Geochemical Indicators of Weathering, Cenozoic Palaeoclimates, and Provenance in Fine-Grained Sediments from CRP-3, Victoria Land Basin, Antarctica

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Abstract - The CRP-3 core, drilled in western McMurdo Sound in October and November 1999, penetrated 823 m of lower Oligocene (to possibly upper Eocene) glacially influenced sediments. The palaeoclimatic record of CRP-3 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 molar 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, so provenance changes have been evaluated by examining the Al_2O_3/TiO_2 ratios and the Sr and Nb contents of the CRP-3 mudstones.

Relatively low Nb contents (<20 ppm) and relatively high Al_2O_3/TiO_2 ratios (generally ≥15) indicate that little or no McMurdo Volcanic Group detritus was incorporated in these sediments. Instead, these sediments appear to be mixtures of Beacon Supergroup, Ferrar Dolerite, and basement (Granite Harbour Intrusives) components; increased Sr contents suggest that the importance of basement-derived material is greatest above ~200 metres below seafloor (mbsf), whereas Beacon Supergroup and/or Ferrar Dolerite components dominate below that level.

Below ~400 mbsf, the CIA profile is irregular and shows no correlation to the Al_2O_3/TiO_2 record; as a result, the effects of weathering and provenance controls have not yet been interpreted for this part of the CIA profile. Above ~400 mbsf, however, four "cycles" of CIA increase/decrease (each spanning 50-100 m of stratigraphic thickness) are superimposed on a general decrease in CIA values upcore, and Al_2O_3/TiO_2 ratios exhibit a matching pattern of "cycles". This correlation indicates that short-term provenance changes occurred during deposition of the upper half of CRP-3, and affected its CIA record. However, the Al_2O_3/TiO_2 profile does not show any long-term trend above ~400 mbsf, so that the general decrease in CIA values above that level does not appear to be provenance-related. Instead, the general upcore decrease in the importance of chemical weathering above ~400 mbsf may record an episode of climatic deterioration prior to ~31 Ma.
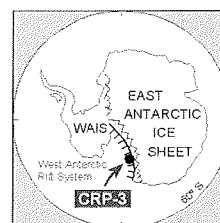
INTRODUCTION

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 (2000).

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 Sr and Nb contents are also considered as independent records of sediment provenance. A similar approach was used by Krissek & Kyle (1998, 2000) to examine the records of palaeoweathering and sediment provenance at CRP-1/CIROS-1 and CRP-2/2A, respectively.

In this paper we present an extensive set of major and trace element analyses of 85 samples of

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mudstones and siltstones. The major element analyses are used to examine the stratigraphic record of CIA values in samples from CRP-3. Only minor reference is made to the trace element analyses to examine the sediment provenance; detailed examination of these data will be made in subsequent publications. The CIA values suggest that chemical weathering effects were relatively low during the early Oligocene (late Eocene?), as would be expected in a glacially influenced environment. Changes in sediment provenance during the early Oligocene/late Eocene(?) also affected the major element geochemistry and, therefore, the CIAs of these sediments. As a result, more definitive interpretations of the palaeoweathering history contained in CRP-3 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

$$CIA = [Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$$

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-3, 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-3 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 Al_2O_3/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 evaluate the relative importance of input from the McMurdo Volcanic Group, a potential source rock with elevated Nb contents, and Sr contents are used to evaluate the relative inputs of "basement" (Granite Harbour Intrusives) vs. the Ferrar Dolerite and the Beacon Supergroup.

MATERIALS AND METHODS

In this study 85 fine grained samples were analyzed for major and trace elements by x-ray fluorescence (XRF; Tab. 1). Sixty-five of the analyzed samples were bulk core collected from the finest grained lithologies (mudstones and siltstones) between 22 to 789 msbf; in relatively thick intervals of fine-grained sediments, samples were taken approximately every 5 m. Twenty of the samples were splits of the <63μm size fraction that remained after foraminifera processing; each of these is indicated by an asterisk in table 1.

The XRF 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 all 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 63 samples by XRF (V, Cr, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Ba, Pb, Th, U) using pressed powder samples (Norrish & Chappell, 1977). The XRF was calibrated using a wide variety of well-analyzed rock standards.

Tab. 1 - Elemental abundances, loss-on-ignition (LOI), total analyzed abundances, CIA values, and Al-oxide/Ti-oxide ratios for samples from CRP-3. "*" indicates sample of <63 µm fraction separated during processing for microfossils. Major element abundances are weight % of the oxide; trace element abundances are in ppm.

