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Molluscan Stable Isotope Temperature Estimates of the Southwestern Ross Sea during the Early Oligocene and Early Miocene, CRP-2/2A and CRP-3, Victoria Land Basin, Antarctica

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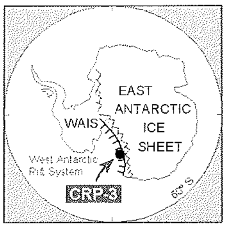
Abstract - Stable isotope analyses of marine bivalve growth increment samples have been used to estimate early Oligocene (29.4 - 31.2) Ma and early Miocene (24.0 Ma) seafloor palaeotemperatures from the southwestern continental margin of the Ross Sea. Measured $\delta^{18}O$ values average +2.5‰ in the early Miocene and range between +1.26 to +3.24‰ in the early Oligocene. The results show that palaeoceanographic conditions in McMurdo Sound during the mid-Cenozoic were significantly different from those of today. The minimum estimated spring through late summer seasonal temperature range was 3°C during the early Miocene and between 1 and 5°C during the early Oligocene. This compares to the equivalent modern day range of <0.5°C within the sound. Absolute seawater temperatures at <100 m depth were of the order of 5 to 7°C during both time slices, compared to modern day values of -1.4 to -1.9°C in the same area. The results are in broad agreement with early Oligocene Mg/Ca temperature estimates from deep Atlantic foraminifera as well as estimates from local terrestrial palynology and palaeobotany.



INTRODUCTION

Estimates of marine palaeotemperatures are critical to our understanding of the long-term evolution of the Antarctic cryosphere. The stable oxygen isotope composition of carbonate subsamples of marine bivalves provides a proxy record of marine temperatures during the lifetime of the organism. In addition, multiple growth increment samples on single bivalve shells may also be used to estimate inter-annual and seasonal temperature variations.

The 624-m-long CRP-2/2A core encountered a succession of Quaternary, Pliocene, Early Miocene, and Oligocene glacimarine sediments. In contrast, only the uppermost *c.* 200 m of the early Oligocene section recovered in CRP-3 contained material suitable for dating and stable isotope analysis. We report here a preliminary stable isotope study of the currently available well preserved aragonitic and calcitic molluscan shell material from the early Miocene and early Oligocene of drillholes CRP-2/2A and CRP-3. The study is intended to provide first-order proxy data to assist in more detailed palaeoceanographic studies of the region.

ANALYTICAL METHODS

Well-preserved biogenic carbonate suitable for stable isotope analyses was obtained from eight horizons within the working halves of the CRP-2/2A and CRP-3 cores. The fragments represent splits of the molluscan shell material used for strontium isotope dating (Lavelle, 2000; Lavelle, this volume). Information on shell preservation and taphonomy are presented in Lavelle (2000) and Lavelle (this volume). Full high-resolution growth increment profiling of individual bivalve fragments proved impossible due to the small size of the available shell fragments (fragment weight averaged 2-5 mg of carbonate). Instead, the fragments were broken along growth lines at *c.* 1 mm spacing to provide 1-4 broad-scale growth increment samples from each specimen. Individual samples covered a shell span of 5-10 growth ridgelets in both the pectinids and the modiolids. The extremely thin nature of the shells, characteristic of many modern cold-water Antarctic bivalves, made it impossible to identify and separate individual crystalline layers with the shells. Whole shell fragments were analysed throughout the study.

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The samples (weighing 40-500 μg) were placed in glass vials, gently crushed, and dried in an oven at 50°C overnight. Individual vials were sealed with a septum and screw cap and analysed using a Micromass Multicarb preparation system attached to a PRISM mass spectrometer in the Godwin Laboratory, University of Cambridge. Results are reported to the international standard V-PDB and the precision was better than +/- 0.08‰ for $\delta^{18}O$ and better than +/- 0.06‰ for $\delta^{13}C$ measurements.

