

The Stable Oxygen Isotope Record of Pleistocene and Miocene Bivalves in the CRP-1 Drillhole, Victoria Land Basin, Antarctica

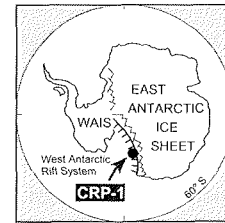
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Received 3 August 1998; accepted in revised form 10 November 1998

Abstract - Bivalve shells from the CRP-1 drillhole, Cape Roberts (Victoria Land Basin), have been analysed for their stable isotope composition to obtain information on Antarctic coastal palaeoceanography during the middle Pleistocene and early Miocene. Shells from a middle Pleistocene carbonate-rich unit (lithostratigraphic Unit 3.1; 33.82-31.89 metres below sea floor) have $\delta^{18}\text{O}$ values between +3.64 and +4.56‰ PDB and $\delta^{13}\text{C}$ between +0.85 and +1.09‰ PDB. Oxygen isotopic compositions are close to or at equilibrium conditions with seawater at a temperature in the range of *c.* -2 to 0°C in the absence of melt water influx. Thus, the CRP-1 carbonate-unit was deposited under "interglacial" polar conditions, comparable to those of the present-day and isotope stage 3 in the Ross Sea. "*Chlamys*" sp. 1, retrieved from a lower Miocene diamictite at 62.19 mbsf, is the only unaltered shell of this age in CRP-1 and yielded a $\delta^{18}\text{O}$ value of -4.64‰ PDB and $\delta^{13}\text{C}$ of -3.35‰ PDB. These values show that palaeoceanographic conditions during early Miocene time were significantly different from those of today. The depleted stable oxygen isotope composition of the Miocene shell reflects both an appreciable input of melt or fresh water and warmer-than-present seawater temperatures.



INTRODUCTION

Isotope palaeontology provides an important method of extracting palaeoenvironmental information from skeletal remains of organisms living in the past oceans (*e.g.* Wefer & Berger, 1991). Two main factors which govern the distribution of oxygen isotopes within the CaCO_3 skeleton are temperature and fluid composition (\sim salinity). Macrofossils of benthic organisms and especially bivalves, have been widely used in the reconstruction of palaeotemperature and palaeosalinity (Stanton & Dodd, 1970; Dodd & Stanton, 1975; Hillaire-Marcel, 1981; Stevens & Vella, 1981; Dodd et al., 1984; Krantz, 1990; Wefer & Berger, 1991; Berkman et al., 1992; Berkman, 1994). Pectinid mollusc shells (scallops) are well suited to isotopic studies because these bivalves secrete shell that is in or very close to equilibrium with ambient fluids (*e.g.* Dodd & Stanton, 1975; Stevens & Vella, 1981; Barrera et al., 1990; Berkman et al., 1992).

The isotopic composition of biogenic carbonates forming under cool- to cold-water conditions is relatively well documented (*e.g.* Hillaire-Marcel, 1981; Rao, 1993,

1996; James et al., 1997), and that of Quaternary Antarctic carbonates is receiving increasing attention (Taviani & Aharon, 1989; Barrera et al., 1990; Taviani, 1991; Baroni et al., 1991; Berkman et al., 1992; Taviani et al., 1993; Berkman, 1994; Rao, 1996; Rao et al., 1996; Marshall et al., 1997). Antarctic marine carbonates occupy a distinct isotopic field due to the peculiarly heavy oxygen isotopic signals driven by subzero temperatures (Taviani, 1991; Rao, 1996).

Pectinid and limid bivalve shells were recovered from both the Quaternary (middle Pleistocene) and Miocene sections of the CRP-1 drillhole, Cape Roberts (Victoria Land Basin). In this paper we present the results of a stable isotope study carried out on shell material (*Adamussium* sp., *Limatula* sp.) from the Pleistocene carbonate-rich lithostratigraphic Unit 3.1. (see Taviani & Claps, this volume) at 33.82-31.89 metres below sea floor (mbsf), and from a lower Miocene diamictite at 62.19 mbsf ("*Chlamys*" sp.1: see Jonkers & Taviani, this volume). Modern counterparts from McMurdo Sound (*Adamussium colbecki*, *Limatula hogdsoni*) and early Pliocene scallops ("*Chlamys*" *tuftsensis*) from the Wright Valley were analysed for comparison (Tab. 1).