Depth(mbsf)	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	L.O.I.	SUM	CIA	Al/Ti	S	Cl	V	Cr	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb	Th	U
*22.23	69.90	0.62	10.61	5.32	0.07	2.88	4.20	1.36	1.74	0.09	2.42	99.22	47.44	16.99		315		64								124					330			
25.77	68.94	0.57	11.04	5.14	0.06	2.60	3.46	1.89	2.05	0.10	3.67	99.52	48.72	19.20	2283	3469	115	54	30	36	52	14	2	76	123	21	187	13	2	366	16	4	1
29.34	71.42	0.53	10.09	4.76	0.06	2.49	3.32	1.77	1.88	0.10	3.14	99.56	47.89	19.03	2010	3381	102	49	27	32	50	13	2	69	118	21	182	12	1	345	12	5	1
35.48	69.42	0.59	11.08	5.01	0.06	2.53	3.28	1.96	2.08	0.11	3.57	99.68	49.20	18.79	2597	3042	111	58	27	30	59	14	3	79	132	20	177	14	2	395	15	6	1
41.09	72.52	0.53	9.52	4.49	0.07	2.43	4.01	1.75	1.55	0.08	2.49	99.43	44.58	18.11	2810	3399	104	55	29	26	42	12	2	55	122	19	201	12	2	303	11	3	2
*44.18	67.68	0.63	11.64	4.94	0.07	2.69	3.74	1.64	2.24	0.11	3.11	98.48	49.42	18.59		512		54							158					408			
45.29	64.56	0.69	12.88	5.34	0.07	2.89	3.72	2.28	2.78	0.14	4.25	99.60	48.80	18.70	2208	4772	110	56	28	24	72	16	4	112	199	25	192	18	2	480	19	9	2
48.97	68.40	0.58	11.03	5.01	0.07	2.64	3.94	1.91	2.06	0.10	3.93	99.67	46.82	19.05	4471	3417	116	67	32	25	61	13	4	79	145	23	182	14	2	514	15	5	2
53.00	66.00	0.62	12.67	5.87	0.06	2.67	2.71	2.01	2.57	0.12	4.62	99.52	53.49	20.45	2470	3813	126	76	31	25	69	16	2	102	124	22	169	13	1	441	20	8	2
57.99	67.55	0.59	11.00	5.17	0.08	2.70	4.36	1.90	2.01	0.10	4.45	99.90	45.38	18.78	3062	2696	122	63	35	29	58	13	3	77	137	23	173	13	2	361	16	5	3
62.83	66.83	0.59	11.87	5.72	0.07	3.08	3.75	2.06	2.10	0.10	3.69	99.85	48.77	20.27	3480	4006	127	66	32	32	59	14	3	80	135	22	172	12	2	383	15	6	2
*62.95	67.71	0.59	11.68	5.50	0.07	3.03	4.40	1.51	1.91	0.09	2.86	99.37	48.19	19.65		438		62							137					376			
67.76	65.95	0.59	12.37	5.90	0.07	3.24	3.89	2.08	2.15	0.11	3.82	100.18	49.09	20.83	1311	4151	131	67	35	37	62	15	2	82	139	23	168	13	2	401	17	8	2
72.97	64.08	0.63	12.97	6.28	0.08	3.23	3.67	2.07	2.36	0.11	4.47	99.94	50.69	20.68	2123	5259	133	68	35	50	67	15	2	91	138	23	177	10	1	402	16	8	2
77.32	63.90	0.62	12.88	6.43	0.08	3.40	3.26	2.00	2.53	0.13	4.63	99.85	51.88	20.74	2047	2179	115	63	33	43	64	15	1	94	159	24	169	10	1	418	18	9	2
82.21	67.90	0.61	11.91	5.63	0.07	2.92	3.49	1.85	2.31	0.11	3.80	100.61	50.06	19.54	2818	1363	120	61	32	40	61	13	2	83	167	22	177	10	1	374	17	8	2
*82.29	67.92	0.61	11.80	5.43	0.07	2.98	4.10	1.43	2.14	0.10	3.13	99.72	49.34	19.24		213		63							174					391			
87.60	62.01	0.52	10.30	4.67	0.14	2.87	9.19	1.51	1.90	0.14	6.80	100.05		19.62	4045	1366	105	61	30	27	46	12	1	66	185	26	188	8	0	344	13	7	2
95.60	68.70	0.56	11.82	5.42	0.06	3.10	2.23	1.81	2.40	0.09	4.12	100.30	55.14	21.16	1772	1214	110	50	27	30	52	14	1	87	191	21	181	10	1	403	17	8	2
106.07	63.50	0.57	12.29	5.20	0.09	2.99	4.35	2.47	2.56	0.12	6.06	100.19	45.47	21.68	1893	964	105	59	30	33	63	13	3	99	308	25	170	11	0	428	18	11	3
*106.36	66.47	0.58	12.57	5.04	0.07	2.84	2.54	1.63	2.46	0.09	4.78	99.06	55.51	21.72		297		56							214					442			
109.09	66.62	0.56	12.56	5.15	0.07	2.91	2.44	2.24	2.50	0.10	4.52	99.67	53.74	22.28	1693	1460	114	52	45	33	55	15	2	99	251	23	172	10	1	455	17	11	3
*123.65	65.87	0.59	12.57	5.01	0.07	2.61	3.18	1.83	2.49	0.10	4.49	98.81	52.25	21.17		316		56							256					443			
128.58	62.21	0.62	13.67	6.27	0.09	3.47	2.48	2.10	2.74	0.13	6.08	99.86	55.59	22.07		1672		63			71				255					456			
130.60	71.83	0.51	9.71	4.58	0.06	2.49	1.92	1.59	1.97	0.08	3.88	98.61	54.11	19.23	6388	1125	107	50	42	25	50	12	2	82	254	19	180	8	1	332	14	7	2
135.23	70.50	0.54	10.65	5.08	0.06	2.80	1.73	1.78	2.13	0.08	4.06	99.41	55.96	19.85	3218	1988	116	52	31	27	52	13	1	87	248	17	166	9	1	353	15	8	1
144.44	70.89	0.51	9.64	4.62	0.07	2.50	3.11	1.66	2.14	0.08	4.09	99.31	47.40	18.76	2644	1460	115	47	28	30	46	12	1	85	150	18	173	9	1	311	13	7	2
