

Geochemical Indicators of Weathering and Cenozoic Palaeoclimates in Sediments from CRP-1 and CIROS-1, McMurdo Sound, Antarctica

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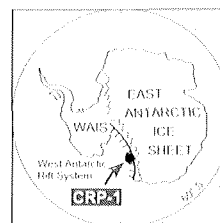
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Abstract - The CRP-1 core penetrated 148 m of Quaternary and lower Miocene glacial sediments. This material complements the Eocene through Miocene section that was cored previously at CIROS-1, 70 km to the south. The palaeoclimatic records of CRP-1 and CIROS-1 have been examined by calculating the Chemical Index of Alteration (CIA) of Nesbitt & Young (1982), using new data for CRP-1 materials and the data of Roser & Pyne (1989) for CIROS-1 mudstones. The CIA is calculated from the relative abundances of Al, K, Ca, and Na, and its magnitude increases as the effects of chemical weathering increase. However, changes in sediment provenance can also affect the CIA, and such changes appear to dominate some parts of the CRP-1 and CIROS-1 records.

Relatively large (47-60) and variable CIA values in the lithologically defined "lower sequence" at CIROS-1 record the influence of chemical weathering during the late Eocene, a result of relatively mild climates and glacial influence, but not glacial dominance. CIA values do decrease upsection through the Eocene, however, suggesting gradual climatic deterioration. The Oligocene and Miocene "upper sequence" at CIROS-1 is characterized by lower (45-50) and more uniform CIA values. This part of the record clearly is affected by an increased contribution of mafic material derived from the McMurdo Volcanic Group, but also may indicate a change in palaeoweathering intensity. CIA values for CRP-1 are uniformly low (<45) and decrease slightly upsection, suggesting glacial dominance, although an increased influx of McMurdo Volcanic Group material is also indicated.



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.

One of the goals 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.

In this paper, the stratigraphic record of CIA values in samples from CRP-1 is presented and discussed. In order to place this record in a longer-term context, the CRP-1 CIA values are compared with CIA values for older sediments recovered from the CIROS-1 drillhole. This combined dataset suggests that chemical weathering effects have been consistently and significantly low in the region since the Oligocene, as would be expected in a glacially

dominated environment. However, changes in sediment provenance during this time have also affected the major element geochemistry and, therefore, the CIAs of these sediments. In particular, an increase in the supply of McMurdo Group Volcanics introduced material whose unweathered composition produces anomalously low CIAs. As a result, more definitive interpretations of the palaeoweathering history contained in CIROS-1 and CRP-1 will be available only after detailed mixing model studies have been performed to remove the effects of changing sediment provenance.

MATERIALS AND METHODS

In this study, 72 CRP-1 samples were analyzed for major and trace elements by x-ray fluorescence (XRF) (Tab. 1). Twenty-five were bulk samples, collected from the finest grained lithologies available and taken at approximately 5 m intervals from 21 to 148 mbsf. The other 57 samples were splits of the bulk fine fraction (<63 µm) generated during processing for foraminifera. These "foram residue" samples were analyzed because they provided a consistently small grain size, which is most appropriate for calculating the CIA.

The XRF analyses were made at New Mexico Tech using a Philips PW2400 spectrometer. For all 72 samples, major elements and selected trace elements (Cr, Ni, Cu,

Tab. 1 - Continued.

