

Temperatures in the Ross Sea During the Early to Mid-Miocene from Clumped Isotope Analysis of ANDRILL-2A Carbonates

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Abstract

Antarctica's peripheral ice shelves are a critical component of the ice sheet's mass balance, contributing to the sensitivity of the Antarctic cryosphere and global sea-level. Despite being a fundamental aspect of ice-sheet dynamics, the relationship between water temperatures on continental shelves and changes in CO₂ conditions has not been clearly determined. This study investigates conditions in the Ross sea over the early and middle Miocene (~23-14 million years ago), when $p\text{CO}_2$ was >400 ppmv, using samples from the Antarctic geologic drilling (ANDRILL) program. Clumped isotope data for primary carbonates indicate average temperatures for shelf waters to be >10°C warmer than the present. Some diagenetic carbonates have low water $\delta^{18}\text{O}$ values, like modern sea ice brines that form from freezing of seawater, with evidence for aragonite-aragonite neomorphism. Given the role of the Ross Sea in affecting ice sheet stability and Antarctic bottom water production, our results can serve as a reference dataset to constrain thresholds for ice shelf disintegration, and Southern Ocean polar amplification.

1. Introduction

The Antarctic Ice Sheet's mass loss has been accelerating over the past two decades, contributing to global sea-level rise (Shepherd et al. 2012; 2018). The acceleration of mass loss is associated with the dynamic interaction of the cryosphere in the thinning or collapse of ice-

sheets which serve to buttress the seaward flow of inland ice. The Ross Ice Shelf, the world's largest ice shelf, is currently close to steady-state, but historical geologic records indicate its sensitivity to global climate and the potential for sudden melting (Stevens et al. 2020; Catania et al. 2012).

1.1 Overview of Antarctic Ice Shelf Interactions

The understanding of ice-ocean-atmosphere interactions is imperative in analyzing the stability of the cryosphere and projecting global sea-level change. Ice shelves, the marine component of ice sheets, are warmed from below by upwelled Circumpolar Deep Water and from above by the atmosphere. However, the response of ice shelves to changing CO₂ concentrations and temperature has not been determined due to difficulties and uncertainties in simulating the complex relationship between wind-driven ocean circulation, ice albedo, bathymetry, and marine ice sheet instability (Solomon 2007). With the relative paucity of modern empirical data, geologic proxy records of past conditions are valuable for constraining the climate evolution of the Antarctic and are vital for testing models against (Solomon 2007).

1.2 Early-Middle Miocene Climate

The middle-Miocene is of critical importance because of its potential as a future warm climate analogue. It is the most recent period in geologic history with atmospheric CO₂ levels comparable to modern projected elevated CO₂ levels (Modestou et al. 2020). According to proxy data, CO₂ concentrations during this interval ranged from 350-500 ppm (Greenop et al. 2014; A. K. Tripathi, Roberts, and Eagle 2009). Geologic records from the Antarctic geologic drilling (ANDRILL) program reveal that water temperatures in the Ross sea were 6-10°C

warmer during the mid-Miocene than in the Ross Sea today (Levy, Harwood, Florindo, Sangiorgi, Tripathi, von Eynatten, et al. 2016). During this warm period, the Antarctic ice sheet retreated well inland of the coast, suggesting that the global climate system and Antarctic ice sheet were highly sensitive during the mid-Miocene (Levy, Harwood, Florindo, Sangiorgi, Tripathi, von Eynatten, et al. 2016).

Previous studies of ANDRILL core 2A (AND-2A) biogenic carbonates found evidence of extensive chemical alteration, primarily dissolution and chemical exchange with pore fluid (Marcano et al. 2015; Beu and Taviani 2014). The residual porewater brines were also found to have $\delta^{18}\text{O}$ values as low as -11‰ (Vienna Standard Mean Ocean Water, VSMOW) (Frank, Gui, and the ANDRILL SMS Science Team 2010). The infiltration and formation of these cryogenic brines are hypothesized to have formed as isolated water masses frozen in the advance and retreat of glaciers (Starinsky and Katz 2003; Frank, Gui, and the ANDRILL SMS Science Team 2010; Staudigel et al. 2018) and make classical temperature proxy measurements, such as $\delta^{18}\text{O}$, difficult to interpret.

Here we report stable isotope-based temperatures and water $\delta^{18}\text{O}$ values from the AND-2A core. Due to the cryogenic, hypersaline brines and large inputs of glacial meltwater at high latitudes, $\delta^{18}\text{O}$ values are biased to lower, meteoric values in this succession (Frank, Gui, and the ANDRILL SMS Science Team 2010). Therefore, constructing a $\delta^{18}\text{O}$ - based temperature history was not feasible. Instead, we use carbonate ‘clumped’ isotope thermometry (Eiler 2007) to determine carbonate mineral precipitation on bivalves (Came et al. 2007; Eagle et al. 2013; Henkes et al. 2013) as well as associated sediments. These temperatures are combined with simultaneously determined carbonate $\delta^{18}\text{O}$ values to calculate water $\delta^{18}\text{O}$ values near the Antarctic coast.

1.3 Background on Clumped Isotopes

A clumped isotope is a molecule containing two or more heavy isotopes. The vibration of a bond between two atoms can be approximated as a simple harmonic oscillator and as the mass of atoms increases, their bond vibrates slower and is more stable, resulting in lower zero-point energy (Urey 1947; Schauble, Ghosh, and Eiler 2006). The lower vibrational energy of clumped isotopes results in thermodynamic favorability towards clumping in association with decreasing internal energy, or in this case, temperature (Eiler 2007).