Tab. 1 - Stable oxygen and carbon isotope composition of bivalve shells from CRP-1, Wright Valley and McMurdo Sound.

Sample No.	Sample location and depth	Age	Species	$\delta^{18}\text{O}$ ‰ PDB	stdv	$\delta^{13}\text{C}$ ‰ PDB	stdv
1	McMurdo Sound	Modern	<i>Adamussium colbecki</i>	3.970	0.0117	2.383	0.0087
2	Wright Valley	Pliocene	" <i>Chlamys</i> " <i>tuftsensis</i>	- 9.760	0.0071	- 0.207	0.0087
3	McMurdo Sound	Modern	<i>Limatula hogdsoni</i>	3.574	0.0098	0.689	0.0081
4	CRP-1 62.19 mbsf	Lower Miocene	" <i>Chlamys</i> " sp. 1	- 4.640	0.0455	- 3.350	0.0367
5	CRP-1 32.05 mbsf	Middle Pleistocene	<i>Adamussium</i> sp.	4.192	0.0109	1.343	0.0049
6	CRP-1 32.05 mbsf	Middle Pleistocene	<i>Limatula</i> sp.	4.387	0.0109	0.982	0.0085
7	CRP-1 32.05 mbsf	Middle Pleistocene	<i>Limatula</i> sp.	3.688	0.0154	1.107	0.0069
8	CRP-1 32.05 mbsf	Middle Pleistocene	<i>Adamussium</i> sp.	4.096	0.0038	1.152	0.0056

MATERIAL AND METHODS

Carbonate chips were broken off the shells and ultrasonically rinsed for 20 seconds in methanol to remove sediment particles. The samples were then rinsed in distilled water up to five times to ensure complete cleaning. The carbonate chips were then transferred to glass vials for isotope measurement. CO_2 was released by dissolving the sample under vacuum with 100% orthophosphoric acid at 75°C in a Carbo Kiel automated carbonate preparation device, in which carbonate samples are dissolved in separate glass vials to minimise "memory" effects. The carbonate device was linked online to a Finnigan MAT 252 mass spectrometer. External reproducibility of $\delta^{18}\text{O}$ as determined from replicate measurements of an internal laboratory standard (Solenhofen Limestone) is better than 0.08‰. The isotope values are referred to the Pee Dee Belemnite (PDB) carbonate isotope scale through calibration of the mass spectrometer with NBS 19 and 20 standards.

To check for potential diagenetic alteration of the bivalve carbonate that would limit the interpretation of its $\delta^{18}\text{O}$ values, carbonate mineralogy of the shells was thus determined by X-ray diffractometry (XRD). The shell chips were powdered in an agate pestle and mortar, and the powder mounted on aluminum sample holders to transfer to the sample cassette. Sample 7 (a Pleistocene *Limatula* shell) that was very small and contained very little carbonate was mounted on a silicon holder to minimise substrate reflections from the sample holder. Sample 4 ("*Chlamys*" sp.1: Jonkers & Taviani, this volume) is unique in that it represents the only unrecrystallised Miocene shell retrieved from core CRP-1. To save the sample for future work, the shell fragment was mounted whole on the sample holder.

XRD measurements were carried out using a Philips PW1820 automated diffractometer with incident and diffracted beam monochromator (cK α radiation at 35mA and 40 kV; scanning angle was 25°-32°). Identification of the d_{hkl} peaks followed the JCPDS reference list (Bayliss et al., 1986). The XRD was calibrated with carbonate and aragonite standards were run to better constrain interpretation of the diffractograms.

RESULTS AND DISCUSSION

The XRD scans of all bivalve specimens show dominant calcite peaks with minor contributions from aragonite in some samples (Fig. 1); pectinid and limid bivalves are known to secrete either calcitic or mixed calcitic/aragonitic shells (e.g. Milliman, 1974). The diffractogram of sample 4 ("*Chlamys*" sp.1) shows considerable background scatter, because of the XRD scan was run on a shell fragment with a curved surface rather than on a powder sample. However, the carbonate peaks and two distinctive aragonite peaks are still clearly visible in the scans. From the presence of aragonite in this sample we infer that this Miocene pectinid species had a mixed calcitic/aragonitic shell and that the shell fragment was not, or only to minor extent, affected by diagenesis and/or recrystallisation; these are important

constraints for the interpretation of the $\delta^{18}\text{O}$ signature of the sample (see below). The only other pre-Pleistocene sample, no. 2, is a shell of "*Chlamys*" *tufisensis* Turner, from Wright Valley on the Antarctic mainland nearby. It is Pliocene in age, and the lack of distinctive aragonite peaks in the XRD scan suggests that diagenetic alteration may have occurred, thus limiting the potential significance of its isotopic composition.