The «cold water» equations used to convert measured carbonate $\delta^{18}O$ to temperature of precipitation are:

Aragonite (Grossman & Ku (1986) as modified by Barrera et al. (1994)):

$$T(°C) = 22.05 - 4.72(\delta^{18}O_{arag} - \delta^{18}O_{water})$$

Calcite (O'Neil et al. (1969) as published by Shackleton (1974)):

$$T(°12C) = 16.9 - 4.38(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.10(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$$

As the $\delta^{18}O$ value of Miocene and Oligocene seawater is unknown, we have produced two palaeotemperature estimates for each sample. Both assume that early Oligocene and early Miocene McMurdo Sound seawater were both warmer and more saline than the average conditions observed today (see palaeoenvironmental summary in Cape Roberts Science Team, 1999, 2000). Implicit in these assumptions is that the Antarctic continent was less glaciated than today (see deep-sea references in «Discussion and Palaeotemperature Estimates»). The Signy meltwater scenario (SS) uses the measured mean modern $\delta^{18}O_{seawater}$ value of –1.2‰ V-SMOW for a coastal high latitude site where normal seawater mixes with freshwater of highly negative isotopic composition (*c.* -35‰ V-SMOW: Marshall et al., 1996). The modern-day McMurdo Sound summer scenario (MS) assumes more frigid conditions and a lowest $\delta^{18}O_{seawater}$ value of –0.7‰ V-SMOW (Barrera et al., 1990).

The age model used throughout this study is that of Lavelle (2000) and Lavelle (this volume).

RESULTS

Interpreted SEM images of the 10 analysed shell fragments (presented in Lavelle (2000) and Lavelle (this volume)) show the preservation of original molluscan aragonite and calcite at the submicron level. Stable oxygen and carbon isotope results are summarised in table 1 and are plotted in figure 1. Carbonate $\delta^{18}O$/ $\delta^{13}C$ values are related to V-PDB throughout.

EARLY MIOCENE

Following the separation of molluscan samples for strontium isotope stratigraphy and taxonomy, a single unidentified aragonitic bivalve fragment large enough for stable isotope analyses was analysed from 246.97 mbsf (metres below sea floor) in CRP-2A. The specimen was dated at 24.0 (+0.4/-0.3) Ma using strontium isotope stratigraphy (Lavelle, 2000). The two coarse scale growth increment samples analysed display a range of 0.7‰ $\delta^{18}O$ (2.13 and 2.83‰) and 1.29‰ $\delta^{13}C$ (1.80 and 3.09‰).

EARLY OLIGOCENE

Thirteen growth increment samples were analysed from 4 aragonitic modiolid bivalve fragments recovered from between 447.69 and 483.18 mbsf in CRP-2A. All of the samples represented fragments broken from the mid-part of the valve – *i.e.* no umbonal, hinge or margin samples were analysed. The mean ages of the samples range from 29.4 to 30.5 Ma. Four growth increment splits of Fragment 2 (447.69 mbsf; 29.4 Ma) displayed a $\delta^{18}O$ range of 1.05‰ (1.50 to 2.55‰) and a $\delta^{13}C$ range of 0.55‰ (0.45 to 1.00‰). Fragment 3, from 460.76 mbsf (29.6 Ma), was divided into 3 samples perpendicular to the valve growth axis. The measured $\delta^{18}O$ range of 1.24‰ is the largest range observed in this study and also exhibits the heaviest Tertiary $\delta^{18}O$ value measured to date (3.24‰). Fragment 4, recovered from 463.36 mbsf (29.9 Ma) and split into 2 samples, was one of the smallest specimens analysed. The small ranges in $\delta^{18}O$ (0.03‰) and $\delta^{13}C$ (0.17‰) are likely to be partially the result of the very close sample spacing. Both $\delta^{18}O$ and $\delta^{13}C$ results are some of the lightest values measured in this study (1.50‰ $\delta^{18}O$ and –0.24‰ $\delta^{13}C$). Fragment 5 was the deepest well-preserved carbonate sample recovered from CRP-2A at 483.15 mbsf (30.5 Ma). The four sub-samples analysed display a small $\delta^{18}O$ range (0.25‰), but a very large range in $\delta^{13}C$ values (2.64‰).

Eleven sub-samples were analysed from five pectinid fragments recovered from between 29.94 and 190.29 mbsf within the CRP-3 drill hole. All of the analysed SEM micrographs revealed the preservation of original cross-foliated calcite (Lavelle, this volume). Fragment 6 (29.94 mbsf; 31.0 Ma) was split into four growth-perpendicular sub-samples. Measured values range 0.86‰ (1.65-2.51‰) for $\delta^{18}O$ and 0.21‰ (2.74-2.95‰) for $\delta^{13}C$. Fragment 7, a small pectinid sample recovered from 47.55 mbsf (31.0 Ma), was split in half and shows a range of 1.07‰ (1.26-2.33‰) in $\delta^{18}O$ and 0.84‰ (-0.03-0.81‰) in $\delta^{13}C$. Three separate fragments were recovered from 190.29 mbsf (31.2 Ma). All five sub-samples display very light $\delta^{18}O$ values (0.57 to -5.23‰). The $\delta^{13}C$ values also display a large scatter, from 0.15‰ to –9.45‰.