Carbonate clumped isotopes are a relatively new geochemical temperature proxy based on the excess abundance of $^{13}\text{C} - ^{18}\text{O}$ bonds in the carbonate lattice compared to a theoretical stochastic (random) distribution (Bernasconi et al. 2018). Δ_{47} is used to quantify the abundance of clumped $^{13}\text{C} - ^{18}\text{O}$ bonds in the carbonate-containing compounds. In the clumped isotope reaction, the equilibrium constant approaches 1 as temperature increases, indicating an increase in stochastically distributed clumped isotopes (Aradhna K. Tripathi et al. 2015). Therefore, the equilibrium constant for this reaction can be used as a paleotemperature indicator. As opposed to conventional paleoclimate proxies, like $\delta^{18}\text{O}$ and Mg/Ca, the clumped isotope proxy allows for the reconstruction of paleoclimates independent of the isotopic composition of the waters in which the mineral grew. Direct evidence for the oxygen isotope concentration of primitive waters has only rarely been studied and glacial-interglacial periods have an unknown but significant effect on seawater composition (Ghosh et al. 2006). Antarctic ice sheet retreat and expansion during the Miocene Climatic Optimum and Miocene Climate transition is evidenced by the ANDRILL project and Ocean Drilling Program Sites 1165 and U1356, suggesting significant changes in the $\delta^{18}\text{O}$ isotopic composition of Antarctic waters over the middle Miocene (Fielding et al. 2011).

In this study, clumped isotope temperature estimates are then combined with simultaneously determined carbonate $\delta^{18}\text{O}$ values to calculate $\delta^{18}\text{O}$ values near the Antarctic coast. The measurement of carbonate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios and clumped isotope temperatures facilitate the calculation of fluid $\delta^{18}\text{O}$ values using carbonate-water fractionation equations, allowing for the construction of a detailed paleoclimate record and providing insights into the fluids associated with diagenesis.

2. Methods

2.1 Sample Preparation

The AND-2A core was drilled in late 2007 to a depth of 1138.54 m from the southwestern McMurdo Sound, Ross Sea, at 77°45.488'S, 165°16.613'E (Acton and Crampton 2008). The AND-2A core records Pleistocene through late Miocene glaciomarine and marine sediments in McMurdo Sound, with the majority of the core recording the interval between 15.5 and 20.2 Ma (Acton and Crampton 2008). Multiple coquina-like shelly deposits occur throughout the core, particularly in the early and middle Miocene interval. Several shell samples are suspected to have been affected by subsurface diagenetic alteration, while other specimens are thought to be pristine based on the detailed study of mineralogy, ultrastructure, cathodoluminescence, trace element abundance, and Sr isotope ratios (Marcano et al. 2009; 2015).

A total of 28 mollusk samples were received from the AND-2A core between 59.75 m and 1063.71 m consisting of bivalves, cirripedes, serpulid tubes, and matrix materials. Because these samples were from a drill core, they had been processed previously and contained very little to no organic material. Some samples were also previously screened for diagenesis based on texture and trace element concentrations (Marcano et al. 2009), while others were visually

examined for diagenesis. Powder x-ray diffraction analysis at Caltech and the University of Michigan was used to determine the mineralogy of the fossil specimens (Marcano et al. 2009).

The 4 mg samples were powdered in preparation for gas-source mass spectrometry for analysis. The isotope measurements were performed on a Thermo MAT 253 dual inlet mass spectrometer at Caltech (Passey et al. 2010; Defliese and Tripathi 2020). Sample replicates were either prepared by the use of a custom-built common acid bath carbonate preparation device (as described in Passey et al. 2010), or by acid digestion in sealed reaction vessels. The samples prepared via the automated carbonate device were reacted with 105% phosphoric acid at 90°C, while offline reactions were conducted at 25°C to produce carbon dioxide. The abundance of clumped carbon dioxide molecules of mass 47, which contain both ^{13}C and ^{18}O isotopes, relative to the expected stochastic distribution of this combination is reported by the parameter Δ_{47} (Bernasconi et al. 2018). Δ_{47} values were standardized and placed on the Absolute Reference Frame (Dennis et al. 2011) by the use of equilibrated gas standards prepared at 1000 and 25 °C that were interspersed with sample unknowns. An acid fractionation factor of +0.092‰ was used to correct for samples reacted at 90°C (Defliese, Hren, and Lohmann 2015).

2.2 Measurement Procedure: Δ_{47} Calculation

All masses were measured simultaneously through the mass spectrometer, allowing us to take the ratio of the smaller masses to the most abundant mass. Δ_{47} values were converted to temperatures using the Δ_{47} -temperature calibration of Eagle et al. (2013) and Bernasconi et al. (2018). Δ_{47} -based temperatures were combined with measured $\delta^{18}\text{O}$ values to calculate water $\delta^{18}\text{O}$ values, using the calcite-water equation of Kim and O'Neil (1997) and aragonite-water equation of Kim et al. (2007). Carbon and oxygen isotope values of carbonates are reported

relative to the Vienna Pee Dee Belemnite (VPDB) Standard and oxygen isotope values of water are reported relative to Vienna Standard Mean Ocean Water (VSMOW).

3. Results

The isotopic values for all samples discussed are displayed in Table 1.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of core matrix cements and macrofossils suspected of diagenetic alteration were significantly more negative than pristine samples. The $\delta^{18}\text{O}$ values of all the samples ranged from -8.2‰ to 4.2‰ where most altered samples exhibited $\delta^{18}\text{O}$ values between -8.2‰ and -0.7‰ and unaltered samples ranged from -3.7‰ to 3.9‰ (Fig. 1). There were some exceptions where isotopic values did not indicate diagenesis, but elemental analysis suggested carbonate alteration (Fig. 1). Samples suspected of alteration also exhibited higher Δ_{47} -based temperatures than pristine samples, with just a few exceptions (Fig. 2). Clumped isotope temperatures from preserved samples ranged from 6.7°C to 13.2°C via the Eagle et al. (2013) calibration, while the Bernasconi (2018) calibration yielded slightly higher temperatures from 7.8°C to 16.6°C. Matrix materials exhibited high Δ_{47} -based temperatures, ranging from 33.6°C to 97.4°C, compared to nearby calcitic bivalves, likely indicating inputs from mixed detrital sediments and fabric-selective thermal resetting.

During the mid-Miocene climatic optimum, growth temperatures for preserved samples average 10.6°C (Eagle et. al 2013 calibration). These likely represent summer temperatures within the water column, given that these specimens grew on the ocean floor, sea surface temperatures were probably higher than the values we report above. Calculated seawater $\delta^{18}\text{O}$ values for the mid-Miocene range from -8.4 to 3.6 ‰ VSMOW, and average -1.9 ‰, indicating some contributions from either glacial meltwater or precipitation runoff to the local seawater.