| CRPI | Sample | SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MnO | MgO | CaO | Na ₂ O | K ₂ O | P ₂ O ₅ | L.O.I. | SUM | CIA | Al ₂ O ₃ / TiO ₂ | V | Cr | Ni | Cu | Zn | Ga | As | Rb | Sr | Y | Zr | Nb | Mo | Ba | Pb | Th | U |
|--------|--------|------------------|------------------|--------------------------------|--------------------------------|-------|------|------|-------------------|------------------|-------------------------------|--------|--------|-------|--|------|-----|------|------|-----|-----|------|------|-----|------|------|-----|------|------|-----|-----|-----|
| Depth | Type | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | wt % | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| 104.72 | B | 69.67 | 0.57 | 11.42 | 4.11 | 0.073 | 2.35 | 4.03 | 2.80 | 2.58 | 0.15 | 1.67 | 99.42 | 43.7 | 20.00 | 78 | 64 | 22 | 4 | 55 | 14 | 2 | 76 | 270 | 21 | 229 | 21 | 435 | 18 | 8 | 2 | |
| 108.85 | FR | 64.22 | 0.84 | 13.05 | 5.69 | 0.100 | 2.80 | 4.87 | 2.88 | 2.65 | 0.19 | 2.44 | 99.73 | 44.2 | 15.59 | 298 | 79 | 30 | 23 | 79 | | | 298 | 413 | 333 | 413 | 510 | 36 | | | | |
| 109.15 | FR | 62.97 | 0.86 | 12.97 | 5.32 | 0.087 | 2.65 | 4.65 | 2.89 | 2.64 | 0.21 | | 44.7 | 14.99 | | | 73 | 27 | 18 | 76 | | | 279 | | | | 454 | 37 | | | | |
| 110.48 | B | 64.31 | 0.93 | 13.08 | 5.39 | 0.086 | 2.42 | 4.10 | 3.29 | 2.98 | 0.27 | 2.93 | 99.78 | 44.8 | 14.07 | 106 | 62 | 26 | 7 | 81 | 17 | 5 | 94 | 314 | 31 | 309 | 42 | 3 | 525 | 17 | 12 | 2 |
| 111.64 | FR | 57.04 | 1.57 | 13.69 | 7.84 | 0.132 | 2.72 | 5.19 | 3.50 | 2.81 | 0.46 | 4.42 | 99.37 | 42.9 | 8.72 | 138 | 73 | 25 | 25 | 117 | 21 | 7 | 85 | 418 | 42 | 446 | 70 | 3 | 461 | 22 | 13 | 4 |
| 113.26 | FR | 57.28 | 1.68 | 13.87 | 7.17 | 0.130 | 2.67 | 5.43 | 3.59 | 2.76 | 0.48 | 3.71 | 98.77 | 42.5 | 8.28 | 133 | 76 | 24 | 18 | 99 | 21 | 6 | 80 | 436 | 43 | 485 | 75 | 4 | 460 | 19 | 14 | 4 |
| 113.70 | B | 60.68 | 1.37 | 12.89 | 6.51 | 0.114 | 2.45 | 4.62 | 3.62 | 2.73 | 0.38 | 4.12 | 99.48 | 42.7 | 9.40 | 131 | 67 | 23 | 7 | 90 | 20 | 4 | 81 | 376 | 37 | 385 | 65 | 3 | 427 | 14 | 12 | 3 |
| 116.43 | FR | 59.78 | 0.79 | 14.19 | 6.70 | 0.079 | 3.00 | 3.94 | 2.50 | 2.99 | 0.18 | 4.16 | 98.31 | 49.4 | 17.96 | 139 | 92 | 36 | 50 | 113 | 18 | 6 | 116 | 244 | 29 | 255 | 22 | 2 | 874 | 69 | 14 | 3 |
| 119.15 | FR | 65.48 | 0.70 | 12.42 | 4.89 | 0.083 | 2.64 | 4.70 | 2.68 | 2.48 | 0.19 | 2.29 | 98.55 | 44.3 | 17.82 | 93 | 79 | 28 | 20 | 65 | 15 | 4 | 81 | 271 | 30 | 345 | 24 | 3 | 443 | 24 | 10 | 3 |
| 119.60 | B | 64.95 | 0.69 | 12.66 | 5.04 | 0.084 | 2.77 | 4.49 | 2.90 | 2.79 | 0.18 | 2.68 | 99.23 | 44.2 | 18.43 | 108 | 76 | 26 | 9 | 67 | 17 | 4 | 93 | 271 | 24 | 231 | 24 | 2 | 456 | 18 | 10 | 2 |
| 120.40 | FR | 60.38 | 0.81 | 13.24 | 6.48 | 0.101 | 3.02 | 4.80 | 2.77 | 2.71 | 0.21 | 3.63 | 98.15 | 44.9 | 16.37 | 84 | 84 | 27 | 44 | 94 | | | 266 | | | 262 | | | 465 | 30 | | |
| 123.84 | FR | 62.10 | 0.89 | 13.67 | 5.43 | 0.094 | 3.06 | 5.34 | 2.99 | 2.67 | 0.22 | 2.81 | 99.28 | 43.8 | 15.34 | 117 | 86 | 29 | 31 | 83 | 18 | 7 | 92 | 302 | 29 | 308 | 30 | 3 | 497 | 45 | 11 | 2 |
| 128.20 | FR | 61.39 | 0.85 | 13.69 | 5.84 | 0.098 | 3.07 | 5.23 | 2.91 | 2.93 | 0.22 | 3.14 | 99.37 | 43.9 | 16.16 | 116 | 79 | 31 | 40 | 87 | 17 | 6 | 98 | 309 | 28 | 292 | 29 | 2 | 501 | 51 | 12 | 3 |
| 129.15 | FR | 59.31 | 1.05 | 13.38 | 6.52 | 0.112 | 3.02 | 5.70 | 3.11 | 2.55 | 0.28 | 3.53 | 98.56 | 42.3 | 12.76 | 88 | 88 | 31 | 32 | 84 | | | 331 | | | 297 | | | 483 | 45 | | |