155.20	71.50	0.45	8.94	5.31	0.05	3.71	1.33	1.73	1.88	0.07	3.94	98.91	55.04	19.93	1513	1993	108	44	32	27	40	12	2	73	120	19	202	7	0	293	10	5	2
161.06	59.63	0.56	12.12	5.39	0.13	3.62	4.81	1.92	2.69	0.13	7.38	98.38	44.99	21.65	1817	1747	114	54	32	38	59	15	3	115	201	27	163	9	0	365	14	8	1
167.20	69.35	0.55	10.80	5.04	0.08	3.49	1.95	1.91	2.31	0.09	3.62	99.17	54.05	19.67	2967	1918	121	56	30	28	51	13	3	90	234	21	191	8	1	370	13	6	2
173.66	79.10	0.39	6.59	3.73	0.06	2.61	1.63	1.69	1.27	0.06	2.22	99.35	48.12	17.11	2607	545	81	35	23	23	28	8	1	45	166	16	188	6	1	246	7	2	1
180.08	76.46	0.44	8.14	3.32	0.07	2.15	1.95	1.72	1.79	0.09	3.51	99.64	49.49	18.61	2549	763	94	35	21	22	32	10	2	69	222	22	206	7	1	298	10	6	2
186.16	73.11	0.50	9.97	4.26	0.07	2.91	0.97	1.73	2.27	0.07	3.88	99.74	58.51	19.86	2381	735	88	44	25	24	44	13	2	96	197	20	185	9	0	378	13	8	2
189.04	67.62	0.57	12.15	5.23	0.08	3.44	1.12	1.95	2.78	0.09	4.69	99.72	59.52	21.48	1414	1027	106	58	29	36	55	14	2	121	241	23	185	9	0	443	16	9	2
*190.77	70.08	0.57	10.70	4.60	0.07	3.18	1.95	1.72	2.43	0.08	4.02	99.40	54.31	18.81		139		55							348					365			
195.00	71.33	0.51	10.45	4.68	0.07	3.30	1.04	1.94	2.29	0.08	4.09	99.79	58.01	20.49	1409	860	97	47	27	31	47	13	2	97	174	20	183	7	0	361	13	7	2
201.44	79.72	0.38	6.95	3.14	0.06	1.97	1.45	1.44	1.62	0.06	2.91	99.71	50.67	18.44	2837	604	69	33	21	18	31	8	2	65	147	16	187	6	1	278	9	3	2
*209.98	73.13	0.57	8.38	4.85	0.05	3.65	1.64	1.68	1.38	0.06	3.76	99.15	53.64	14.82		190		48							104					240			
213.60	76.91	0.44	8.02	3.69	0.04	2.42	1.22	1.95	1.67	0.06	3.08	99.51	52.58	18.26	1050	449	88	37	23	17	29	10	1	64	86	15	226	6	1	294	9	4	2
217.37	80.26	0.38	6.65	3.11	0.04	1.72	1.57	2.02	1.23	0.05	2.95	99.98	46.97	17.61	1113	826	82	41	20	10	24	7	2	42	113	13	267	5	1	230	5	1	1
229.50	72.98	0.43	9.67	4.59	0.05	2.49	0.98	1.65	2.32	0.07	4.26	99.47	58.00	22.53	1496	916	102	46	27	26	39	12	2	95	73	16	164	6	1	339	10	3	2
232.80	69.74	0.50	11.48	4.74	0.05	2.11	1.08	1.62	2.94	0.08	4.80	99.15	59.48	23.01	2792	1478	110	52	32	30	47	14	1	123	77	20	172	7	0	403	14	6	2
241.30	67.36	0.57	13.05	5.49	0.06	2.51	0.87	1.64	3.58	0.08	4.70	99.92	61.52	22.79	858	901	124	54	31	35	55	16	2	153	82	22	172	8	1	467	15	7	2
258.76	76.31	0.47	9.56	3.15	0.04	0.95	1.40	1.29	2.74	0.08	3.62	99.64	55.58	20.25	1245	1554	93	41	20	23	44	11	1	122	87	19	206	8	1	364	13	6	3
269.95	68.65	0.50	11.24	5.33	0.13	1.20	2.29	1.16	3.31	0.07	5.85	99.74	53.80	22.31	3067	738	104	53	31	30	43	13	0	156	73	21	169	7	0	411	14	8	1
275.53	70.00	0.50	10.43	4.91	0.06	1.83	2.84	1.39	2.77	0.07	5.35	100.16	49.94	20.85	2833	589	114	50	30	31	45	13	2	126	84	18	167	7	0	343	12	5	1
286.80	77.16	0.47	9.09	3.87	0.04	1.22	0.84	1.14	2.85	0.07	3.18	99.92	58.34	19.53	3712	405	96	42	19	22	41	12	2	134	75	15	170	8	0	314	11	4	2
292.62	66.13	0.53	11.59	6.90	0.09	3.14	0.80	1.33	4.06	0.09	4.72	99.38	59.08	21.79	845	759	133	56	38	44	51	13	2	231	64	19	154	8	0	395	12	6	1
308.75	86.02	0.23	4.09	1.93	0.03	1.08	1.53	0.99	1.32	0.04	2.35	99.61	41.12	17.49	2873	2713	46	23	16	12	12	6	1	46	56	9	179	4	1	181	5	2	1
*311.14	73.87	0.50	8.66	4.13	0.06	2.67	2.00	1.17	2.15	0.06	3.77	99.04	52.34	17.41		106		41							83					318			
313.13	75.75	0.48	8.96	4.34	0.05	2.54	1.09	1.55	2.16	0.06	3.08	100.06	56.58	18.65	2332	616	102	39	23	22	38	10	1	93	81	16	189	8	1	331	10	6	2
319.91	68.23	0.59	11.79	5.47	0.08	3.54	1.10	2.04	2.92	0.09	4.04	99.89	58.04	19.98	3371	928	130	53	32	33	57	14	2	134	89	22	174	9	0	398	13	6	3
324.20	69.04	0.56	11.01	5.47	0.07	3.34	1.21	1.77	2.84	0.08	4.43	99.82	57.33	19.50	2441	868	125	52	31	31	55	14	2	131	88	21	176	9	0	401	14	6	2
331.68	68.24	0.55	11.38	5.91	0.06	3.70	0.89	1.58	3.26	0.09	3.84	99.50	59.47	20.56	1714	666	118	52	32	31	56	14	3	159	88	20	196	11	0	434	15	7	3
337.66	76.19	0.50	6.98	4.27	0.05	3.28	1.73	1.38	2.29	0.06	3.19	99.91	46.93	13.96	1997	685	104	49	24	11	31	8	2	98	78	17	328	7	1	313	7	4	2