Global seawater at this time had a $\delta^{18}\text{O}$ value of approximately -0.50‰ (Lear et al. 2000), so only a small contribution of glacial meltwater ($\sim 30\text{‰}$ VSMOW) would be necessary to reach the more negative seawater values calculated for the mid-Miocene.

4. Discussion

In both altered and pristine carbonates, the Δ_{47} -based temperatures decrease with increasing depth, indicating formation and recrystallization of carbonates at increasingly higher temperatures (Fig. 3). Our Δ_{47} -based temperatures generally agree with the proxy-derived temperatures for ANDRILL 2A carbonates as described in Levy et al. (2016) and Staudigel et al. (2018) (Fig. 4, 5). Furthermore, insufficient core coverage and sample availability results in discontinuous coverage between 2.5 and 11.3 Ma, and 11.7 to 15.9 Ma.

4.1 Isotopic Comparisons

The $\delta^{18}\text{O}$ values of porewater are considerably greater than those of pristine core matrix cements and macrofossils. The correspondence between carbonate and porewater oxygen isotope values indicate alteration in the biogenic carbonate samples and confirm alteration in the labeled samples. Isotopic analysis of the altered carbonate samples yielded significantly more negative $\delta^{13}\text{C}$ values ranging between -6.1‰ and 2.1‰ . Variations in the calcite $\delta^{13}\text{C}$ values suggest differences in carbon derivation, where negative values are hypothesized to have been derived from the oxidation of methane and positive values are derived from a mixture of respired organic material and seawater carbonate (Staudigel et al. 2018).

The $\delta^{18}\text{O}_{\text{water}}$ values derived from carbonate Δ_{47} and $\delta^{18}\text{O}$ values are within a similar range to $\delta^{18}\text{O}$ values for porewater brines. There are several proposed models for diagenetic

incorporation of porewater brines which explain the shifting of $\delta^{18}\text{O}$ values in either the positive or negative direction, such as the “Pulse”, “Pulse+Constant”, and “2x brine rate” models that simulate rates of cementation using a conventional exponential decay function, as further described in Staudigel et al. (2018).

The calculated water $\delta^{18}\text{O}$ values reveal that many samples that otherwise appear to remain pristine aragonite have interacted with porewater brines during their burial history, as they are in equilibrium with measured porewater $\delta^{18}\text{O}$ values (Frank, Gui, and the ANDRILL SMS Science Team 2010, our graph/table), which are significantly more negative than seawater values. This is in itself a significant finding, representing a case of aragonite to aragonite neomorphic replacement, which under normal conditions is thermodynamically unfavorable. However, the enhanced Mg:Ca ratio in the porewater brines may enable precipitation of aragonite, as aragonite precipitation is favored over calcite at ratios above 4:1 Mg to Ca (Morse, Wang, and Tsio 1997).

Non-linear sedimentary mixing of Δ_{47} isotopes may have led to the temperature disparities found when our Δ_{47} -based temperatures are compared to isotopic analyses done by Staudigel et al. (2018) (Defliese and Lohmann 2015). Δ_{47} -based temperatures are also higher at shallower core depths compared to findings from (Levy et al. 2016) and Staudigel et al. (2018) (Fig. 5).

4.2 Mid-Miocene Temperature

Our unaltered carbonate Δ_{47} -based temperatures during the mid-Miocene Climatic Optimum largely align with the temperatures found in Levy et al. (2016) (Fig. 4) though there is limited core coverage from 11.67 to 16.05 Ma. This alignment supports that our clumped data

used for temperature reconstruction was isotopically unaltered. Notably there is a significant temperature peak from 16.05 to 16.36 Ma which concur with both a peak in sea level and elevated atmospheric CO₂ concentrations (Levy, Harwood, Florindo, Sangiorgi, Tripathi, Eynatten, et al. 2016). Proxy data show that atmospheric CO₂ concentrations were >500 ppm during the warmth episode between 16.4 and 15.8 Ma, suggesting the presence of higher climate sensitivity to CO₂ concentrations than climate models present (Greenop et al. 2014; Kürschner, Kvaček, and Dilcher 2008; Goldner, Herold, and Huber 2014).

5. Conclusion

Our clumped isotope-based temperatures indicate that the formation and recrystallization of carbonates occurred at increasingly higher temperatures in relation to increasing core-depth and age. These temperature reconstructions for the mid-Miocene climatic optimum suggest that the Antarctic shelf was significantly warmer (~+10 °C) than present, with minimum summer sea temperatures of 6.9 °C just off the coast of Antarctica. This supports the multiproxy evidence for increased temperatures at high latitudes during the mid-Miocene climatic optimum in conjunction with increased *p*CO₂. Reconstructed seawater δ¹⁸O values indicate inputs of glacial meltwater or precipitation runoff, likely from cryogenic porewater brines that were likely present after the Miocene Climatic Optimum.