| 129.57 | B | 65.38 | 0.63 | 12.59 | 5.00 | 0.088 | 2.96 | 4.91 | 2.90 | 2.64 | 0.16 | 2.10 | 99.35 | 43.2 | 20.11 | 104 | 77 | 31 | 14 | 68 | 16 | 4 | 86 | 282 | 23 | 229 | 20 | 2 | 481 | 17 | 9 | 2 |
| 131.80 | FR | 60.11 | 0.85 | 13.24 | 5.63 | 0.099 | 3.02 | 5.30 | 2.89 | 2.64 | 0.21 | 2.69 | 96.68 | 43.4 | 15.63 | 80 | 80 | 29 | 21 | 76 | | | 286 | | | 281 | | | 485 | 31 | | |
| 133.94 | FR | 60.11 | 1.19 | 13.71 | 6.25 | 0.107 | 3.02 | 5.70 | 3.14 | 2.38 | 0.29 | 3.26 | 99.36 | 42.8 | 11.49 | 134 | 98 | 33 | 30 | 87 | 18 | 6 | 83 | 352 | 32 | 331 | 40 | 3 | 501 | 48 | 12 | 2 |
| 134.75 | B | 65.64 | 0.64 | 12.42 | 4.95 | 0.086 | 2.88 | 4.78 | 2.89 | 2.61 | 0.16 | 1.99 | 99.05 | 43.3 | 19.50 | 98 | 76 | 29 | 6 | 60 | 15 | 2 | 83 | 277 | 23 | 224 | 20 | 2 | 464 | 20 | 8 | 2 |
| 136.92 | FR | 61.57 | 0.81 | 13.62 | 5.97 | 0.100 | 3.23 | 5.16 | 2.98 | 2.73 | 0.19 | 3.07 | 99.43 | 44.1 | 16.92 | 98 | 85 | 33 | 38 | 85 | | | 284 | | | 282 | | | 484 | 75 | | |
| 141.19 | FR | 62.71 | 0.74 | 13.82 | 5.65 | 0.089 | 3.15 | 4.79 | 2.81 | 2.80 | 0.18 | 3.09 | 99.83 | 45.8 | 18.70 | 114 | 84 | 33 | 36 | 90 | 17 | 5 | 97 | 272 | 26 | 266 | 22 | 2 | 489 | 48 | 11 | 2 |
| 141.80 | FR | 62.72 | 1.02 | 13.65 | 6.43 | 0.097 | 3.12 | 5.16 | 2.89 | 2.67 | 0.27 | 3.35 | 101.37 | 44.5 | 13.37 | 123 | 91 | 31 | 56 | 92 | 17 | 5 | 92 | 401 | 31 | 322 | 33 | 3 | 548 | 10 | 12 | 2 |
| 142.13 | B | 60.71 | 0.98 | 13.53 | 6.83 | 0.096 | 3.22 | 4.73 | 3.15 | 2.98 | 0.26 | 4.10 | 100.59 | 44.3 | 13.78 | 84 | 84 | 30 | 24 | 85 | | | 340 | | | 278 | | | 546 | 13 | | |
| 142.20 | FR | 60.91 | 1.01 | 13.48 | 6.43 | 0.097 | 3.16 | 5.09 | 2.92 | 2.76 | 0.27 | 3.62 | 99.75 | 44.2 | 13.32 | 123 | 85 | 28 | 23 | 83 | 18 | 5 | 95 | 358 | 32 | 309 | 35 | 2 | 537 | 23 | 13 | 2 |
| 142.59 | FR | 57.33 | 1.07 | 14.09 | 7.58 | 0.094 | 3.42 | 4.10 | 3.10 | 3.35 | 0.27 | 5.33 | 99.73 | 46.5 | 13.12 | 84 | 84 | 37 | 63 | 115 | | | 290 | | | 255 | | | 507 | 64 | | |
| 143.55 | B | 59.68 | 0.95 | 13.42 | 6.30 | 0.090 | 2.96 | 4.44 | 3.31 | 3.26 | 0.25 | 3.80 | 98.46 | 44.1 | 14.16 | 118 | 72 | 26 | 16 | 88 | 18 | 5 | 106 | 310 | 31 | 279 | 39 | 3 | 510 | 17 | 13 | 4 |
| 144.60 | FR | 61.15 | 0.91 | 13.87 | 6.56 | 0.096 | 3.04 | 4.76 | 2.79 | 3.07 | 0.24 | | 45.6 | 15.23 | | 76 | 76 | 30 | 49 | 103 | | | 332 | | | 291 | | | 529 | 131 | | |
| 145.92 | FR | 59.24 | 0.98 | 13.56 | 6.54 | 0.095 | 3.12 | 4.72 | 2.92 | 2.98 | 0.27 | 3.84 | 98.27 | 44.9 | 13.78 | 122 | 80 | 30 | 34 | 93 | 19 | 5 | 106 | 323 | 30 | 282 | 38 | 3 | 505 | 41 | 13 | 3 |
| 146.92 | B | 59.17 | 1.03 | 13.36 | 6.58 | 0.092 | 3.08 | 4.45 | 3.32 | 3.19 | 0.27 | 4.16 | 98.69 | 43.0 | 13.01 | 124 | 74 | 26 | 15 | 87 | 18 | 3 | 106 | 327 | 31 | 271 | 38 | 3 | 642 | 19 | 14 | 3 |
| 147.33 | FR | 55.01 | 1.50 | 13.30 | 7.45 | 0.120 | 3.51 | 5.71 | 3.33 | 2.65 | 0.36 | 4.97 | 97.91 | 41.5 | 8.85 | 128 | 128 | 32 | 25 | 101 | | | 367 | | | 374 | | | 486 | 27 | | |
| Mean | | 61.59 | 0.96 | 12.81 | 6.01 | 0.10 | 2.81 | 4.72 | 3.22 | 2.85 | 0.53 | 3.45 | 43.1 | 14.54 | 108 | 78 | 28 | 29 | 88 | 17 | 4 | 87 | 308 | 30 | 326 | 38 | 3 | 482 | 34 | 11 | 3 | |
| Sigma | | 3.8 | 0.3 | 0.0 | 1.1 | 0.0 | 0.5 | 0.7 | 0.6 | 0.3 | 0.8 | 1.1 | 2.1 | 4.1 | 22.9 | 22.7 | 8.2 | 21.3 | 17.7 | 2.7 | 1.5 | 15.6 | 55.4 | 6.7 | 85.0 | 16.8 | 1.3 | 83.5 | 27.1 | 2.5 | 0.7 | |