DISCUSSION AND PALAEOTEMPERATURE ESTIMATES

In converting the measured carbonate $\delta^{18}O$ values to ambient marine temperatures, it is necessary to make two major assumptions:

The shell was deposited in equilibrium with the surrounding seawater.

In dealing with extinct species, as in this study, this assumption is difficult to validate. However, in the case of the pectinid fragments from CRP-3, the nearest living Antarctic relative of this species (*Adamussium colbecki*; B. Jonkers, pers. comm.) has been shown to precipitate its exterior shell layers in isotopic equilibrium with ambient seawater (Barrera et al., 1990; Barrera et al., 1994). For this reason, our multi-layer analyses of the relatively thin-shelled CRP-3 pectinid are assumed to reflect ambient seawater conditions at the time of precipitation. Vital effect assumptions with respect to the modiolid samples recovered from CRP-2A are more tenuous, since there is no known modern occurrence of the family within Antarctica today. However, work on warmer water members of the mussel family shows that they also commonly precipitate their shells in isotopic equilibrium with surrounding seawater (*e.g.* van der Putten et al., 2000). The possibility of discrete areas of non-equilibrium precipitation within individual shells (*e.g.* Barrera et al., 1994, Marshall et al., 1996) cannot be quantified with the small number of samples available for the current study. Our procedure of selecting samples from the centre of the valve, away from extreme growth rate areas such as the shell margin and the hinge region should minimise this effect.

The local $\delta^{18}O_{seawater}$ at the time of deposition can be estimated.

The most common procedure is to make a single assumption of the early glacial value of Eocene to early Oligocene seawater at nearshore sites (*e.g.* –1.2‰, Andreasson & Schmitz, 1996; –1‰, Dutton et al., 2000). Deep sea $\delta^{18}O_{seawater}$ estimates for the early Oligocene range between –0.2‰ (Lear et al., 2000) and -0.5‰ (Zachos et al., 1994; Ivany et al., 2000). Independent palaeoenvironmental evidence based on sedimentology and palaeontology (Cape Roberts Science Team 1999, 2000) suggests that the CRP sites were more temperate than today, with iceberg influence a common feature throughout the Cenozoic section. The presence of a small but measurable local meltwater flux has also been proposed (Aghib F.S., pers. comm.). Our McMurdo Sound Summer scenario (MS) $\delta^{18}O_{seawater}$ value of –0.7‰ V-SMOW assumes a 0.5‰ decrease in average salinity from the measured modern seawater value (salinity = 34.8‰; $\delta^{18}O_{seawater}$ = -0.2‰), due to a postulated increase in meltwater flux ($\delta^{18}O_{meltwater}$ = -35‰). The Signy Summer scenario (SS) (-1.2‰) takes a more extreme view,

