of sediment provenance changes on the CIA record from CRP-2/2A.

As a reminder, the CIA is calculated as

$$\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

where the elemental abundances are expressed as molar proportions, and CaO* represents the CaO contained only in the silicate fraction. For these samples, the CaO content of the silicate fraction is assumed to equal the CaO content

of the bulk sample; *i.e.*, biogenic and diagenetic carbonates and biogenic apatite are assumed to contribute little or CaO to the bulk sample. The CaO contributions from biogenic and diagenetic carbonates are judged to be low because "loss-on-ignition" (LOI) values for this sample set are relatively low and fairly uniform between samples (Tab. 1). Samples analyzed by Dietrich *et al.* (this vol.) contain up to 3% carbonate above 300 mbsf and up to 8–13% carbonate below 300 mbsf. However, the majority of this carbonate is diagenetic and is distributed very irregularly through the core (as indicated by downhole logging results; Brink *et al.*, this vol.), so the low LOI values remain the best indicators of low CaO contributions from carbonates in this dataset. CaO contents also have been corrected for a contribution from biogenic apatite in some other studies (*e.g.*, Fedo *et al.*, 1995) by assuming that all P_2O_5 is present as biogenic apatite. Such a correction has not been made for the CRP-2/2A samples because the P_2O_5 is uniformly low (<0.2 wt % below 300 mbsf and <0.4 wt % between 0 and 300 mbsf), and because the McMurdo Volcanic Group is a potential source rock and is usually enriched in P_2O_5 . The small variations in P_2O_5 in the upper 300 meters of the core are undoubtedly due to varying amounts of McMurdo Volcanic Group detritus, which is clearly shown by elevated levels of Nb (Tab. 1) and is discussed further below.

Because a detailed age-depth model is not presently available for CRP-2/2A, the CIA, Al_2O_3/TiO_2 and Nb profiles are plotted as a function of subbottom depth (Figs. 1, 2 and 3).

DATA AND RESULTS

The complete data set, the calculated CIAs, and the calculated Al_2O_3/TiO_2 ratios for the 104 samples from CRP-2/2A are presented in table 1.

The stratigraphic profile of CIA values for CRP-2/2A is presented in figure 1. CIAs generally range between 40 and 50. The CIAs decrease slightly upsection, from an average value of 47 for the lower Oligocene/upper Eocene(?) (624–443 mbsf) to average values of 44, 45, and 44 for the Oligocene (443–307 mbsf), upper Oligocene (307–130 mbsf), and lower Miocene (130–28 mbsf), respectively. The range of CIAs also decreases upsection, most notably within the upper Oligocene section.

On first examination, the low CIA values throughout the CRP-2/2A profile suggest that this site consistently received sediment that had undergone little or no chemical weathering during the Oligocene and the early Miocene. This interpreted input of unweathered or weakly weathered material is in agreement with the importance of glaciogenic lithofacies throughout CRP-2/2A. However, the fact that CIA values for CRP-2/2A are consistently less than 50, which is the value cited for unweathered feldspar by Nesbitt & Young (1982), indicates that primary phases with higher original K/Al, Ca/Al, or Na/Al ratios than those found in feldspars must be present. As a result, the possible effects of provenance changes on this profile must be considered, because the upsection decrease in CIAs at CRP-2/2A could be produced either by a decrease

in the amount of weathering or by an increase in the relative importance of material whose low "apparent CIA" is independent of its weathering history.

Roser & Pyne (1989) summarized the representative geochemical compositions of six source rock types thought to have supplied sediment to CIROS-1; because CRP-2/2A and CIROS-1 are located only 70 km apart and are in similar geologic settings, similar source rock types can be expected to have supplied sediment to CRP-2/2A. As a result, the source rock compositions summarized by Roser & Pyne (1989) are used here to examine the potential effects of provenance changes on the CIA record at CRP-2/2A. The six potential source rock types are: 1) basement rocks (*e.g.*, granitoids of Ferrar Valley), 2) lower Beacon Supergroup sediments (Weller Coal Measures through the Windy Gully Sandstone), 3) Ferrar Dolerite, 4) McMurdo Volcanic Group basanites, 5) McMurdo Volcanic Group trachybasalts to trachytes, and 6) Lashly Formation sediments. Selected major element oxide abundances for these six source rock types are listed in table 2, together with the resulting CIAs and Al_2O_3/TiO_2 ratios.