Zn, Sr, Zr, Ba, Pb) were determined on 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%Pt5%Au crucible at 1 200°C. There was sufficient sample available for 34 samples to allow additional trace elements to be determined on pressed powder samples (Norrish & Chappell, 1977). The XRF was calibrated using a wide variety of well-analyzed rock standards. In-house standards were used to monitor the analytical precision, and proficiency tests administered by the International Association of Geoanalysts provide data on the analytical accuracy.

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-1. Instead, the complete dataset is listed here primarily for use by other workers. The Al-oxide and Ti-oxide data, however, are also used here in a preliminary effort to evaluate the effect of sediment provenance changes on the CIA record from CRP-1.

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 CRP-1 samples, the CaO content of the silicate fraction is assumed to equal the CaO content of the bulk sample; *i.e.*, biogenic carbonate and biogenic apatite are assumed to contribute little or no CaO to the bulk sample. The CaO contribution from biogenic carbonate is judged to be insignificant for two reasons: 1) with one exception, total carbon abundances (carbonate carbon + total organic carbon) measured previously in samples from CRP-1 are 0.6% or less (Cape Roberts Science Team, 1998). The one exception is a carbonate-rich interval at 31.89 - 33.82 mbsf, but that interval has not been sampled for this study of CIAs; and 2) "loss-on-ignition" (LOI) values for this sample set are relatively low (Tab. 1). CaO contents have been corrected for a contribution from biogenic apatite in some other studies (*e.g.*, Fedo *et al.*, 1995) by assuming that all P₂O₅ is present as biogenic apatite. Such a correction has not been made for the CRP-1 samples because high-P volcanics (the McMurdo Volcanic Group) are a potential source rock and may contain P in inorganic forms.

The CIA is generally used to provide an indication of the abundance of "unweathered" original material relative to the abundance of 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-1, 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-1 and CIROS-1 because potential source rocks include two basic igneous units, the McMurdo Group Volcanics and the Ferrar Dolerite, whose bulk geochemistries produce CIA values lower than the CIAs of unweathered feldspar.

CIAs for sediments from CIROS-1 were calculated using the published geochemical data of Roser & Pyne (1989), without correcting for CaO contained in carbonate or biogenic apatite. Only the pertinent data for these samples is reproduced in table 2; the complete dataset is tabulated in Roser & Pyne (1989). Only samples from the CIROS-1 mudstone lithofacies were used, in order to minimize the effects on grain size variations on the calculated CIA values. After the initial CIA calculation, mudstone samples with CaO abundances greater than 5% were deleted from the CIROS-1 dataset, on the assumption that these samples might contain carbonate phases. This assumption could not be evaluated independently because mineral compositions were not provided for these samples.

Because a detailed age-depth model is not presently available for samples from CRP-1, the CIA profile for CRP-1 is plotted as a function of sub-bottom depth. A more detailed age-depth model is available for samples from CIROS-1 (Wilson *et al.*, 1998), but that age-depth model is not used here because of the limitations on age assignments at CRP-1. Instead, the CIROS-1 CIAs are plotted in two ways: first, as a function of sub-bottom depth at CIROS-1, and second, on a simple cumulative depth section constructed by placing the base of CRP-1 at the top of CIROS-1. This cumulative depth section places the CIROS-1 and CRP-1 data in the proper stratigraphic order, even if the absolute positions of samples within the overall stratigraphic section are incorrect.

DATA AND RESULTS

The complete dataset, the calculated CIAs, and the calculated Al-oxide/Ti-oxide ratios for the 72 samples from CRP-1 are presented in table 1. Selected major element abundances (from Roser & Pyne, 1989), LOIs, total elemental abundances, Al-oxide/Ti-oxide ratios, and CIAs for the 50 mudstone samples from CIROS-1 are presented in table 2.

In order to assess the possible effect of larger grain sizes on the CRP-1 CIA values, the CIAs of bulk samples were compared to the CIAs of nearby "foram residue" samples. Twenty-one pairs of samples were identified in

Tab. 2 - Selected elemental abundances, LOIs, total analysed abundances, CIAs, and Al-oxide/Ti-oxide ratios for mudstone samples from CIROS-1 (data from Roser & Pyne, 1989).