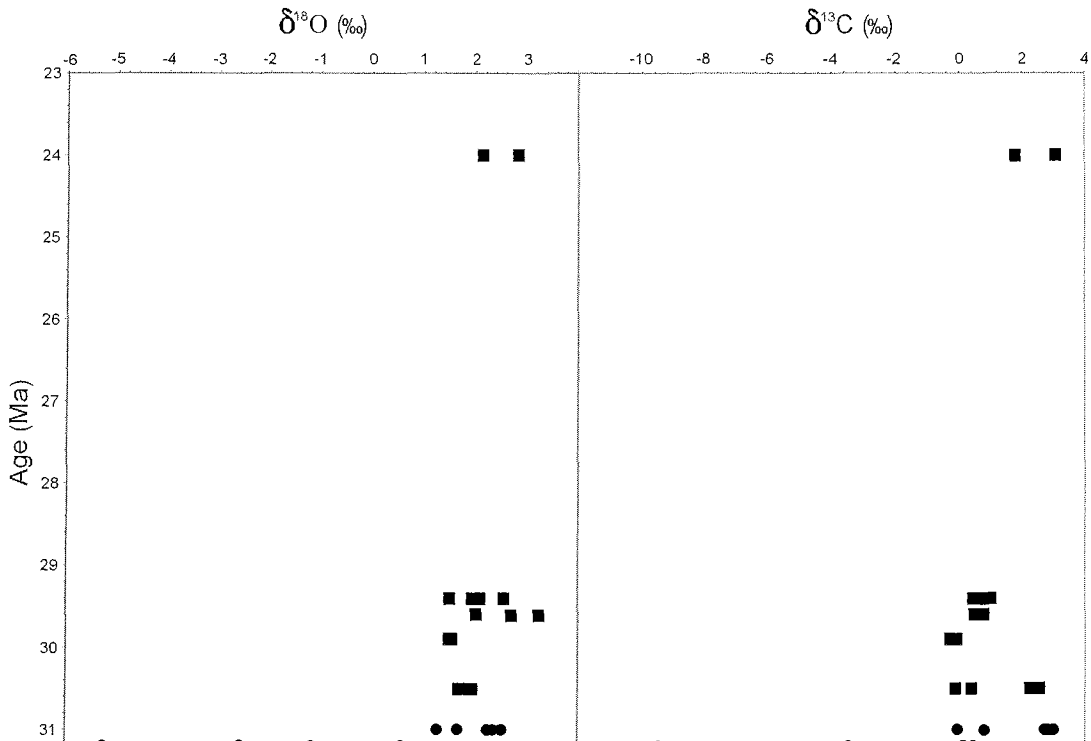

Fig. 1 - $\delta^{18}O$ and $\delta^{13}C$ data *vs.* depositional age for CRP-2/2A and CRP-3 drillholes. Filled squares = aragonite shells; filled circles = calcite shells. Measurement errors fall within the symbols.

Tab. 1 - Stable isotope data for marine bivalve fragments from the CRP-2/2A and CRP-3 drillholes.

Depth (mbsf) (*max*)	Sample	Mineralogy	Age (Ma)	$\delta^{18}O$ (*‰ V-PDB*)	$\delta^{13}C$ (*‰ V-PDB*)	T(°C) *Signy Mean*	T(°C) *McMurdo Summer*
247.00	Unidentified fragment	Aragonite	24.0	2.13	1.80	6.3	8.7
247.00	Unidentified fragment	Aragonite	24.0	2.83	3.09	3.0	5.4
447.81	Modiolid fragment	Aragonite	29.4	2.55	0.72	4.4	6.7
447.81	Modiolid fragment	Aragonite	29.4	1.97	0.80	7.1	9.4
447.81	Modiolid fragment	Aragonite	29.4	1.50	0.45	9.3	11.7
447.81	Modiolid fragment	Aragonite	29.4	2.07	1.00	6.6	9.0
460.78	Modiolid fragment	Aragonite	29.6	2.00	0.53	6.9	9.3
460.78	Modiolid fragment	Aragonite	29.6	3.24	0.63	1.1	3.5
460.78	Modiolid fragment	Aragonite	29.6	2.69	0.75	3.7	6.0
463.38	Modiolid fragment	Aragonite	29.9	1.53	-0.24	9.2	11.5
463.38	Modiolid fragment	Aragonite	29.9	1.50	-0.07	9.3	11.7
483.18	Modiolid fragment	Aragonite	30.5	1.93	2.53	7.3	9.6
483.18	Modiolid fragment	Aragonite	30.5	1.73	2.26	8.2	10.6
483.18	Modiolid fragment	Aragonite	30.5	1.89	0.41	7.5	9.8
483.18	Modiolid fragment	Aragonite	30.5	1.67	-0.11	8.5	10.9
29.96	Pectinid fragment	Calcite	31.0	2.51	2.95	2.0	3.9
29.96	Pectinid fragment	Calcite	31.0	2.24	2.87	3.0	4.9
29.96	Pectinid fragment	Calcite	31.0	2.50	2.74	2.1	3.9
29.96	Pectinid fragment	Calcite	31.0	1.65	2.87	5.2	7.2
47.57	Pectinid fragment	Calcite	31.0	1.26	-0.03	6.7	8.7
47.57	Pectinid fragment	Calcite	31.0	2.33	0.81	2.7	4.5
190.31	Pectinid fragment	Calcite	31.2	0.57	0.15	n/a	n/a
190.31	Pectinid fragment	Calcite	31.2	-1.15	0.16	n/a	n/a
190.31	Pectinid fragment	Calcite	31.2	-1.16	0.44	n/a	n/a
190.31	Pectinid fragment	Calcite	31.2	-2.56	-3.44	n/a	n/a
190.31	Pectinid fragment	Calcite	31.2	-5.23	-9.45	n/a	n/a

assuming a maritime Antarctic climate with seasonal ice cover, as currently observed around the sub-Antarctic Islands. In both cases, sub-surface inter-seasonal salinity changes are minimal (Barrera et al., 1990; Marshall et al., 1996).