340.76	75.36	0.47	8.73	4.08	0.04	2.53	0.73	1.23	2.96	0.07	3.41	99.61	57.09	18.40	949	603	98	41	24	20	35	10	1	139	72	16	205	7	0	367	11	6	2
*359.21	61.27	0.74	9.02	10.11	0.06	5.96	2.26	0.84	1.76	0.05	6.60	98.66	54.99	12.21		613		188							82					254			
360.10	66.74	0.54	13.33	5.05	0.05	2.36	0.54	1.18	4.13	0.07	5.39	99.37	64.33	24.85																			
363.69	65.64	0.58	14.36	5.59	0.05	2.17	0.45	1.12	4.33	0.07	5.34	99.70	66.13	24.68	952	655	108	53	29	34	56	17	0	213	66	21	164	9	0	529	22	10	3
406.44	68.43	0.55	10.94	5.72	0.06	3.68	1.50	1.61	3.29	0.08	4.22	100.07	55.02	20.00	600	308	134	56	33	33	47	12	2	158	85	19	179	7	0	405	11	4	1
409.82	64.35	0.60	12.88	6.35	0.06	4.12	0.77	1.64	4.24	0.09	4.85	99.95	59.76	21.39	640	496	142	58	34	43	58	15	2	206	83	21	167	8	0	490	13	6	3
*410.38	64.43	0.61	12.49	6.10	0.06	4.10	1.26	1.15	3.74	0.08	5.18	99.19	60.28	20.51		217		58							86					457			
411.78	75.69	0.46	8.59	3.91	0.04	2.66	0.93	1.34	2.87	0.06	3.08	99.65	55.05	18.79	2513	623	97	39	33	21	34	11	2	130	74	15	199	7	1	338	9	5	2
*457.42	73.51	0.54	5.31	5.08	0.07	2.03	4.16	0.59	1.57	0.05	5.99	98.89		9.89		498		81							54					174			
459.38	65.60	0.24	4.53	2.16	0.17	1.07	12.08	0.75	1.35	0.06	11.17	99.18		18.84	4597	251	58	20	16	11	15	6	1	56	76	16	157	3	0	204	6	2	0
461.77	60.16	0.55	13.49	7.09	0.08	3.64	1.44	1.49	4.92	0.09	6.00	98.95	56.47	24.49	3384	1986	144	55	35	44	58	18	1	245	62	20	144	7	0	429	16	8	3
475.59	86.68	0.16	3.09	1.75	0.02	1.09	0.65	0.74	1.33	0.03	4.69	100.23	44.59	19.53	4184	1966	43	19	18	9	6	5	1	54	37	8	145	3	1	201	5	3	1
522.77	82.53	0.39	7.20	2.02	0.02	0.51	0.57	0.92	2.84	0.05	2.73	99.75	56.12	18.38	2478	1384	93	36	15	26	30	8	0	127	52	13	211	6	0	335	7	3	1
*584.49	44.53	0.42	5.40	12.15	0.11	3.45	13.07	0.42	0.86	0.03	18.48	98.92		12.72		858		149							81					103			
601.42	86.36	0.18	4.35	1.64	0.01	1.04	0.51	1.01	1.54	0.03	2.91	99.59	50.56	24.07	653	2142	59	25	16	11	12	5	1	57	49	8	132	3	1	246	5	3	1
*621.8	52.58	0.31	6.46	11.31	0.12	5.32	7.11	0.69	0.94	0.03	14.06	98.94		20.57		876		126							92					106			
635.92	79.87	0.25	5.44	3.69	0.03	3.35	1.25	1.48	1.00	0.04	3.32	99.72	48.39	21.97	1165	1116	89	44	32	17	21	6	0	34	75	11	134	3	1	223	5	3	2
640.40	81.42	0.23	5.24	2.73	0.04	2.07	1.71	1.48	1.07	0.04	3.69	99.72	43.85	22.52		1804		40			17				72					210			
*640.76	65.31	0.60	8.36	7.62	0.07	5.98	3.12	1.25	1.40	0.11	5.62	99.44	47.47	13.90		424		117							107					221			
*656.59	60.16	0.31	8.77	7.45	0.07	9.49	1.48	1.02	1.23	0.03	9.36	99.38	60.61	28.47		311		134							100					156			
*697.34	50.36	0.42	7.95	12.29	0.11	14.58	2.45	0.83	0.66	0.03	9.87	99.54	54.97	19.05		340		209							127					93			
710.70	77.84	0.30	6.15	4.91	0.05	3.67	1.14	1.30	1.07	0.04	3.34	99.82	53.34	20.70	684	404	99	44	30	18	26	9	3	40	87	15	132	4	0	215	6	2	2
*731.33	52.17	0.48	7.94	11.72	0.13	13.67	2.41	0.80	0.86	0.03	9.45	99.65	51.58	16.53		172		218							108					108			
*751.36	61.77	0.60	9.49	8.15	0.09	8.27	2.62	1.34	1.28	0.06	6.56	100.25	53.15	15.92		137		126							130					233			
762.41	72.70	0.37	8.39	5.00	0.05	4.42	1.61	1.73	1.59	0.05	3.87	99.79	52.82	22.57	588	493	121	54	37	16	32	9	1	53	115	15	153	4	0	257	8	6	1
765.10	70.02	0.46	9.90	5.54	0.06	4.50	1.88	1.88	2.06	0.05	4.14	100.50	53.13	21.33	544	645	122	47	34	22	37	11	1	65	133	17	151	5	0	295	8	4	2
776.70	78.20	0.35	6.70	4.44	0.03	2.83	1.39	1.31	1.29	0.05	3.11	99.72	52.39	18.99	881	433	108	53	29	21	27	8	1	48	92	12	151	4	0	230	6	5	2
781.20	71.19	0.46	9.66	5.61	0.04	3.62	1.94	1.77	2.08	0.05	3.50	99.93	52.59	20.96	576	929	147	70	40	20	37	10	1	78	120	13	182	4	1	322	8	6	2
*781.29	65.33	0.59	11.20	7.25	0.05	4.63	2.40	1.40	2.18	0.06	4.84	99.94	55.40	18.88		307		95							113					319			
788.87	72.55	0.40	8.50	5.68	0.04	3.82	1.37	1.54	2.14	0.05	3.61	99.70	53.65	21.22	590	773	128	66	34	19	33	10	0	77	107	13	159	4	0	282	7	5	1