| Depth | SiO ₂ wt% | Al ₂ O ₃ wt% | CaO wt% | Na ₂ O wt% | K ₂ O wt% | TiO ₂ wt% | LOI wt% | Sum wt% | CIA | Al ₂ O ₃ /TiO ₂ |
|--------|----------------------|------------------------------------|---------|-----------------------|----------------------|----------------------|---------|---------|------|--|
| 59.35 | 63.72 | 12.99 | 3.97 | 2.80 | 3.06 | 1.08 | 3.59 | 100.02 | 46.2 | 12.03 |
| 61.56 | 64.17 | 13.06 | 3.74 | 2.45 | 3.13 | 0.88 | 3.61 | 99.73 | 47.9 | 14.84 |
| 64.11 | 65.68 | 13.49 | 3.67 | 3.47 | 3.03 | 0.86 | 2.29 | 99.57 | 46.3 | 15.69 |
| 94.30 | 63.22 | 13.08 | 3.48 | 2.61 | 3.01 | 1.19 | 3.97 | 99.40 | 48.5 | 10.99 |
| 100.46 | 61.47 | 13.44 | 3.89 | 2.85 | 3.43 | 0.97 | 4.52 | 99.43 | 46.5 | 13.86 |
| 110.26 | 63.01 | 13.27 | 4.59 | 2.51 | 3.15 | 0.96 | 3.99 | 99.66 | 45.5 | 13.82 |
| 116.82 | 61.47 | 13.46 | 3.89 | 2.46 | 3.12 | 1.04 | 4.38 | 99.56 | 48.1 | 12.94 |
| 129.92 | 61.42 | 13.52 | 5.62 | 2.86 | 3.09 | 0.88 | 4.17 | 99.38 | 42.5 | 15.36 |
| 173.26 | 64.20 | 12.66 | 5.59 | 1.99 | 2.88 | 0.70 | 4.45 | 100.30 | 43.3 | 18.09 |
| 215.74 | 61.59 | 13.33 | 4.30 | 1.90 | 2.87 | 0.81 | 5.30 | 100.12 | 48.7 | 16.46 |
| 222.91 | 63.00 | 13.68 | 3.65 | 2.19 | 2.88 | 0.69 | 4.86 | 100.16 | 50.6 | 19.83 |
| 224.26 | 60.01 | 12.80 | 5.07 | 1.61 | 2.75 | 0.68 | 6.39 | 99.90 | 46.3 | 18.82 |
| 224.91 | 61.48 | 13.19 | 4.02 | 2.35 | 2.93 | 0.76 | 5.22 | 100.03 | 47.9 | 17.36 |
| 276.43 | 72.21 | 10.93 | 3.51 | 1.19 | 2.35 | 0.62 | 2.84 | 99.58 | 50.1 | 17.63 |
| 296.68 | 70.23 | 11.71 | 2.94 | 1.83 | 2.54 | 0.75 | 3.63 | 99.40 | 51.3 | 15.61 |
| 300.14 | 61.80 | 11.73 | 4.65 | 1.67 | 2.58 | 0.75 | 7.01 | 99.58 | 45.6 | 15.64 |
| 310.07 | 72.48 | 11.43 | 3.12 | 1.97 | 2.54 | 0.54 | 2.93 | 99.58 | 49.5 | 21.17 |
| 390.55 | 68.34 | 10.29 | 5.70 | 1.08 | 2.23 | 0.53 | 4.13 | 99.76 | 41.4 | 19.42 |
| 393.76 | 67.84 | 11.09 | 5.39 | 0.91 | 2.50 | 0.54 | 3.90 | 99.47 | 44.2 | 20.54 |
| 395.35 | 67.72 | 11.41 | 5.00 | 0.79 | 2.51 | 0.53 | 3.91 | 99.68 | 46.5 | 21.53 |
| 418.05 | 68.93 | 11.56 | 4.65 | 0.91 | 2.57 | 0.56 | 3.34 | 99.42 | 47.6 | 20.64 |
| 422.57 | 70.87 | 11.22 | 3.68 | 0.77 | 2.44 | 0.52 | 3.44 | 99.80 | 51.4 | 21.58 |
| 442.20 | 66.44 | 10.27 | 5.95 | 1.01 | 2.88 | 0.51 | 6.59 | 99.85 | 39.7 | 20.14 |
| 454.07 | 71.31 | 10.36 | 2.70 | 1.35 | 2.48 | 0.58 | 3.43 | 99.95 | 51.4 | 17.86 |
| 460.53 | 77.41 | 8.35 | 1.74 | 0.95 | 1.95 | 0.44 | 2.58 | 99.82 | 55.0 | 18.98 |
| 475.56 | 68.97 | 11.06 | 3.46 | 1.81 | 2.66 | 0.56 | 3.24 | 100.21 | 47.7 | 19.75 |
| 494.52 | 69.49 | 11.29 | 3.62 | 0.80 | 2.45 | 0.55 | 3.20 | 99.24 | 51.7 | 20.53 |
| 498.04 | 74.24 | 10.15 | 2.86 | 0.52 | 2.31 | 0.52 | 2.39 | 99.91 | 54.3 | 19.52 |
| 525.52 | 73.14 | 10.37 | 1.26 | 1.52 | 2.46 | 0.55 | 3.36 | 99.65 | 58.2 | 18.85 |
| 541.07 | 65.52 | 11.08 | 3.85 | 1.52 | 2.64 | 0.60 | 8.01 | 99.39 | 47.3 | 18.47 |
| 548.96 | 69.94 | 11.12 | 1.97 | 1.46 | 2.70 | 0.63 | 4.79 | 99.73 | 55.5 | 17.65 |
| 569.45 | 63.81 | 12.21 | 2.53 | 1.93 | 2.92 | 0.72 | 6.05 | 99.18 | 52.8 | 16.96 |
| 573.22 | 65.66 | 11.42 | 3.68 | 1.86 | 2.79 | 0.62 | 5.81 | 99.99 | 47.2 | 18.42 |
| 582.19 | 71.83 | 9.97 | 2.33 | 1.64 | 2.47 | 0.50 | 4.95 | 99.64 | 50.9 | 19.94 |
| 599.44 | 66.86 | 11.34 | 2.76 | 1.55 | 2.83 | 0.62 | 6.12 | 99.32 | 51.6 | 18.29 |
| 615.75 | 64.91 | 12.28 | 2.07 | 1.83 | 2.78 | 0.74 | 5.32 | 99.43 | 55.7 | 16.59 |
| 618.83 | 69.47 | 11.67 | 1.68 | 1.47 | 2.62 | 0.60 | 4.20 | 100.03 | 58.4 | 19.45 |
| 620.03 | 60.09 | 11.56 | 1.58 | 2.31 | 2.73 | 0.63 | 3.94 | 100.15 | 54.6 | 18.35 |
| 634.54 | 67.62 | 11.31 | 3.46 | 1.16 | 2.56 | 0.57 | 4.72 | 99.56 | 50.8 | 19.84 |
| 641.03 | 70.84 | 10.89 | 3.16 | 1.23 | 2.59 | 0.51 | 3.74 | 100.12 | 50.7 | 21.35 |
| 644.66 | 74.14 | 8.83 | 3.00 | 1.40 | 2.08 | 0.43 | 3.63 | 99.47 | 46.9 | 20.53 |
| 655.51 | 65.34 | 12.94 | 3.24 | 1.09 | 2.95 | 0.59 | 4.50 | 99.56 | 54.3 | 21.93 |
| 658.06 | 75.36 | 10.37 | 1.45 | 0.94 | 2.40 | 0.50 | 2.98 | 99.82 | 60.5 | 20.74 |
| 662.75 | 60.59 | 10.95 | 8.31 | 0.84 | 2.41 | 0.52 | 9.29 | 99.39 | 36.4 | 21.06 |
| 674.88 | 66.08 | 13.65 | 1.29 | 1.39 | 3.06 | 0.68 | 5.25 | 100.13 | 63.2 | 20.07 |
| 677.83 | 65.67 | 12.78 | 2.99 | 1.63 | 2.99 | 0.65 | 4.79 | 99.63 | 53.0 | 19.66 |
| 682.10 | 63.27 | 13.74 | 2.60 | 1.48 | 3.45 | 0.68 | 6.02 | 99.04 | 55.8 | 20.21 |
| 685.67 | 70.80 | 10.03 | 2.36 | 0.75 | 2.63 | 0.52 | 5.22 | 99.58 | 54.5 | 19.29 |
| 692.58 | 61.85 | 12.28 | 2.25 | 2.23 | 2.02 | 1.11 | 7.61 | 99.84 | 55.3 | 11.06 |
| 696.98 | 69.97 | 11.78 | 1.67 | 1.68 | 2.52 | 0.57 | 5.74 | 99.03 | 58.0 | 20.67 |