The relative importance of these sediment sources to deposition at CRP-2/2A did change from the early Oligocene/late Eocene(?) to the early Miocene, as indicated by the stratigraphic profile of Al_2O_3/TiO_2 ratios (Fig. 2). The Al_2O_3/TiO_2 ratios at CRP-2/2A decrease upsection, averaging 19, 17, 17, and 14 for the lower Oligocene/upper Eocene(?) (624–443 mbsf), Oligocene (443–307 mbsf), upper Oligocene (307–130 mbsf), and lower Miocene (130–28 mbsf) sections, respectively. The Al_2O_3/TiO_2 ratio decreases just below 300 mbsf, and also becomes more variable upsection. Comparing the Al_2O_3/TiO_2 values of the potential source rock types, listed in table 2, to the CRP-2/2A profile indicates that the sediments above ~300 mbsf must contain McMurdo Volcanic Group detritus, which has a low Al_2O_3/TiO_2 ratio. Concentrations of the trace element Nb are an even better indicator of the presence of McMurdo Volcanic Group detritus in the core, and the Nb data (Fig. 3) suggest that such detritus is absent below 300 mbsf. These observations are consistent with provenance shifts that were recognized previously at 350–280 mbsf in the sand fraction, the clast population, and the bulk quartz/feldspar contents of CRP-2/2A (Cape Roberts Science Team, 1999), and that have been defined in more detail by post-drilling studies (heavy mineral assemblages (Polozek, this vol.), lonestone clast type (Talarico *et al.*, this vol.), whole-rock geochemistry (Bellanca *et al.*, this vol.; Armienti *et al.*, this vol.), sand composition (Smellie, this vol.), and fine fraction mineralogy (Ehrmann, this vol.; Neumann & Ehrmann, this vol.)). Taken together, these indicators record a shift from older sediments dominated by Ferrar Dolerite and Beacon Supergroup components to younger sediments derived more from the crystalline basement and the McMurdo Volcanic Group. This upsection shift from Ferrar Dolerite and Beacon Supergroup detritus to crystalline basement input appears to record long-term uplift and erosion of the Transantarctic Mountains, whereas the influx from the McMurdo Volcanic Group was controlled by the timing of McMurdo Volcanic Group activity.

The input of McMurdo Volcanic Group detritus above

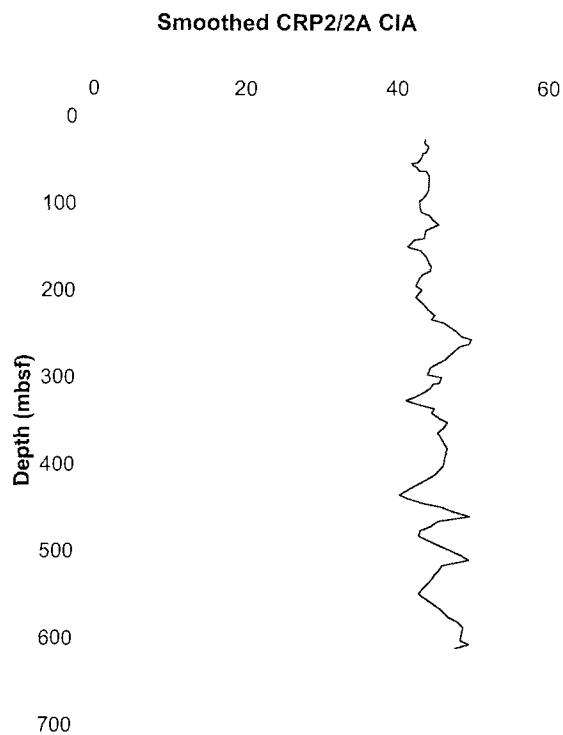


Fig. 1 - CIA profile for CRP-2/2A, smoothed with a 5-point moving average and plotted vs. subbottom depth. Note slight decrease in CIA values upsection.