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.

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-3. All the data are listed in table 1 so as to be useful to other investigators. The Al_2O_3, TiO_2 Nb, and Sr analyses are used here in a preliminary effort to

evaluate the effect of sediment provenance changes on the CIA record from CRP-3.

In calculating CIA values, the CaO* abundance used is only the CaO contained in the silicate fraction. For the vast majority of CRP-3 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 no CaO to the bulk sample. The CaO contributions from

biogenic and diagenetic carbonates for these samples are judged to be low because: 1) measured CaO contents for the majority of samples are consistent with the CaO contents of most potential source rocks (< 5 wt. %; Roser & Pyne, 1989), and 2) "loss-on-ignition" (LOI) values for the majority of samples also are relatively low (Tab. 1). The exceptions are four samples with CaO contents greater than 5%; CIAs for these samples have not been included in this study because the elevated CaO contents suggest a contribution from non-silicate sources. Carbonate analyses were not conducted during initial characterization of the CRP-3 cores, but diagenetic carbonates were identified during visual core description, particularly below 234 mbsf (Cape Roberts Science Team, 2000). Post-drilling analysis of carbonate contents confirms this depth distribution, but also shows that carbonate contents vary significantly over short stratigraphic intervals (Dietrich and others, this volume). In addition, the diagenetic carbonates were concentrated in sandstone lithologies, which were not sampled for this study, so the low LOI values and source-consistent CaO contents remain the best indicators of low CaO contributions from carbonates to most samples in this dataset. In some other studies (e.g., Fedo et al., 1995), CaO contents also have been corrected for a contribution from biogenic apatite by assuming that all P_2O_5 is present as biogenic apatite. Such a correction has not been made for the CRP-3 samples because the P_2O_5 is uniformly low (<0.2 wt % throughout CRP-3), and because the McMurdo Volcanic Group is a potential source rock and is usually enriched in P_2O_5.

Because a detailed age-depth model is not presently available for CRP-3, all data are presented as stratigraphic profiles vs. subbottom depth.

DATA AND RESULTS

The complete data set, the calculated CIAs, and the calculated Al_2O_3/TiO_2 ratios for the 85 samples from CRP-3 are presented in table 1. The stratigraphic profiles of the calculated CIAs, the calculated Al_2O_3/TiO_2 ratios, and the Nb and Sr contents are shown in figures 1, 2, 3, and 4, respectively.

CIA values in CRP-3 (Fig. 1) generally range between 45 and 60, and the CIA profile can be subdivided into two parts: 1) a lower part (below ~400 mbsf), where CIAs are relatively high at 750-800 mbsf, low at ~600 mbsf, and increase irregularly toward 400 mbsf, and 2) an upper part (above ~400 mbsf), where an overall upsection decrease in CIA values is overprinted by four smaller, quasi-cyclic changes, each occurring over 50-100 m of stratigraphic thickness.

On first examination, the low CIA values that are distributed throughout the CRP-3 profile suggest that