which the bulk sample and the “foram residue” sample were taken within approximately one metre of each other; the linear regression line for these 21 pairs of CIA values had a slope of 0.967 and an r value of 0.97, indicating that the CIA values for the bulk and the “foram residue” samples were essentially equal. This suggests that the CRP-1 CIA values are not affected significantly by the presence of sand-sized or larger grains.

The stratigraphic profile of CIA values for the entire CRP-1 dataset (both bulk samples and “foram residue” samples) is presented in figure 1. The average CIA is 42.4, with a standard deviation of 1.3, and only a few samples have CIAs less than 40 or greater than 45. The CIA profile shows a slight decrease upsection, although without any major stepwise changes.

On first examination, the low CIA values throughout the CRP-1 profile suggest that this site consistently received sediment that had undergone little or no chemical

weathering during the early Miocene and the Quaternary. This interpreted input of unweathered or weakly weathered material is in agreement with the importance of glacial lithofacies throughout CRP-1. However, the fact that CIA values for CRP-1 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-1 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) summarised the representative geochemical compositions of six source terrains thought to have supplied sediment to CIROS-1; because CRP-1 and CIROS-1 are located only 70 km apart and are in

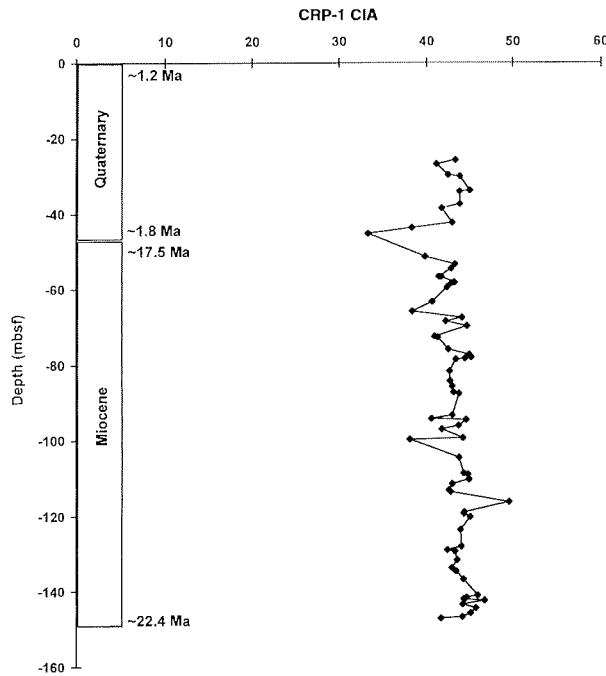


Fig. 1 - CIA values for all samples (bulk and foram residue) from CRP-1, plotted vs sub-bottom depth. General age boundaries are shown for the Quaternary and Miocene sections of the core. Note slight decrease in CIA values upsection.

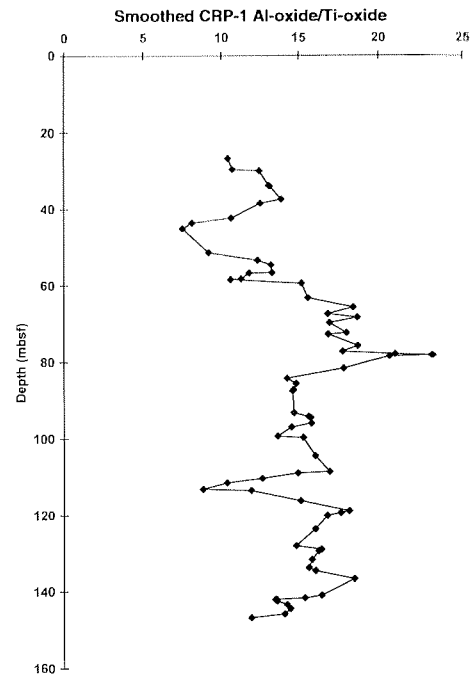


Fig. 2 - Al-oxide/Ti-oxide ratios for all samples from CRP-1, smoothed with a 5-point moving average and plotted vs sub-bottom depth. Note major decrease in the ratio at 62 mbsf, resulting from increased supply of McMurdo Volcanic Group material.

similar geologic settings, similar source terrains can be expected to have supplied sediment to CRP-1. As a result, the source terrain compositions summarised by Roser & Pyne (1989) are used here to examine the potential effects of provenance changes on the CIA record at CRP-1 (and subsequently, at CIROS-1). The six potential source terrains are: 1) basement rocks (*e.g.*, granitoids of Ferrar Valley), 2) lower Beacon Supergroup sediments (Weller Coal Measures through to 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 terrains are listed in table 3, together with the resulting CIAs and Al-oxide/Ti-oxide ratios.