PLEISTOCENE

$\delta^{18}\text{O}$ values of the modern and Pleistocene shells are all within, or close to, the range of equilibrium values determined from today's seawater temperature and $\delta^{18}\text{O}$ in Antarctica (Fig. 2). Our data fit well within the field of Quaternary marine carbonates (Fig. 3). The temperature range today of surface-subsurface waters down to 50 m is between -2 and +1°C. Seawater $\delta^{18}\text{O}$ is around -0.3‰ SMOW (Standard Mean Ocean Water) but can be as low as -0.7‰ SMOW (Weiss et al., 1979; Jacobs et al., 1985; Östlund et al., 1987; Rao et al., 1996). Using the cold-water palaeotemperature equation of Shackleton (1974), equilibrium $\delta^{18}\text{O}$ for calcite is estimated at between +3.0‰ and +4.2‰ PDB. $\delta^{18}\text{O}$ values of both modern specimens (samples 1, *Adamussium colbecki*, and 3, *Limatula hogdsoni*) are +3.0‰ and +3.7‰ PDB, and are at the "cold" end of the modern range of equilibrium $\delta^{18}\text{O}$. The close correspondence of these values with estimated equilibrium $\delta^{18}\text{O}$ values confirms the equilibrium or near-equilibrium $\delta^{18}\text{O}$ signature of these bivalves (see also Krantz, 1990), and is consistent with other Southern Ocean cold-water carbonates (Taviani & Aharon, 1989; Barrera et al., 1990; Taviani et al., 1993; Berkman, 1994; Rao, 1996; Rao et al., 1996). Samples 5 (*Adamussium* sp.), 7 (*Limatula* sp.), and 8 (*Adamussium* sp.) have $\delta^{18}\text{O}$ values between +3.7 and +4.2‰ PDB, and thus also contain isotope signatures within the range of modern equilibrium values. The values imply that the species lived during interglacial climates when global ice volume was small and environmental conditions at Cape Roberts were similar to those of today.

The $\delta^{18}\text{O}$ value of sample 6 (*Limatula* sp.) of +4.4‰ PDB is slightly higher than the most positive modern equilibrium $\delta^{18}\text{O}$ of +4.2‰ PDB that occurs near the freezing point of seawater at -2°C. Because temperature could not have been lower than that, the high $\delta^{18}\text{O}$ may represent heavier seawater, either because of enhanced global ice volume and/or decreased runoff of local melt water. This would imply "semi-glacial" conditions such as occur during the early onset of glacial conditions, or during the final transition into an interglacial. Applying a sea-level change of 10 m per 0.1‰ increment in seawater $\delta^{18}\text{O}$ (Labeyrie et al., 1987; Fairbanks, 1989), the 0.2‰ increase in $\delta^{18}\text{O}$ over the highest modern equilibrium value in the area suggests that sea level was lowered about 20 m below its present interglacial level, compared with the full-glacial sea-level lowering evident during the last glacial maximum of between 120 m and 150 m (Fairbanks, 1989; Peltier, 1994; Bard et al., 1996). Thus, if the increased bivalve $\delta^{18}\text{O}$ reflects increased global ice volume, the