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Figures and Tables

Core Depth	Mineralogy	No. of Replicates run	$\delta^{13}\text{C}$ PDB avg	1 s.d.	$\delta^{18}\text{O}$ PDB avg	1 s.d.	$\Delta 47$ avg	1 s.e.	Bernasconi (2018) Average	1 s.e.	Eagle (2013) Average Temperature	1 s.d.	$\delta^{18}\text{O}$ water SMOW avg	1 s.d.	Preservation
59.75	Calcite	1	-0.6	0.007	1.2	0.025	0.710	0.009	14.4	5.1	9.7	2.8	0.7	0.025	
66.24	Calcite	1	-0.9	0.003	-1.8	0.006	0.610	0.035	45.3	16	49.1	16.3	2.2	0.006	Altered
66.24	Calcite	1	1.5	0.002	3.6	0.003	0.698	0.010	17.6	6.2	13.6	3.2	3.6	0.003	
66.92	Calcite	1	-0.6	0.004	-5.8	0.003	0.528	0.012	79.5	28.1	97.4	8.4	2.2	0.003	Altered
67.56	Calcite	1	2.3	0.003	3.1	0.007	0.761	0.015	1.9	0.7	-5.4	3.9	0.5	0.007	
144.03	Calcite	3	1.8	0.014	4.2	0.029	0.718	0.006	12.3	1.5	7	1.8	3.4	0.422925517	
144.03	Calcite	3	1.7	0.086	3.9	0.235	0.706	0.005	15.4	1.5	10.9	1.9	3.6	0.608558354	Preserved
144.03	Calcite	1	0.3	0.005	-6.3	0.004	0.529	0.015	79.1	28	96.8	10.4	1.6	0.004	Altered
175.4	Calcite	1	-2.5	0.004	-2.4	0.006	0.644	0.011	33.5	11.8	33.6	4.4	0.1	0.006	Altered
208.96	Calcite	1	2.1	0.004	-0.7	0.004	0.690	0.009	20.0	7.1	16.5	3	-0.2	0.004	Altered
366.8	Calcite	1	4.0	0.005	1.9	0.013	0.734	0.013	8.2	2.9	2.1	3.7	0.4	0.013	Preserved
416.78	Calcite	1	-6.1	0.002	-5.9	0.004	0.610	0.005	45.1	15.9	48.9	2.4	-1.9	0.004	Altered
429.98	Aragonite	3	-2.2	0.031	-3.3	0.024	0.733	0.005	8.4	1.2	2.4	1.8	-5.5	0.317632449	
429.98		3	-2.1	0.139	-3.7	0.175	0.703	0.008	16.3	2.2	12	2.4	-4.6	0.460331626	Altered
430.41	Aragonite	1	-3.6	0.003	-4.1	0.004	0.729	0.011	9.6	3.4	3.7	3.2	-6.1	0.004	Altered
430.49	Aragonite	1	1.2	0.004	-0.4	0.007	0.708	0.008	15.0	5.3	10.4	2.5	-0.7	0.007	Preserved
430.54	Calcite	2	3.7	0.005	0.6	0.034	0.702	0.004	16.6	1.1	12.3	2	0.5	0.288641781	Preserved
430.54	Calcite	4	3.5	0.039	0.5	0.436	0.736	0.012	7.8	3	1.7	1.8	-1.0	0.78684698	Preserved
430.54	Calcite	5	2.8	0.253	-0.5	1.035	0.708	0.015	14.8	4	10.2	2.1	-0.9	1.787679183	Preserved
430.54	Calcite	5	2.7	0.233	-0.7	0.612	0.703	0.009	16.3	2.6	12	2	-0.8	1.13414446	Preserved
450.54	Calcite	3	2.3	0.170	-1.5	0.956	0.714	0.006	13.3	1.5	8.3	1.8	-2.1	1.200520045	Preserved
450.54	Calcite	2	1.9	0.304	-2.1	0.620	0.715	0.026	13.1	6.7	8.1	3.1	-2.7	2.174813603	Preserved
576.29	Calcite	1	-5.2	0.002	-6.9	0.004	0.735	0.010	7.9	2.8	1.8	3	-8.4	0.004	Altered
605.56	Calcite	3	-4.0	0.022	-8.2	0.002	0.617	0.039	42.6	11.4	45.5	6	-7.4	3.74450421	Altered
605.61		1	-6.4	0.002	-6.8	0.003	0.606	0.010	46.5	16.5	50.8	4.5	-2.6	0.003	Altered
970.74	Calcite	4	2.3	1.136	0.4	0.124	0.744	0.014	5.8	3.6	-0.8	1.9	-5.4	1.204515302	
986.01	Calcite	1	0.0	0.003	-3.7	0.004	0.688	0.007	20.3	7.2	9.7	2.3	-3.2	0.004	Altered
1063.71	Calcite	2	3.8	0.018	1.2	0.617	0.726	0.027	10.3	6.9	4.7	2.4	0.0	1.028483006	Preserved

Table 1. Isotopic composition of carbonate materials analyzed in this study.

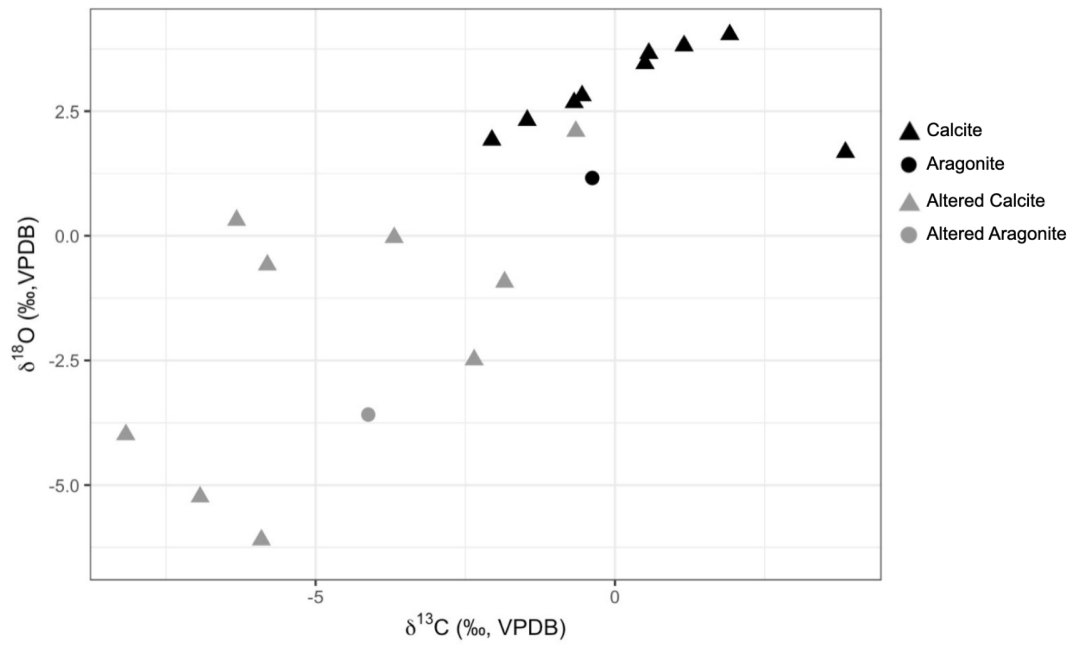


Fig. 1. $\delta^{13}\text{C}$ v. $\delta^{18}\text{O}$ plot with indications of mineralogy and preservation. There is a strong positive correlation between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, as expected, with a Pearson's coefficient of 0.82. The altered samples have significantly more negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values than pristine samples.