The Al-oxide/Ti-oxide 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. As shown in

figure 2, Al-oxide/Ti-oxide ratios in CRP-1 average approximately 15 below 62 mbsf, and vary from approximately 8 to 24. The Al-oxide/Ti-oxide value decreases markedly at 62 mbsf, and averages approximately 11 above that level. Comparing the Al-oxide/Ti-oxide values of the potential source terrains, listed in table 3, to the CRP-1 profile indicates that the sediments below 62 mbsf could be developed by mixing McMurdo Volcanic Group material with Ferrar Dolerite, basement rocks, or Beacon/Lashly sediments. The only explanation for the Al-oxide/Ti-oxide decrease above 62 mbsf, however, is an increase in the relative contribution of McMurdo Volcanic Group material. This shift in overall sediment provenance at 62 mbsf (approximately 18-19 Ma) has also been recognized in the sand fraction of CRP-1, where the abundance of sand-sized volcanic detritus increases markedly at 62 mbsf (Cape Roberts Science Team, 1998).

The upsection decrease in Al-oxide/Ti-oxide ratios at CRP-1 indicates that McMurdo Volcanic Group material is relatively more abundant above 62 mbsf; this provenance change must also be examined for its possible effects on the CIA profile. As listed in table 3, the CIA values for unweathered McMurdo Volcanic Group material are low

Tab. 3 - Selected geochemical data for CIROS-1 sediment source terrains (from Roser & Pyne, 1989).

| Source Terrain | 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 |

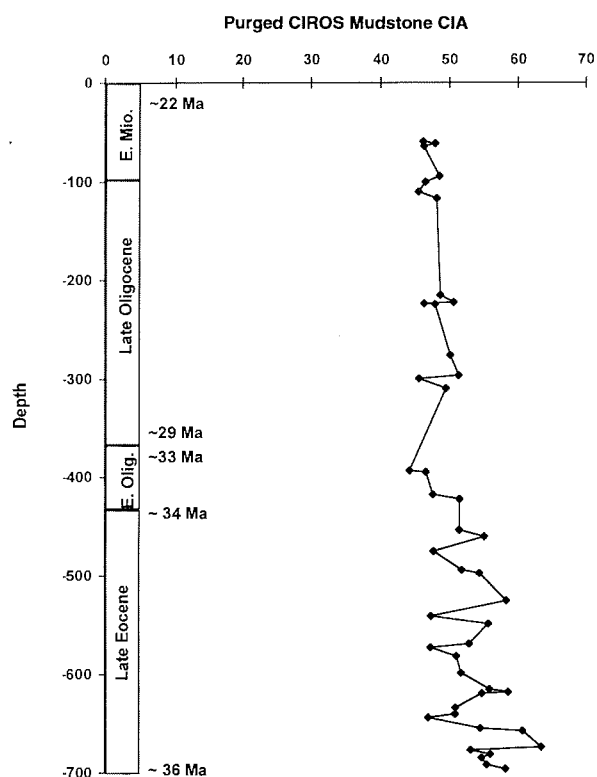


Fig. 3 - CIA values for all mudstone samples from CIROS-1, plotted vs sub-bottom depth. General age boundaries are shown. Note decreasing CIA values and large variability between 700 and ~380 mbsf, and relatively constant CIA values above ~380 mbsf.

compared with the CIA values for the basement rocks and the Beacon/Lashly sediments. As a result, the increased contribution of McMurdo Volcanic Group material above 62 mbsf does appear to be responsible for at least some portion of the upsection decrease in “apparent” CIAs. Detailed compositional modelling, beyond the scope of the present study, will be needed to remove the overprint of provenance changes from the CIA record, so that the true palaeoweathering signal can be extracted and interpreted.

The stratigraphic profile of CIA values for CIROS-1 mudstones is presented in figure 3, plotted as a function of sub-bottom depth at CIROS-1. These CIA values are generally larger and more variable than the CIA values at CRP-1. On first examination, these characteristics suggest that these sediments, on average, experienced a greater amount of chemical weathering than the younger sediments recovered at CRP-1. However, the potential effects of provenance changes must be evaluated for CIROS-1, as they were for CRP-1.

In general, CIAs decrease upsection from the base of CIROS-1 to approximately 380 mbsf, and CIAs are relatively variable in this interval (Fig. 3). Al-oxide/Ti-oxide ratios are relatively uniform through the same interval (Fig. 4), ranging from 19 to 21. These Al-oxide/Ti-oxide values suggest that Ferrar Dolerite, basement, and Beacon/Lashly sources (Tab. 3) supplied most of the sediment to the lower part of CIROS-1, an interpretation consistent with the findings of Hambrey et al. (1989), George (1989), and Roser & Pyne (1989) based on clast composition, sand provenance, and sediment

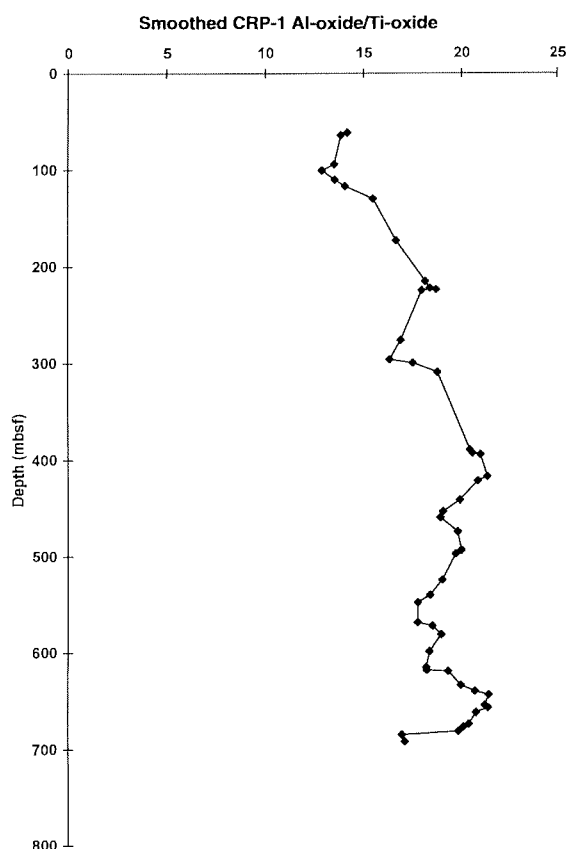


Fig. 4 - Al-oxide/Ti-oxide ratios for all mudstone samples from CIROS-1, smoothed with a 5-point moving average and plotted vs sub-bottom depth. Decreasing ratios above approximately 380 mbsf reflect an increased supply of McMurdo Volcanic Group material.