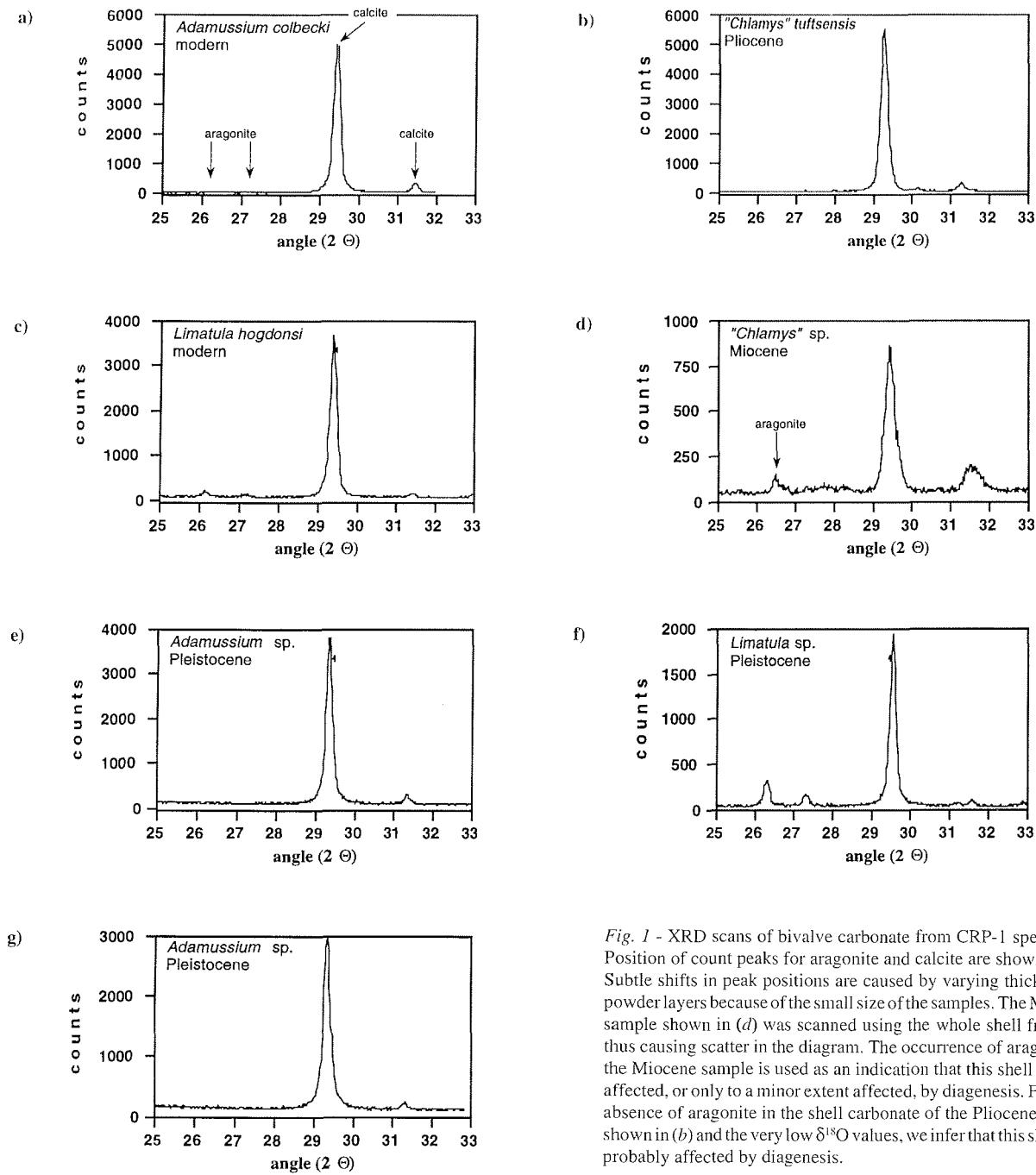


Fig. 1 - XRD scans of bivalve carbonate from CRP-1 specimens. Position of count peaks for aragonite and calcite are shown in (a). Subtle shifts in peak positions are caused by varying thickness of powder layers because of the small size of the samples. The Miocene sample shown in (d) was scanned using the whole shell fragment thus causing scatter in the diagram. The occurrence of aragonite in the Miocene sample is used as an indication that this shell was not affected, or only to a minor extent affected, by diagenesis. From the absence of aragonite in the shell carbonate of the Pliocene sample shown in (b) and the very low $\delta^{18}\text{O}$ values, we infer that this shell was probably affected by diagenesis.

