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

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Abstract - Bivalve shells from the CRP-1 drillhole, Cape Roberts (Victoria Land Basin), have been analysed for their stable isotopic 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 δ18O values between +3.64% and +4.56% and δ13C between +0.85% and +1.09%. Oxygen isotopic compositions are close to or at equilibrium conditions with seawater at a temperature in the range of 2°C to 0°C in the absence of melt water inflow. Thus, the CRP-1 carbonate-rich 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 δ18O value of -4.64% and δ13C of -3.35%. 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 CaCO₃ skeleton are temperature and fluid composition (e.g. 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 (Adamiissium 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 (Adamiissium colbecki, Limatula hogdsoni) and early Pleistocene scallops ("Chlamys" tuftsensis) from the Wright Valley were analysed for comparison (Tab. 1).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample location and depth</th>
<th>Age</th>
<th>Species</th>
<th>δ18O % PDB</th>
<th>stdv</th>
<th>δ13C % PDB</th>
<th>stdv</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>McMurdo Sound</td>
<td>Modern</td>
<td><em>Adamiissium</em> colbecki</td>
<td>3.970</td>
<td>0.0117</td>
<td>2.383</td>
<td>0.0087</td>
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<td>2</td>
<td>Wright Valley</td>
<td>Pliocene</td>
<td>&quot;Chlamys&quot; tuftsensis</td>
<td>-9.760</td>
<td>0.0071</td>
<td>-0.207</td>
<td>0.0087</td>
</tr>
<tr>
<td>3</td>
<td>McMurdo Sound</td>
<td>Modern</td>
<td><em>Limatula</em> hogdsoni</td>
<td>3.574</td>
<td>0.0098</td>
<td>0.689</td>
<td>0.0081</td>
</tr>
<tr>
<td>4</td>
<td>CRP-1 62.19 mbsf</td>
<td>Lower Miocene</td>
<td>&quot;Chlamys&quot; sp. 1</td>
<td>4.640</td>
<td>0.0455</td>
<td>3.350</td>
<td>0.0367</td>
</tr>
<tr>
<td>5</td>
<td>CRP-1 32.05 mbsf</td>
<td>Middle Pleistocene</td>
<td><em>Adamiissium</em> sp.</td>
<td>4.192</td>
<td>0.0109</td>
<td>1.343</td>
<td>0.0049</td>
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<td>6</td>
<td>CRP-1 32.05 mbsf</td>
<td>Middle Pleistocene</td>
<td><em>Limatula</em> sp.</td>
<td>4.387</td>
<td>0.0109</td>
<td>0.982</td>
<td>0.0085</td>
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<td>7</td>
<td>CRP-1 32.05 mbsf</td>
<td>Middle Pleistocene</td>
<td><em>Limatula</em> sp.</td>
<td>3.988</td>
<td>0.0154</td>
<td>1.107</td>
<td>0.0069</td>
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<td>8</td>
<td>CRP-1 32.05 mbsf</td>
<td>Middle Pleistocene</td>
<td><em>Adamiissium</em> sp.</td>
<td>4.096</td>
<td>0.0038</td>
<td>1.152</td>
<td>0.0056</td>
</tr>
</tbody>
</table>
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. CO₂ 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 δ¹⁸O as determined from replicate measurements of an internal laboratory standard (Solenhofen Limestone) is better than 0.08‰. The isotopic 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 δ¹⁸O 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 minimize 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 (CuKα radiation at 35mA and 40kV, scanning angle was 25°-32°). Identification of the d₄₀₀ 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 δ¹⁸O signature of the sample (see below). The only other pre-Pleistocene sample, no. 2, is a shell of "Chlamys" tufsaensis 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

δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O 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 paleotemperature equation of Shackleton (1974), equilibrium δ¹⁸O for calcite is estimated at between +3.0‰ and +4.2‰ PDB. δ¹⁸O 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 δ¹⁸O. The close correspondence of these values with estimated equilibrium δ¹⁸O values confirms the equilibrium or near-equilibrium δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O value of sample 6 (Limatula sp.) of +4.4‰ PDB is slightly higher than the most positive modern equilibrium δ¹⁸O 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 δ¹⁸O 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 δ¹⁸O (Labeuyrie et al., 1987; Fairbanks, 1989), the 0.2‰ increase in δ¹⁸O 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 δ¹⁸O reflects increased global ice volume, the
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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 δ¹⁸O values, we infer that this shell was probably affected by diagenesis.

Fig. 2 - Temperature-δ¹⁸O of seawater (dw) diagram showing equilibrium δ¹⁸O of calcite (dc) fractionation lines and δ¹⁸O values of CRP-1 bivalve mollusc specimens. dc lines were computed using Shackleton’s (1974) “cold” palaeotemperature equation. We have chosen to use a T-δ diagram in conjunction with predicted δ¹⁸O equilibrium fractionation to infer environmental conditions from CRP-1 bivalves, rather than a conventional T-S diagram. δ¹⁸O values of modern samples 1 and 3, and of Pleistocene samples 5, 7, and 8, are all within the range of estimated equilibrium dc for today’s T and dw conditions in the area. The slightly increased δ¹⁸O value of specimen 6 implies a pre- or post-glacial occurrence of this specimen. The Miocene sample (number 4) displays a depleted δ¹⁸O value, suggesting substantially different environmental conditions from today during the life span of this individual.
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 tuftensis") and the Miocene specimen (sample 4, "Chlamys" sp.1) have strongly depleted δ18O values of -9.8‰ and -4.6‰ PDB. The XRD scan indicates that aragonite is present in sample 4, arguing against diageneisis as a cause for the negative δ18O 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 δ18O 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 δ18O conditions, temperatures in excess of 35°C are needed to achieve this negative δ18O 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°C<T<+1°C is maintained, seawater δ18O needs to be around -9‰ to -8‰ SMOW to arrive at equilibrium δ18O values of -4.6‰ PDB. If we allow for a slightly warmer temperature range similar to that in today's subpolar South Atlantic, 5°C<T<7°C, then seawater δ18O would be around -7‰ SMOW (Fig. 2). Applying plausible seawater temperatures, the negative δ18O values from bivalves imply seawater substantially depleted in δ18O. 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 δ18O values of seawater in different ways (Craig & Gordon, 1965). Whereas freezing enhances sea-water salinity but leaves δ18O of seawater virtually unchanged, the injection of melt-waters lowers both salinity and δ18O of seawater. Very negative δ18O values (as low as -54‰ SMOW) for melt-waters have been inferred from extrapolation of δ18O: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 δ18O value close to -0.5‰ SMOW (Weiss et al., 1979). Depletion to -7‰ SMOW, as inferred from the δ18O 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 δ18O 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 δ18O 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.

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