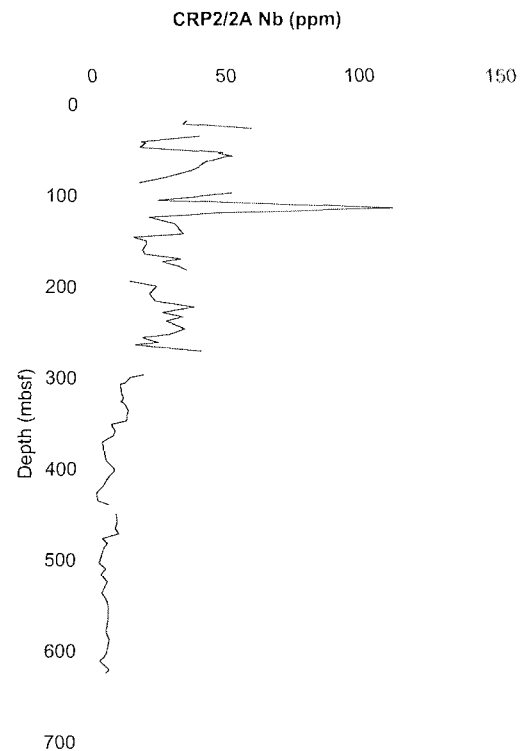


Fig. 3 - Nb concentrations with depth in CRP 2/2A cores. The sharp and rapid increase at ~300 mbsf clearly marks the incoming of McMurdo Volcanic Group detritus.

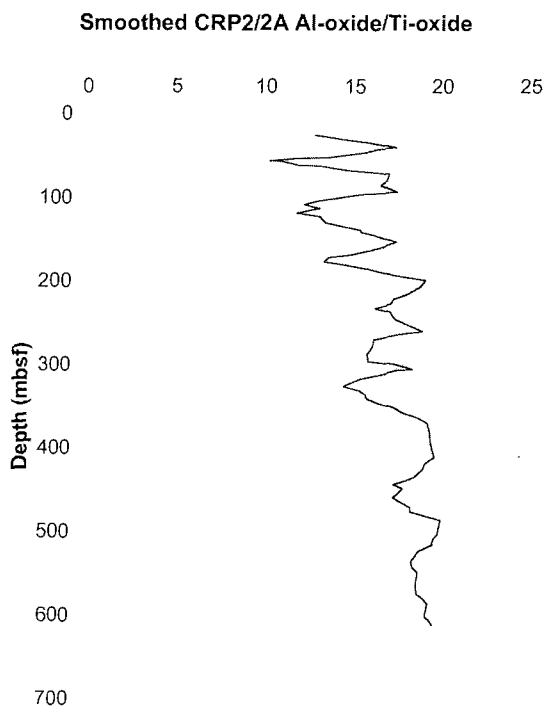


Fig. 2 - Al_2O_3/TiO_2 ratio profile for CRP-2/2A, smoothed with a 5-point moving average and plotted vs. subbottom depth.

300 mbsf might also be expected to affect the CIA profile, but CIA values do not change significantly above that level (Fig. 1). As listed in table 2, the CIA values for unweathered McMurdo Volcanic Group material are low compared to the CIA values for the basement rocks and the Beacon/Lashly sediments. However, the CIA value for

unweathered intermediate McMurdo Volcanic Group material is approximately the same as the CIA for unweathered Ferrar Dolerite. As a result, the replacement of a Ferrar Dolerite component by McMurdo Volcanic Group detritus at ~300 mbsf would lower the Al_2O_3/TiO_2 ratio and increase the Nb contents without producing a significant CIA decrease. Testing this hypothesis will require more detailed compositional modeling to remove the overprint of provenance changes from the CIA record; if this hypothesis is correct, however, then the relatively uniform CIA profile indicates relatively consistent palaeoweathering intensities throughout the Oligocene and the Early Miocene in the sediment sources for CRP-2/2A. In contrast, clay mineral data (Ehrmann, this vol.; Setti et al., this vol.) have been interpreted as showing that enhanced chemical weathering influenced the sediments below approximately 490 mbsf in CRP-2/2A. Such inconsistencies in the interpreted palaeoweathering history at CRP-2/2A may result from the preliminary nature of both the geochemical and the clay mineral studies, or may reflect differences in the sensitivities of the various palaeoweathering indicators. Regardless of their cause, these inconsistencies should be examined by additional, more detailed studies.

SUMMARY AND CONCLUSIONS

The major provenance change recorded at CRP-2/2A is a rapid onset of a McMurdo Volcanic Group component above ~300 mbsf. This provenance change is not apparent in the CIA profile, however, which shows relatively uniform values throughout CRP-2/2A. The CIA profile would have been unaffected by this provenance change if

Tab. 2 - Selected geochemical data for CIROS-1 sediment source rocks (from Roser & Pyne, 1989).