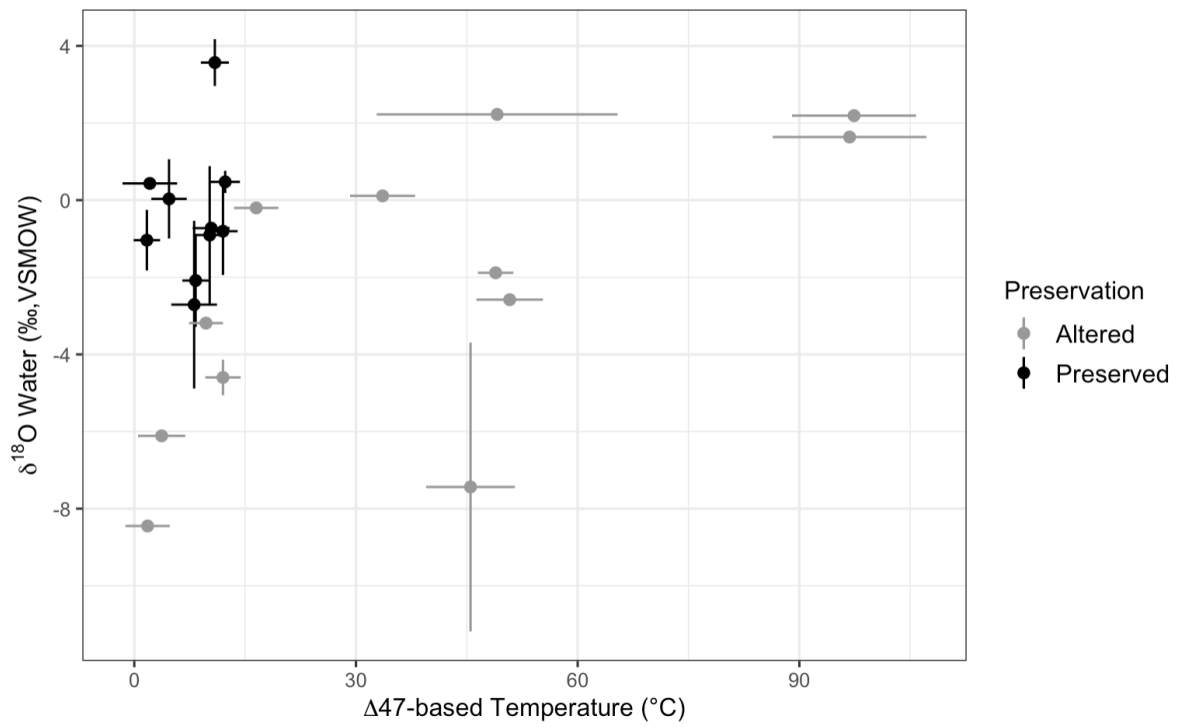
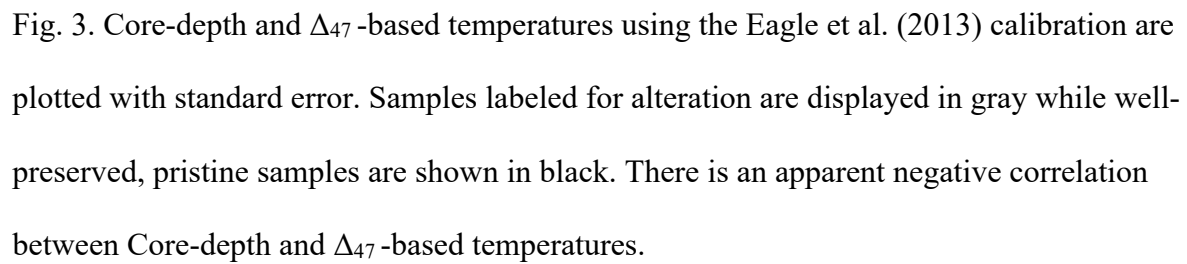


Fig. 2. $\delta^{18}\text{O}$ v. Δ_{47} -based temperature plot using the Eagle et al. (2013) temperature calibration. Samples labeled for alteration are displayed in gray while well-preserved, pristine samples are shown in black.