this site consistently received sediment that had undergone little or no chemical weathering during the early Oligocene (and late Eocene?). This interpreted input of unweathered or weakly weathered material is in agreement with the importance of glacigenic or glacially influenced lithofacies throughout the Cenozoic portion of CRP-3. However, CIA values close to, or less than, 50 occur throughout CRP-3; since 50 is the CIA value cited for unweathered feldspar by Nesbitt & Young (1982), the presence of values less than 50 in CRP-3 indicates that primary phases with original K/Al, Ca/Al, or Na/Al ratios higher than those found in feldspars must be present. Based on these low CIAs, and reinforced by conclusions drawn from studies of CRP-1 and CRP-2/2A (Krissek & Kyle, 1998, 2000), the possible effects of provenance changes on the CIA profile for CRP-3 must be considered before the CIA profile is interpreted solely as an indicator of palaeoweathering. For example, the overall upsection decrease in CIAs above ~400 mbsf in CRP-3 could be produced either by a decrease in the amount of weathering or by an
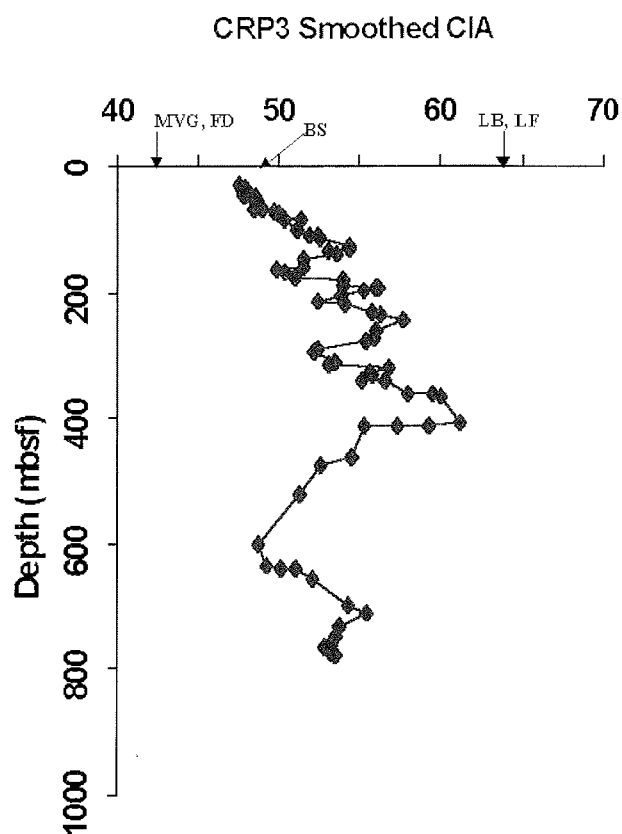
CRP3 Smoothed CIA
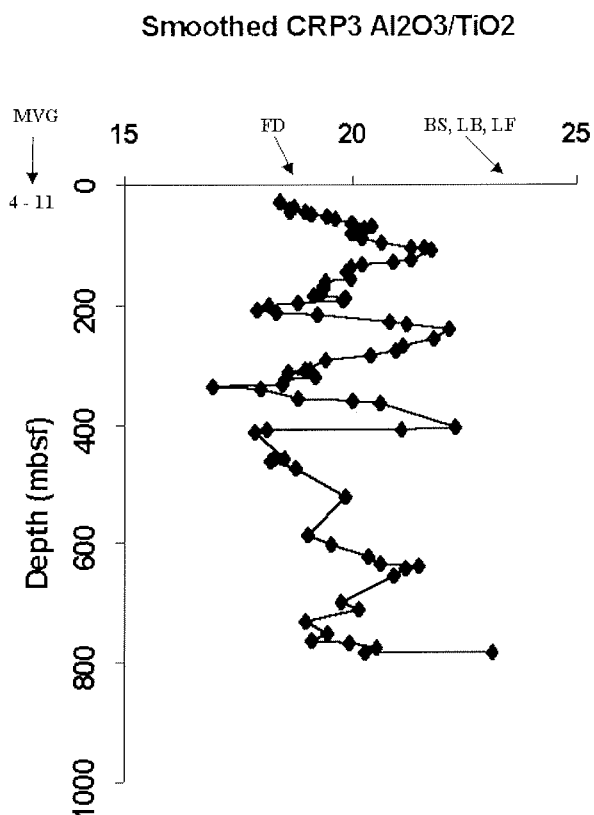

Fig. 1 - CIA profile for CRP-3, smoothed with a 5-point moving average and plotted vs. subbottom depth. Labeled arrows indicate CIA values calculated for potential source rock types from data of Roser & Pyne (1989); MVG = McMurdo Volcanic Group, FD = Ferrar Dolerite, LF = Lashley Formation, LB = Lower Beacon Supergroup sediments, and BS = crystalline basement. Note irregular CIA profile below ~400 mbsf, short-term fluctuations ("quasi-cycles") above ~400 mbsf, and overall decrease in CIA values above ~400 mbsf.

increase in the relative importance of material whose low "apparent CIA" is independent of its weathering history. In a similar manner, the four CIA"quasi-cycles" above 400 mbsf may also record provenance changes, palaeoweathering changes, or a combination of these two.

Roser & Pyne (1989) summarized the representative geochemical compositions of six source rock types thought to have supplied sediment to CIROS-1; because CRP-3 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-3. 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-3. 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 (upper Beacon Supergroup 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, and their Sr and Nb contents; these values are also shown and labeled on figures 1, 2, 3, and 4.

The relative importance of these sediment sources to deposition at CRP-3 did vary during the early Oligocene/late Eocene(?), as indicated by the stratigraphic profile of Al_2O_3/TiO_2 ratios (Fig. 2). The Al_2O_3/TiO_2 ratios at CRP-3 show little or no trend over the entire stratigraphic interval, instead fluctuating repeatedly between ~18 and ~23. These variations are best-developed as three or four "quasi-cycles" above ~400 mbsf. Comparing the Al_2O_3/TiO_2 values of the potential source rock types (listed in table 2 and shown in figure 2) to the CRP-3 profile indicates that these sediments must contain little or no McMurdo Volcanic Group detritus, which is characterized by very low Al_2O_3/TiO_2 ratios (between 3.6 and 11). The paucity of McMurdo Volcanic Group detritus in CRP-3 is also indicated by low concentrations of the trace element Nb (Fig. 3). Small amounts of McMurdo Volcanic Group detritus may be present above ~50 mbsf, but Nb contents below that level in CRP-3 are consistent with sediment supply solely from the Ferrar Dolerite, the Beacon

Fig. 2 - Al_2O_3/TiO_2 ratio profile for CRP-3, smoothed with a 5-point moving average and plotted *vs.* subbottom depth. Labeled arrows indicate Al_2O_3/TiO_2 ratios calculated for potential source rock types from data of Roser & Pyne (1989); MVG = McMurdo Volcanic Group, FD = Ferrar Dolerite, LF = Lashley Formation, LB = Lower Beacon Supergroup sediments, and BS = crystalline basement. Note irregular Al_2O_3/TiO_2 profile below ~400 mbsf, short-term fluctuations ("quasi-cycles") above ~400 mbsf, and absence of overall trend in values above ~400 mbsf.

Supergroup, and the Granite Harbour Intrusives. The absence of McMurdo Volcanic Group detritus also was noted during initial studies of CRP-3 clasts and sandstone framework grains (Cape Roberts Science Team, 2000).