Table 1 lists both MS and SS estimates of early Oligocene and early Miocene seafloor temperatures. Palaeoecological evidence suggests that the bivalves inhabited nearshore water depths of <100 m (Cape Roberts Science Team, 1999, 2000). Figure 2 shows the calculated palaeotemperature ranges, plotted against depositional age. Our calculations are unlikely to reflect the full local seasonal temperature range since: (1) the dominant period of bivalve shell growth in the region is from spring through late summer (Barrera et al., 1990); (2) the combination of slow growth rates and small sample size restricted our ability to recover full multisample growth profiles. Extensive sedimentological evidence of ice rafting across the site suggests winter surface water temperatures may have been close to freezing (Cape Roberts Science Team, 1999, 2000).

Early Miocene (24.0 Ma) benthic shallow marine temperature estimates are 3.0 to 6.3°C (SS) and 5.4 to 8.7°C (MS). This compares to the modern McMurdo Sound shelf bottom water temperature range of -1.9 to -1.4°C. Early Oligocene palaeotemperatures vary between 1.1 to 9.3°C (SS) or 3.5 to 11.7°C (MS). Of note is the small apparent summer warming between 31.0 Ma [2.0 to 6.7°C (SS); 3.9 to 8.7°C (MS)] and 30.5 Ma [7.3 to 8.5°C (SS); 9.6 to 10.9°C (MS)].

These estimates are in broad agreement with:

i. Deep Atlantic marine temperature estimates for the early Oligocene from Mg/Ca ratios in foraminifera (6 to 7°C; Lear et al., 2000).
ii. Estimates from terrestrial palynology for the mean warmest month land surface air temperature at Cape Roberts during the late Oligocene to early Miocene (7 to 10°C; Raine, 1998; Cape Roberts Science Team, 1999) and early Oligocene (10-12°C; Raine & Askin, this volume). The latter estimate was based on modern altitudinal and latitudinal treeline climate of *c.* 10°C for the mean temperature of the warmest month (Cantrill, this volume). These are based on minimum daily maximum summer temperatures for *Nothofagus* growth (*e.g.* Hill & Jordan, 1996).

The large scatter and relatively light $\delta^{18}O$ and $\delta^{13}C$ values measured in the two deepest fragments (9 and 10) recovered from CRP-3 are assumed to reflect either increased meltwater flux at this time, or a small