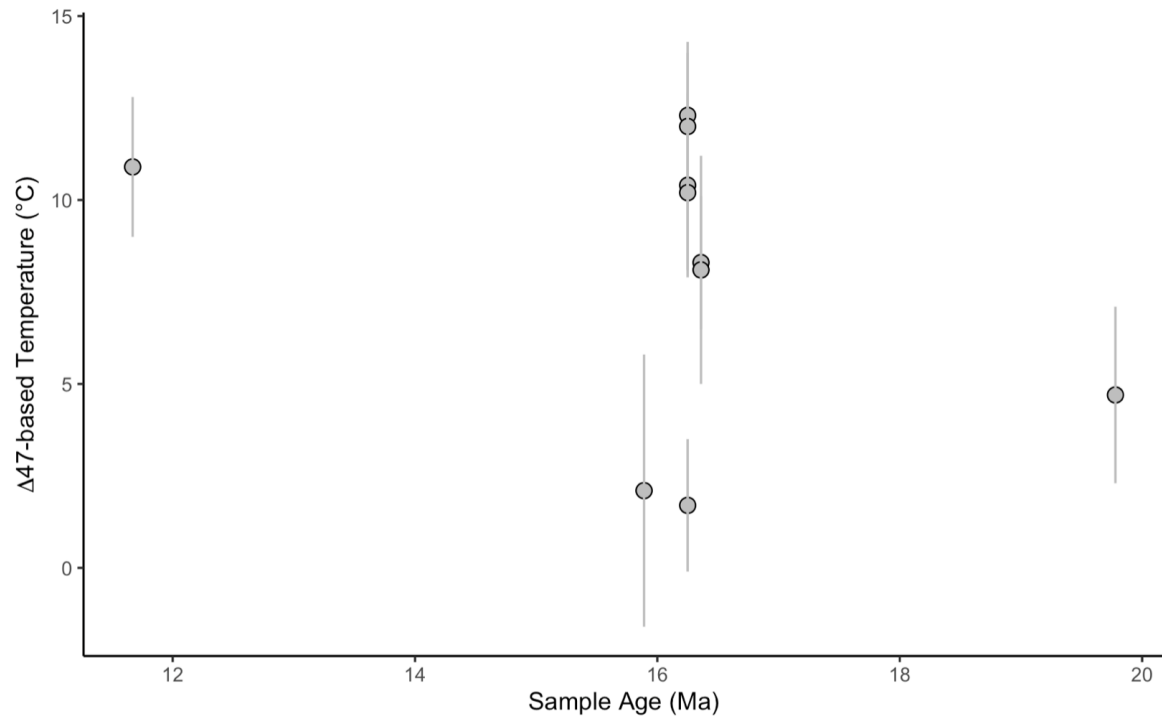


Fig. 4. Sample Age and Δ_{47} -based temperatures using the Eagle et al. (2013) calibration are plotted with standard error. Results from unaltered carbonate samples in this study are shown in gray circles.

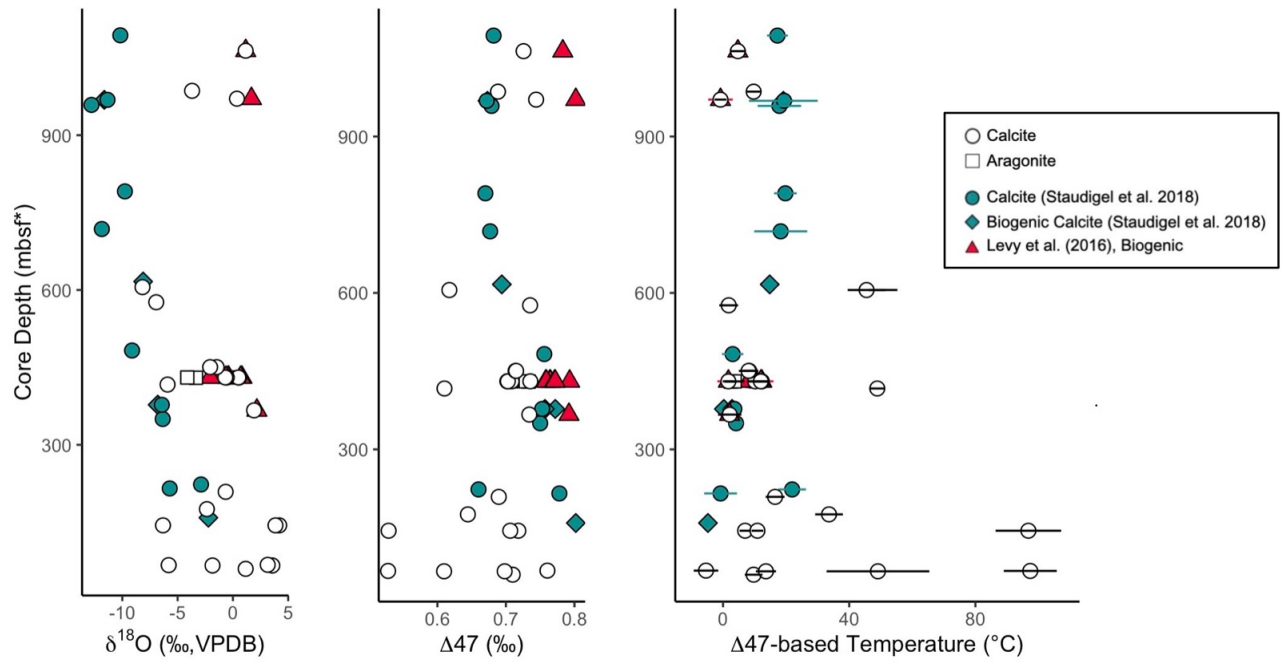


Fig. 5. Plots for AND-2A carbonates. Calcite and aragonite samples from this study are shown as unfilled (white). Calcite (circles) and biogenic calcite (diamonds) described by Staudigel et al. (2018) are plotted as green points relative to core depth. Unaltered biogenic material as described in Levy et al. (2016) are plotted as red triangles. All of the temperatures were calibrated according to Eagle et al. (2013). Plot A: $\delta^{18}\text{O}$ of carbonates (standard error omitted). Plot B: Δ_{47} (standard error omitted). Plot C: Δ_{47} -based temperatures (standard error included). *mbsf = meters below sea floor

References

- Acton, G, and J Crampton. 2008. "Preliminary Integrated Chronostratigraphy of the AND-2A Core, ANDRILL Southern McMurdo Sound Project, Antarctica," 12.
- Bernasconi, Stefano M., Inigo A. Müller, Kristin D. Bergmann, Sebastian F. M. Breitenbach, Alvaro Fernandez, David A. Hodell, Madalina Jaggi, Anna Nele Meckler, Isabel Millan, and Martin Ziegler. 2018. "Reducing Uncertainties in Carbonate Clumped Isotope Analysis Through Consistent Carbonate-Based Standardization." *Geochemistry, Geophysics, Geosystems* : *G(3)* 19 (9): 2895–2914.
<https://doi.org/10.1029/2017GC007385>.
- Beu, Alan, and Marco Taviani. 2014. "Early Miocene Mollusca from McMurdo Sound, Antarctica (ANDRILL 2A Drill Core), with a Review of Antarctic Oligocene and Neogene Pectinidae (Bivalvia)." *Palaeontology* 57 (2): 299–342.
<https://doi.org/10.1111/pala.12067>.
- Came, Rosemarie E., John M. Eiler, Ján Veizer, Karem Azmy, Uwe Brand, and Christopher R. Weidman. 2007. "Coupling of Surface Temperatures and Atmospheric CO₂ Concentrations during the Palaeozoic Era." *Nature* 449 (7159): 198–201.
<https://doi.org/10.1038/nature06085>.
- Catania, Ginny, Christina Hulbe, Howard Conway, T. A. Scambos, and C. F. Raymond. 2012. "Variability in the Mass Flux of the Ross Ice Streams, West Antarctica, over the Last Millennium." *Journal of Glaciology* 58 (210): 741–52.
<https://doi.org/10.3189/2012JoG11J219>.
- Defliese, William F., Michael T. Hren, and Kyger C. Lohmann. 2015. "Compositional and Temperature Effects of Phosphoric Acid Fractionation on $\Delta 47$ Analysis and Implications