Source Rock	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CIA	Al ₂ O ₃ /TiO ₂
Basement	65.25	16.14	0.72	3.88	3.63	3.69	0.17	48.7	22.4
Lower Beacon	89.73	5.7	0.24	0.68	0.2	1.44	0.02	64.6	23.8
Ferrar Dolerite	57.17	15.83	0.83	8.67	2.65	1.28	0.11	42.4	19.1
McMurdo Volcanic Group (basic)	42.69	13.83	3.82	10.78	3.53	1.49	0.86	33.9	3.6
McMurdo Volcanic Group (intermediate)	52.76	19.1	1.73	5.06	7.23	3.86	0.58	43	11
Lashly Formation	77.86	12.7	0.53	1.06	1.72	2.26	0.03	63.7	24

an older supply of Ferrar Dolerite material was replaced by a younger supply derived from intermediate McMurdo Volcanic Group rocks. If this interpretation is correct, then the relatively uniform CIA profile indicates relatively consistent palaeoweathering intensities throughout the Oligocene and early Miocene in the sediment sources for CRP-2/2A. A more detailed interpretation of the palaeoweathering and palaeoclimatic component of the CIA record, however, will only be possible after the overprint of provenance changes has been removed using mixing models and comprehensive trace element analyses.

ACKNOWLEDGEMENTS

Lawrence Kressek was supported by Office of Polar Programs, NSF grant OPP-9527008. Philip Kyle was supported by Office of Polar Programs, NSF grant OPP-9527329. The XRF facility at New Mexico Tech was partially funded by NSF grant EAR-9316467. Irradiation of samples at Texas A&M University was supported by the DOE reactor sharing program. We gratefully acknowledge the efforts of the Cape Roberts Project drillers and core processors, the Antarctica New Zealand support staff at the Cape Roberts camp, and the Antarctic Support Associates personnel at McMurdo Station. Grant Young, Bernhard Diekmann, and Werner Ehrmann provided helpful reviews.

REFERENCES

- Barrett P.J., 1997. *Cape Roberts Project Science Plan*. Antarctic Data Series, no. 20, Victoria University of Wellington, 59 p.
- Barrett P.J. & Davey F.J., 1992. Cape Roberts Project Workshop Report. *Royal Society of New Zealand, Miscellaneous Series*, **23**, 38 p.
- Cape Roberts Science Team, 1999. Initial Report on CRP-2/2A. *Terra Antarctica*, **6**(1/2), 1-173.
- Fedo C.M., Nesbitt H.W. & Young G.M., 1995. Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. *Geology*, **23**, 921-934.
- Hallett R.B., & Kyle P.R. 1993. XRF and INAA determinations of major and trace elements in Geological Survey of Japan igneous and sedimentary rock standards. *Geostandards Newsletter*, **17**, 127-133.
- International Steering Committee, 1994. Cape Roberts Project - coring for Antarctic tectonic and climatic history. *EOS*, **75**(1), 2-3.
- Krissek L.A. & Kyle P.R., 1998. Geochemical indicators of weathering and Cenozoic palaeoclimates in sediments from CRP-1 and CIROS-1, McMurdo Sound, Antarctica. *Terra Antarctica*, **5**(3), 673-680.
- Krissek L.A. & Kyle P.R., 1999. Geochemical indicators of weathering and Cenozoic paleoclimates in sediments from CRP-1, CRP-2/2A, and CIROS-1, McMurdo Sound, Antarctica. *EOS, Trans. Am. Geophysical Union*, xxx.
- LeMaitre R.W., 1976. The chemical variability of some common igneous rocks. *J. Petrology*, **17**, 589-637.
- Nesbitt H.W., 1979. Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature*, **279**, 206-210.
- Nesbitt H.W. & Young G.M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*, **299**, 715-717.
- Norrish K. & Chappell B.W., 1977. X-ray fluorescence spectrometry. In: Zussman J. (ed.), *Physical Methods in Determinative Mineralogy*. 2nd ed. Academic Press, New York, 210-272.
- Roser B.P. & Pyne A.R., 1989. Wholerock geochemistry. In: Barrett P.J. (ed.), *Antarctic Cenozoic History from the CIROS-1 Drillhole, McMurdo Sound, Antarctica, DSIR Bulletin*, **245**, 175-184.
- Young G.M. & Nesbitt H.W., 1998. Processes controlling the distribution of Ti and Al in weathering profiles, siliciclastic sediments and sedimentary rocks. *J. Sed. Research*, **68**(3), 448-455.