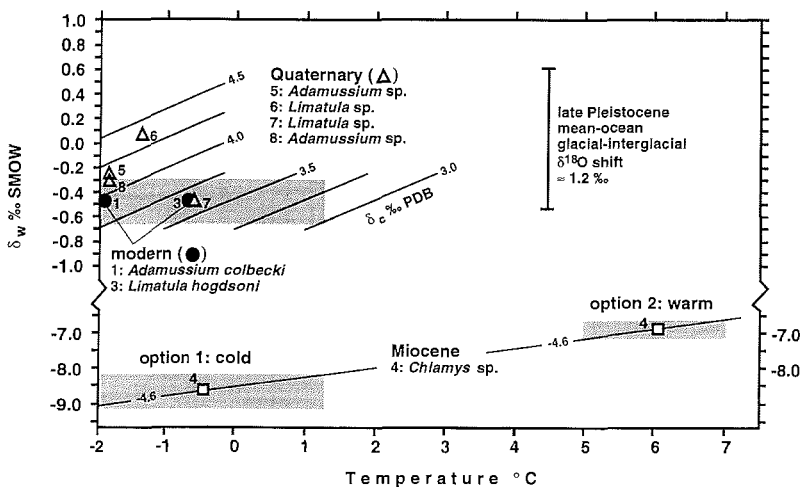
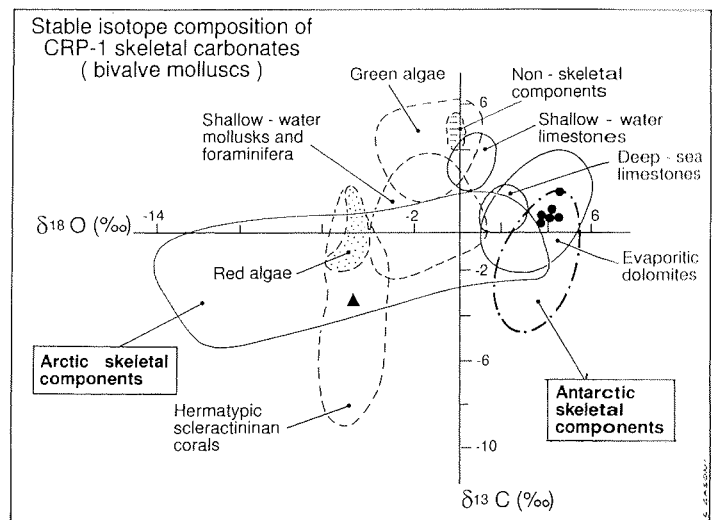


Fig. 2 - Temperature- $\delta^{18}\text{O}$ of seawater (d_w) diagram showing equilibrium $\delta^{18}\text{O}$ of calcite (d_c) fractionation lines and $\delta^{18}\text{O}$ values of CRP-1 bivalve mollusc specimens. d_c lines were computed using Shackleton's (1974) "cold" palaeotemperature equation. We have chosen to use a T- δ_w diagram in conjunction with predicted $\delta^{18}\text{O}$ equilibrium fractionation to infer environmental conditions from CRP-1 bivalves, rather than a conventional T-S diagram. $\delta^{18}\text{O}$ values of modern samples 1 and 3, and of Pleistocene samples 5, 7, and 8, are all within the range of estimated equilibrium d_c for today's T and d_w conditions in the area. The slightly increased $\delta^{18}\text{O}$ value of specimen 6 implies a pre- or post-glacial occurrence of this specimen. The Miocene sample (number 4) displays a depleted $\delta^{18}\text{O}$ value, suggesting substantially different environmental conditions from today during the life span of this individual.

Fig. 3 - Stable isotopic composition of marine Quaternary carbonates (slightly modified after Taviani, 1991). Note that CRP-1 Pleistocene samples (circles) all fall within the range of Antarctic carbonates, whilst the only sample from the Miocene section (triangle) falls within the field of Arctic carbonates.



inferred sea-level drop of 20 m would again suggest a pre- or post-glacial occurrence of this specimen.

MIOCENE

Both the Pliocene specimen (sample 2, "*Chlamys tuftsensis*") and the Miocene specimen (sample 4, "*Chlamys*" sp.1) have strongly depleted $\delta^{18}\text{O}$ values of -9.8‰ and -4.6‰ PDB. The XRD scan indicates that aragonite is present in sample 4, arguing against diagenesis as a cause for the negative $\delta^{18}\text{O}$ signal. For sample 2, the lack of aragonite peaks in the XRD scans hints at diagenetic alteration that may also have caused a fractionation of $\delta^{18}\text{O}$ towards negative value and it is therefore excluded from the following interpretation.