- for Discrepant Calibrations.” *Chemical Geology* 396 (March): 51–60.
<https://doi.org/10.1016/j.chemgeo.2014.12.018>.
- Defliese, William F., and Kyger C. Lohmann. 2015. “Non-Linear Mixing Effects on Mass-47 CO₂ Clumped Isotope Thermometry: Patterns and Implications.” *Rapid Communications in Mass Spectrometry* 29 (9): 901–9. <https://doi.org/10.1002/rcm.7175>.
- Defliese, William F., and Aradhna Tripathi. 2020. “Analytical Effects on Clumped Isotope Thermometry: Comparison of a Common Sample Set Analyzed Using Multiple Instruments, Types of Standards, and Standardization Windows.” *Rapid Communications in Mass Spectrometry* 34 (8). <https://doi.org/10.1002/rcm.8666>.
- Dennis, Kate J., Hagit P. Affek, Benjamin H. Passey, Daniel P. Schrag, and John M. Eiler. 2011. “Defining an Absolute Reference Frame for ‘Clumped’ Isotope Studies of CO₂.” *Geochimica et Cosmochimica Acta* 75 (22): 7117–31.
<https://doi.org/10.1016/j.gca.2011.09.025>.
- Eagle, R. A., J. M. Eiler, A. K. Tripathi, J. B. Ries, P. S. Freitas, C. Hiebenthal, A. D. Jr Wanamaker, et al. 2013. “The Influence of Temperature and Seawater Carbonate Saturation State on ¹³C–¹⁸O Bond Ordering in Bivalve Mollusks.” *Biogeosciences* 10 (7): 4591–4606. <https://doi.org/10.5194/bg-10-4591-2013>.
- Eiler, John M. 2007. “‘Clumped-Isotope’ Geochemistry—The Study of Naturally-Occurring, Multiply-Substituted Isotopologues.” *Earth and Planetary Science Letters* 262 (3–4): 309–27. <https://doi.org/10.1016/j.epsl.2007.08.020>.
- Fielding, Christopher R., Greg H. Browne, Brad Field, Fabio Florindo, David M. Harwood, Lawrence A. Krissek, Richard H. Levy, Kurt S. Panter, Sandra Passchier, and Stephen F. Pekar. 2011. “Sequence Stratigraphy of the ANDRILL AND-2A Drillcore, Antarctica: A

- Long-Term, Ice-Proximal Record of Early to Mid-Miocene Climate, Sea-Level and Glacial Dynamism.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 305 (1–4): 337–51. <https://doi.org/10.1016/j.palaeo.2011.03.026>.
- Frank, Tracy D., Zi Gui, and the ANDRILL SMS Science Team. 2010. “Cryogenic Origin for Brine in the Subsurface of Southern McMurdo Sound, Antarctica.” *Geology* 38 (7): 587–90. <https://doi.org/10.1130/G30849.1>.
- Ghosh, Prosenjit, Jess Adkins, Hagit Affek, Brian Balta, Weifu Guo, Edwin A. Schauble, Dan Schrag, and John M. Eiler. 2006. “ ^{13}C – ^{18}O Bonds in Carbonate Minerals: A New Kind of Paleothermometer.” *Geochimica et Cosmochimica Acta* 70 (6): 1439–56. <https://doi.org/10.1016/j.gca.2005.11.014>.
- Goldner, A., N. Herold, and M. Huber. 2014. “The Challenge of Simulating the Warmth of the Mid-Miocene Climatic Optimum in CESM1.” *Clim. Past* 10 (2): 523–36. <https://doi.org/10.5194/cp-10-523-2014>.
- Greenop, Rosanna, Gavin L. Foster, Paul A. Wilson, and Caroline H. Lear. 2014. “Middle Miocene Climate Instability Associated with High-Amplitude CO_2 Variability.” *Paleoceanography* 29 (9): 845–53. <https://doi.org/10.1002/2014PA002653>.
- Henkes, Gregory A., Benjamin H. Passey, Alan D. Wanamaker, Ethan L. Grossman, William G. Ambrose, and Michael L. Carroll. 2013. “Carbonate Clumped Isotope Compositions of Modern Marine Mollusk and Brachiopod Shells.” *Geochimica et Cosmochimica Acta* 106 (April): 307–25. <https://doi.org/10.1016/j.gca.2012.12.020>.
- Kim, Sang-Tae, and James R. O’Neil. 1997. “Equilibrium and Nonequilibrium Oxygen Isotope Effects in Synthetic Carbonates.” *Geochimica et Cosmochimica Acta* 61 (16): 3461–75. [https://doi.org/10.1016/S0016-7037\(97\)00169-5](https://doi.org/10.1016/S0016-7037(97)00169-5).