In the absence of McMurdo Volcanic Group detritus, the stratigraphic profile of Al_2O_3/TiO_2 ratios (Fig. 2) can be interpreted to record repeated variations in relative inputs from the Ferrar Dolerite (with an Al_2O_3/TiO_2 ratio of ~19) and the Beacon Supergroup + "basement" (Granite Harbour Intrusives; both with Al_2O_3/TiO_2 ratios of 22-24). Sr contents (Fig. 4) help to distinguish inputs from the Beacon

Tab. 2 - Selected geochemical data for CIROS-1 sediment source rocks (from Roser & Pyne, 1989). Major element abundances are weight % of the oxide; trace element abundances are in ppm.

Source Terrane	SiO2	Al2O3	TiO2	CaO	Na2O	K2O	P2O5	CIA	Al2O3/TiO2	Nb	Sr
Basement	65.25	16.14	0.72	3.88	3.63	3.69	0.17	48.7	22.4	13	516
Lower Beacon	89.73	5.7	0.24	0.68	0.2	1.44	0.02	64.6	23.8	5	47
Ferrar Dolerite	57.17	15.83	0.83	8.67	2.65	1.28	0.11	42.4	19.1	8	144
McMurdo Volcanic	42.69	13.83	3.82	10.68	3.53	1.49	0.86	33.9	3.6	114	970
McMurdo Volcanic	52.76	19.1	1.73	5.06	7.23	3.86	0.58	43	11	204	951
Lashly Formation	77.86	12.7	0.53	1.06	1.72	2.26	0.03	63.7	24	12	147

CRP3 Nb

LB   FD   LF, BS

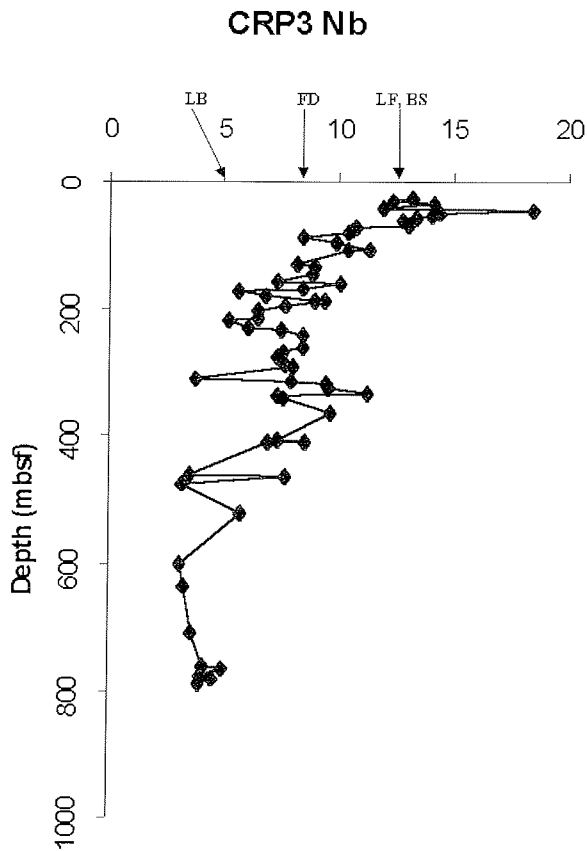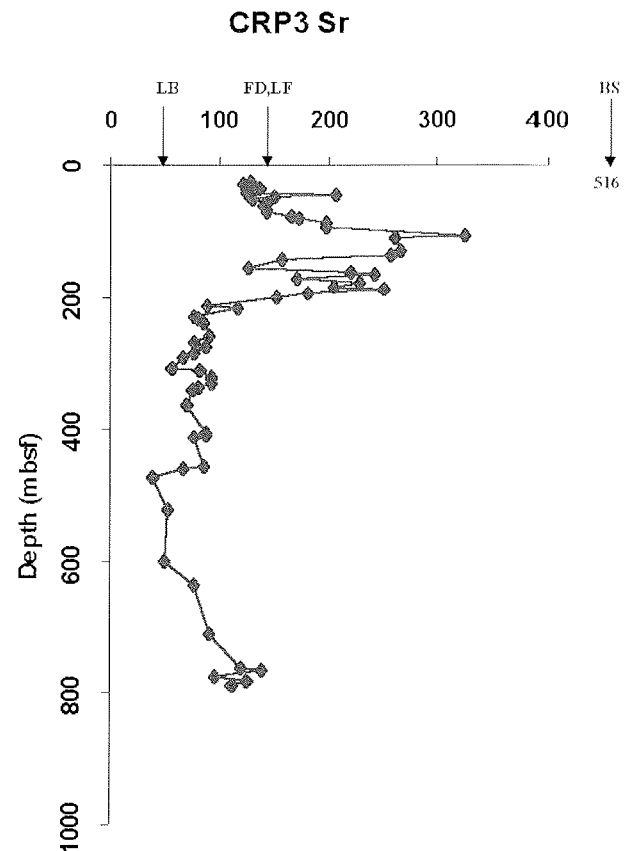0   5   10   15   20

Depth (mbsf)

Fig. 3 - Nb concentrations with depth in CRP-3. Labeled arrows indicate Nb contents for potential source rock types from data of Roser & Pyne (1989); MVG = McMurdo Volcanic Group, FD = Ferrar Dolerite, LF = Lashley Formation, LB = Lower Beacon Supergroup sediments, and BS = crystalline basement. Low Nb contents indicate little or no supply of McMurdo Volcanic Group detritus to CRP-3.

CRP3 Sr

LB   FD,LF   BS

0   100   200   300   400

516

Depth (mbsf)

Fig. 4 - Sr concentrations with depth in CRP-3. Labeled arrows indicate Sr contents for potential source rock types from data of Roser & Pyne (1989); MVG = McMurdo Volcanic Group, FD = Ferrar Dolerite, LF = Lashley Formation, LB = Lower Beacon Supergroup sediments, and BS = crystalline basement. Increased Sr contents above ~200 mbsf indicate increased importance of basement-derived detritus above that level.