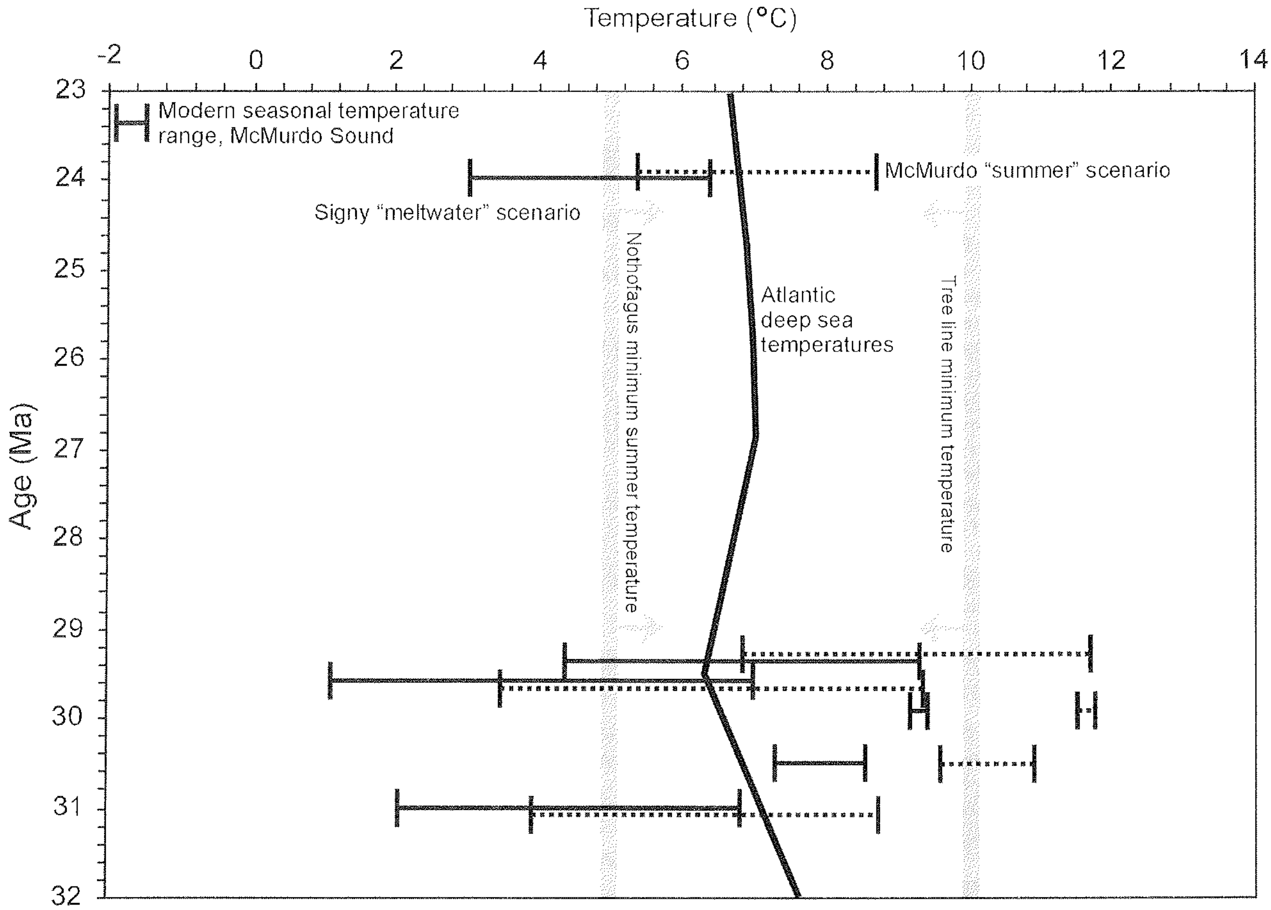

Fig. 2 - Marine palaeotemperature estimates *vs.* depositional age for shelf waters in the McMurdo Sound region during the early Oligocene and earliest Miocene. Atlantic deep sea temperatures are from Lear et al. (2000).

degree of unrecognised diagenetic carbonate within the samples. This conclusion is supported by $\delta^{18}O$ and $\delta^{13}C$ values of -10‰ and -15‰, respectively, measured in a sample of diagenetic carbonate at 141 mbsf in CRP-3 (Aghib F.S., pers. comm.). Note that in either case, the amount of meltwater or secondary contamination involved must be very small, since the $^{87}Sr/^{86}Sr$ values of fragments 9 and 10 are identical to those of other well preserved samples within CRP-3 (Lavelle, this volume).

The $\delta^{13}C$ variations measured in molluscan carbonate are rarely in equilibrium with the $\delta^{13}C$ value of associated seawater inorganic carbon (*e.g.* van der Putten et al, 2000). Respiration rate, feeding mode, changes in the dissolved bicarbonate composition, *etc.*, all result in fluctuations in the contribution of metabolic carbon to the shell. The detailed interpretation of the $\delta^{13}C$ record is beyond the scope of this core characterisation study, although the data are fully reported (Tab. 1). The previous suggestion that the unusual occurrence of modiolid bivalves in CRP-2A may have been linked to methane gas seepage (Cape Roberts Science Team, 1999) is unlikely based on the relatively heavy $\delta^{13}C$ values measured, and by inference, the absence of authigenic carbon.

CONCLUSIONS

For alternative assumed initial seawater $\delta^{18}O$ values (modern McMurdo Sound summer, MS; and modern Signy Island meltwater-influenced seawater, SS), our calculated mean of the measured ranges of McMurdo shelf bottom water temperatures are 7.1°C (MS) and 4.6°C (SS) for the early Miocene and 7.6°C (MS) and 5.2°C (SS) for the early Oligocene.

Independent of our assumptions of $\delta^{18}O_{seawater}$, minimum inter-seasonal temperature ranges are 3.3°C in the early Miocene and range between 1.2 and 4.9°C in the early Oligocene (using fragments with a minimum of 4 analysed growth increment samples only).

Careful note should be taken of our estimates of regional Tertiary $\delta^{18}O_{seawater}$ in the final palaeotemperature calculations. While we believe the assumptions made and ranges used are realistic, unrecognised variations in this value remain the largest potential source of error in our calculations.

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