The negative value of sample 4 of -4.6‰ PDB suggests that environmental conditions were significantly different from those of today. Under present-day seawater $\delta^{18}\text{O}$ conditions, temperatures in excess of 35°C are needed to achieve this negative $\delta^{18}\text{O}$ values from bivalves. This is an unrealistic scenario for the Miocene Southern Ocean and is not considered further. Conversely, if the modern temperature range of $-2^\circ\text{C} < T < +1^\circ\text{C}$ is maintained, seawater $\delta^{18}\text{O}$ needs to be around -9‰ to -8‰ SMOW to arrive at equilibrium $\delta^{18}\text{O}$ values of -4.6‰ PDB. If we allow for a slightly warmer temperature range similar to that in today's subpolar South Atlantic, $5^\circ\text{C} < T < 7^\circ\text{C}$, then seawater $\delta^{18}\text{O}$ would be around -7‰ SMOW (Fig. 2). Applying plausible seawater temperatures, the negative $\delta^{18}\text{O}$ values from bivalves imply seawater substantially depleted in $\delta^{18}\text{O}$. This contention is also supported by the fact that the CRP-1 Miocene sample falls well within the isotopic field of Arctic marine carbonates (Fig. 3), which is characterised by significant mixing with melt-water (e.g. Hillaire-Marcel, 1981).

Today, the composition of coastal waters in the Southern Ocean is largely controlled by sea-ice freezing and melt-water contribution. Both factors change salinity on a seasonal basis but affect $\delta^{18}\text{O}$ values of seawater in different ways (Craig & Gordon, 1965). Whereas freezing enhances sea-water salinity but leaves $\delta^{18}\text{O}$ of seawater virtually

unchanged, the injection of melt-waters lowers both salinity and $\delta^{18}\text{O}$ of seawater. Very negative $\delta^{18}\text{O}$ values (as low as -54‰ SMOW) for melt-waters have been inferred from extrapolation of $\delta^{18}\text{O}$:salinity relations at near-shore sites on the Antarctic shelf (Weiss et al., 1979). However, the contribution of these melt-waters is small, since no more than approximately 0.3% to the coastal waters around Antarctica that have seawater $\delta^{18}\text{O}$ value close to -0.5‰ SMOW (Weiss et al., 1979). Depletion to -7‰ SMOW, as inferred from the $\delta^{18}\text{O}$ value of the Miocene bivalve specimen, requires that fresh-water fluxes must have been significantly higher and/or isotopically less depleted, suggestive of a warmer and wetter climate compared to the cold and dry climate of today. Because of the proposed near-shore location of CRP-1 (Cape Roberts Science Team, 1998), it is reasonable to infer that the negative values most likely represent a local anomaly close to a source of freshwater runoff.

The existence of rhythmic $\delta^{18}\text{O}$ fluctuations in Miocene benthic foraminiferal isotope records has been used to infer alternations between ice sheet growth and decay on Antarctica (Miller et al., 1991; Wright et al., 1992; Mackensen et al., 1992). High-resolution records of $\delta^{18}\text{O}$ from benthic foraminifera, and coarse-fraction variation in Miocene sediments from the western equatorial Atlantic, contain periodicities of orbital eccentricity, obliquity, and precession further supporting the contention of ice-sheet forcing during the Miocene (Zachos et al., 1997). The amplitudes of these changes (0.5‰ ; Shackleton et al., 1995; Zachos et al., 1997) are less than half of those of the glacial-interglacial ones observed in benthic isotope records of late Pleistocene time. This suggests that either ice volumes involved in the Miocene climatic cycles were smaller or their isotopic signature was more positive.

There is much debate concerning whether Antarctica underwent significant modifications during the Neogene or whether its modern landscape was already shaped by the Miocene or earlier (see Wilson, 1995 and Miller & Mabin, 1998, for a review of the problem). Our result from the early Miocene CRP-1 diamictite indeed suggests that the coastal environment in this sector of the Ross Sea was

significantly different from the truly Antarctic polar regime that we know today. The presence of significant melt water, coupled with warmer surface temperatures during the early Miocene, seems to match better the conditions that are found today in subantarctic or subarctic settings.

ACKNOWLEDGEMENTS

We thank Peter Webb, Gary Wilson, and Scott Borg for their help in obtaining shell material from McMurdo Sound and the Wright Valley; Alan Beu and Bert Jonkers kindly provided information concerning fossil scallops. We are grateful to Warren Dickinson and Paul Aharon for their critical review of the manuscript, to Mike Hambrey and Ken Woolfe for editorial handling, and to Paul Berkman and Mike Thomson for useful discussions. This work was supported by the Italian *Programma Nazionale di Ricerche in Antartide* (PNRA). This is IGM scientific contribution no. 1145.

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