Supergroup *vs.* those from "basement", and indicate that detritus from the Granite Harbour Intrusives is most important above ~200 mbsf. Below that level, the low Sr contents (generally ~100 ppm) are consistent with sediment supply dominated by the Ferrar Dolerite and the Beacon Supergroup. Taken together, the Al_2O_3/TiO_2 ratios and Sr contents suggest that sediments above ~200 mbsf in CRP-3 were supplied from all three possible source rock types: the Ferrar Dolerite, the Beacon Supergroup, and the Granite Harbour Intrusives. Sediments below ~200 mbsf in CRP-3, however, appear to have been supplied primarily from only two of these sources, the Ferrar Dolerite and the Beacon Supergroup.

For comparison to these geochemically based interpretations of sediment provenance, preliminary studies of clasts in CRP-3 (Cape Roberts Science Team, 2000) identified a "lower clast assemblage", present below ~150 mbsf and dominated by Beacon Supergroup and Ferrar Dolerite clasts, and an "upper clast assemblage", present above ~150 mbsf and dominated only by Ferrar Dolerite clasts. "Basement" clasts were observed discontinuously through the Cenozoic section, generally in low and variable

proportions. The composition of sandstone framework grains also records the importance of Ferrar-derived material, especially above ~180 mbsf, and input from the Beacon Supergroup (Cape Roberts Science Team, 2000; Smellie, this volume). In summary, then, all three data sets (mudrock geochemistry, clast composition, and sandstone framework grain composition) indicate both the importance of the Ferrar Supergroup as a sediment source throughout the deposition of CRP-3, and the importance of Beacon Supergroup sources below 150-200 mbsf. These three data sets provide a less consistent picture of inputs from the Beacon Supergroup above 150-200 mbsf and from the basement. These are inconsistencies in describing less important sources, however, and may arise from either: 1) the preliminary nature of these data sets and their interpretations, or 2) differences in sample locations superimposed on variable inputs from these sources. As more detailed studies are completed, a comprehensive interpretation of sediment provenance will be an important step toward understanding the tectonic and unroofing histories of the adjacent Transantarctic Mountains.

The stratigraphic variations in sediment provenance at CRP-3, identified from the Al_2O_3/TiO_2 ratios (Fig. 2) and the Sr contents (Fig. 4), might be expected to also affect the CIA profile (Fig. 1), since unweathered Beacon Supergroup material has a higher apparent CIA (~64; Tab. 2) than unweathered Ferrar Dolerite (~42) or unweathered basement (~49). Below ~400 mbsf, however, the CIA and Al_2O_3/TiO_2 profiles show little covariation, suggesting that the observed CIA fluctuations are a complex signal, influenced both by shifts in provenance and by changes in palaeoweathering. Deciphering these two influences, in order to develop a palaeoweathering curve for the lower 400 m of the CRP-3 Cenozoic sequence, will require more detailed compositional modeling to remove the overprint of provenance; this will be the objective of future work. Above ~400 mbsf, however, the CIA and Al_2O_3/TiO_2 profiles show strikingly similar patterns of short-term variation ("quasi-cycles"), clearly recording repeated changes in sediment provenance that strongly influence the CIA record. The cause(s) of the provenance changes is not known at present, but possibilities include episodic uplift in the Transantarctic Mountains and glacial advance/retreat. These possible explanations will be evaluated after the profiles of contributions from the three possible source rock types are calculated using linear mixing models. In addition, changes in source rock contributions will be compared to independent indicators of tectonism or palaeoenvironment, such as sequence stratigraphic boundaries.

Above ~400 mbsf in CRP-3, the CIA and Al_2O_3/TiO_2 profiles show strikingly similar patterns of short-term variation; the overall trends of these two profiles above ~400 mbsf, however, show a subtle, but perhaps important, difference. In the CIA profile, the "quasi-cycles" are superimposed on a general decrease in CIA values upsection; the "baseline" value at ~400 mbsf is ~55, whereas the "baseline" value above the shallowest "quasi-cycle" is 50 or less. In contrast, the "baseline" for the "quasi-cycles" in the Al_2O_3/TiO_2 profile remains relatively constant throughout the interval above ~400 mbsf. This difference in long-term behavior suggests that palaeoweathering intensities were decreasing during deposition of the uppermost 400 m of CRP-3, even as shorter-term, but relatively consistent, provenance changes also influenced the CIA record. If this hypothesis is correct, then the decrease in palaeoweathering may record climatic deterioration (cooling and/or drying) between ~33 Ma and ~31 Ma. Testing this hypothesis will require more detailed compositional modeling to remove the overprint of provenance changes from the CIA record.

SUMMARY AND CONCLUSIONS

Sediments deposited at CRP-3 during the early Oligocene/late Eocene(?) were supplied from the Ferrar Dolerite, the Beacon Supergroup, and local basement (the Granite Harbour Intrusives); the McMurdo Volcanic Group supplied little or no material. Elevated Sr contents suggest that basement-derived material is most important above ~200 mbsf, whereas Beacon Supergroup and/or Ferrar Dolerite components dominate below that level. Below ~400 mbsf, the CIA and Al_2O_3/TiO_2 profiles show little or no covariation, suggesting that the CIA record is influenced by both provenance and palaeoweathering. Above ~400 mbsf, however, the CIA and Al_2O_3/TiO_2 profiles show strikingly similar short-term fluctuations, indicating a strong provenance influence on the CIA record. The cause of such repeated provenance changes, however, is presently unknown. CIA values exhibit a general decrease when viewed over the entire interval above ~400 mbsf, whereas Al_2O_3/TiO_2 values remain uniform. This difference suggests that palaeoweathering intensity decreased during deposition of the upper 400 m of CRP-3, as would be expected during a time of climatic deterioration (cooling and/or drying). 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 analyses of major element and trace element data.

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