geochemistry, respectively. Because these Al-oxide/Ti-oxide ratios suggest that sediment provenance remained relatively uniform through this interval, the upsection decrease in CIAs might be interpreted as resulting primarily from a decrease in the importance of chemical weathering through the late Eocene. The variability of CIAs through this interval may indicate that a mixture of chemically weathered and relatively unweathered material was supplied through this time, but may also record more subtle changes in the relative importance of the various sediment sources. More detailed modelling of sediment mixing will be needed to differentiate the provenance and palaeoweathering signals.

CIAs shift to lower and more uniform values above approximately 380 mbsf in CIROS-1 (Fig. 3), whereas Al-oxide/Ti-oxide ratios consistently decrease upsection (Fig. 4). The decrease in the Al-oxide/Ti-oxide ratio indicates an increased input of McMurdo Volcanic Group material, as interpreted previously on the basis of geochemical data (Roser & Pyne, 1989), sand provenance (George, 1989), and clast composition (Hambrey et al., 1989). This increased contribution of McMurdo Volcanic Group material helps to explain the drop in CIA values at about 380 mbsf (Tab. 3). However, the fact that CIAs remain relatively constant above 380 mbsf as the Al-oxide/Ti-oxide ratios continue to decrease upsection suggests that either: 1) chemical weathering effects actually increased through the late Oligocene and early Miocene,

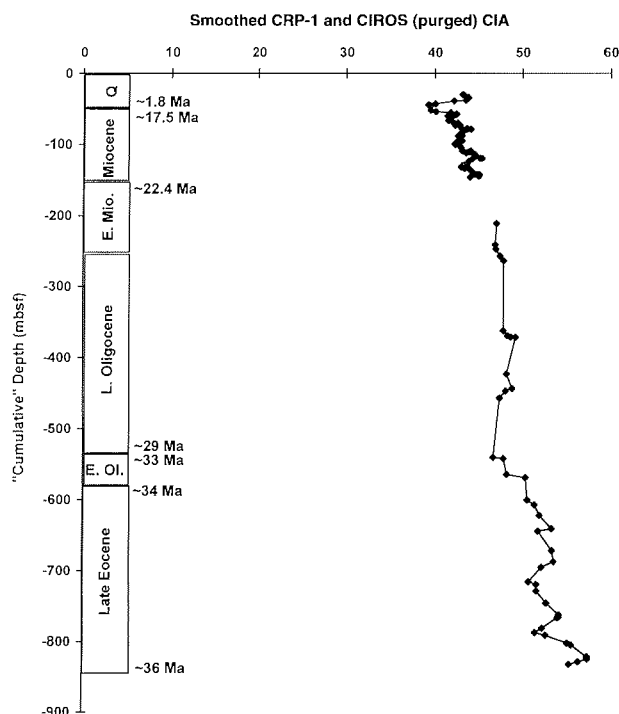


Fig. 5 - Composite CIA profile for samples from CRP-1 and CIROS-1, smoothed with a 5-point moving average. "Cumulative" depth produced by placing CRP-1 on top of CIROS-1. Upsection decreases in CIA values suggest increased effects of physical weathering during the late Eocene and the Miocene, but provenance changes obscure the palaeoweathering signal in the Oligocene and Miocene intervals.

which is inconsistent with lithostratigraphic evidence of continued cooling (Hambrey et al., 1989), or 2) this provenance change cannot be explained by simple two-component mixing. This question will be addressed in future work by more detailed modelling of sediment mixing.

Al-oxide/Ti-oxide values in the upper 300 m of CIROS-1 range from 12 to 19, which are approximately the same as Al-oxide/Ti-oxide values below 62 mbsf in CRP-1. These similar Al-oxide/Ti-oxide ratios suggest relatively similar source area contributions, yet the CIAs of the CRP-1 sediments are consistently and significantly lower than those from the upper 300 m of CIROS-1. This apparent decrease in chemical weathering effects may indicate climatic cooling during the Miocene, but may also be affected by the complexities of multi-component sediment mixing. The resolution of this question will require more detailed modelling of sediment mixing.

SUMMARY AND CONCLUSIONS

The combined CIA profiles for CIROS-1 and CRP-1 are presented in figure 5, plotted on a simple "cumulative" depth scale that places the 148 m recovered at CRP-1 on top of the section recovered at CIROS-1. In addition, both CIA profiles have been smoothed with a 5-point moving average, in order to highlight major trends. The smoothed record clearly shows: 1) the upsection decrease in CIAs through the late Eocene, which appears to result from a decrease in the extent of chemical weathering, 2) the step

to lower and more uniform values for the Oligocene, which carries a signal of provenance changes, perhaps accompanied by changes in the extent of chemical weathering, 3) the decrease from CIROS-1 Miocene sediments to CRP-1 Miocene sediments, which appears to indicate a further decrease in chemical weathering, and 4) the provenance-dominated decrease in the late Miocene. Some of these CIA decreases record increased glacial influence that also can be recognized in sedimentary lithofacies; the most notable is the step from glacial influence to glacial predominance at or near the Eocene/Oligocene boundary. 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.

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