- Kim, Sang-Tae, James R. O'Neil, Claude Hillaire-Marcel, and Alfonso Mucci. 2007. "Oxygen Isotope Fractionation between Synthetic Aragonite and Water: Influence of Temperature and Mg^{2+} Concentration." *Geochimica et Cosmochimica Acta* 71 (19): 4704–15. <https://doi.org/10.1016/j.gca.2007.04.019>.
- Kürschner, Wolfram M., Zlatko Kvaček, and David L. Dilcher. 2008. "The Impact of Miocene Atmospheric Carbon Dioxide Fluctuations on Climate and the Evolution of Terrestrial Ecosystems." *Proceedings of the National Academy of Sciences* 105 (2): 449. <https://doi.org/10.1073/pnas.0708588105>.
- Levy, Richard, David Harwood, Fabio Florindo, Francesca Sangiorgi, Robert Tripathi, Hilmar von Eynatten, Edward Gasson, et al. 2016. "Antarctic Ice Sheet Sensitivity to Atmospheric CO_2 Variations in the Early to Mid-Miocene." *Proceedings of the National Academy of Sciences* 113 (13): 3453. <https://doi.org/10.1073/pnas.1516030113>.
- Levy, Richard, David Harwood, Fabio Florindo, Francesca Sangiorgi, Robert Tripathi, Hilmar von Eynatten, Edward Gasson, et al. 2016. "Antarctic Ice Sheet Sensitivity to Atmospheric CO_2 Variations in the Early to Mid-Miocene." *Proceedings of the National Academy of Sciences* 113 (13): 3453–58. <https://doi.org/10.1073/pnas.1516030113>.
- Marcano, Maria C., Tracy D. Frank, Samuel B. Mukasa, Kyger C Lohmann, and Marco Taviani. 2015. "Diagenetic Incorporation of Sr into Aragonitic Bivalve Shells: Implications for Chronostratigraphic and Palaeoenvironmental Interpretations." *The Depositional Record* 1 (1): 38–52. <https://doi.org/10.1002/dep2.3>.
- Marcano, Maria C., Samuel Mukasa, Kyger C. Lohmann, Christopher Stefano, Marco Taviani, and Alex Andronikov. 2009. "Chronostratigraphic and Palaeoenvironmental Constraints Derived from the $^{87}Sr/^{86}Sr$ and $\Delta^{18}O$ Signal of Miocene Bivalves, Southern McMurdo

Sound, Antarctica.” *Global and Planetary Change* 69 (3): 124–32.

<https://doi.org/10.1016/j.gloplacha.2009.05.001>.

Modestou, S. E., T. J. Leutert, A. Fernandez, C. H. Lear, and A. N. Meckler. 2020. “Warm Middle Miocene Indian Ocean Bottom Water Temperatures: Comparison of Clumped Isotope and Mg/Ca-Based Estimates.” *Paleoceanography and Paleoclimatology* 35 (11): e2020PA003927. <https://doi.org/10.1029/2020PA003927>.

Morse, John W., Qiwei Wang, and Mai Yin Tsio. 1997. “Influences of Temperature and Mg:Ca Ratio on CaCO₃ Precipitates from Seawater.” *Geology* 25 (1): 85–87. [https://doi.org/10.1130/0091-7613\(1997\)025<0085:IOTAMC>2.3.CO;2](https://doi.org/10.1130/0091-7613(1997)025<0085:IOTAMC>2.3.CO;2).

Passey, Benjamin H., Naomi E. Levin, Thure E. Cerling, Francis H. Brown, and John M. Eiler. 2010. “High-Temperature Environments of Human Evolution in East Africa Based on Bond Ordering in Paleosol Carbonates.” *Proceedings of the National Academy of Sciences of the United States of America* 107 (25): 11245–49. <https://doi.org/10.1073/pnas.1001824107>.

Schauble, Edwin A., Prosenjit Ghosh, and John M. Eiler. 2006. “Preferential Formation of ¹³C–¹⁸O Bonds in Carbonate Minerals, Estimated Using First-Principles Lattice Dynamics.” *Geochimica et Cosmochimica Acta* 70 (10): 2510–29. <https://doi.org/10.1016/j.gca.2006.02.011>.

Shepherd, Andrew, Erik R. Ivins, Geruo A, Valentina R. Barletta, Mike J. Bentley, Srinivas Bettadpur, Kate H. Briggs, et al. 2012. “A Reconciled Estimate of Ice-Sheet Mass Balance.” *Science* 338 (6111): 1183. <https://doi.org/10.1126/science.1228102>.

Shepherd, Andrew, Erik Ivins, Eric Rignot, Ben Smith, Michiel van den Broeke, Isabella Velicogna, Pippa Whitehouse, et al. 2018. “Mass Balance of the Antarctic Ice Sheet from

- 1992 to 2017.” *Nature* 558 (7709): 219–22. <https://doi.org/10.1038/s41586-018-0179-y>.
- Solomon, Susan, ed. 2007. *Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge ; New York: Cambridge University Press.
- Starinsky, Abraham, and Amitai Katz. 2003. “The Formation of Natural Cryogenic Brines.” *Geochimica et Cosmochimica Acta* 67 (8): 1475–84. [https://doi.org/10.1016/S0016-7037\(02\)01295-4](https://doi.org/10.1016/S0016-7037(02)01295-4).
- Staudigel, Philip T., Sean Murray, Daniel P. Dunham, Tracy D. Frank, Christopher R. Fielding, and Peter K. Swart. 2018. “Cryogenic Brines as Diagenetic Fluids: Reconstructing the Diagenetic History of the Victoria Land Basin Using Clumped Isotopes.” *Geochimica et Cosmochimica Acta* 224 (March): 154–70. <https://doi.org/10.1016/j.gca.2018.01.002>.
- Stevens, Craig, Christina Hulbe, Mike Brewer, Craig Stewart, Natalie Robinson, Christian Ohneiser, and Stefan Jendersie. 2020. “Ocean Mixing and Heat Transport Processes Observed under the Ross Ice Shelf Control Its Basal Melting.” *Proceedings of the National Academy of Sciences* 117 (29): 16799–804. <https://doi.org/10.1073/pnas.1910760117>.
- Tripati, A. K., C. D. Roberts, and R. A. Eagle. 2009. “Coupling of CO₂ and Ice Sheet Stability Over Major Climate Transitions of the Last 20 Million Years.” *Science* 326 (5958): 1394–97. <https://doi.org/10.1126/science.1178296>.
- Tripati, Aradhna K., Pamela S. Hill, Robert A. Eagle, Jed L. Mosenfelder, Jianwu Tang, Edwin A. Schauble, John M. Eiler, et al. 2015. “Beyond Temperature: Clumped Isotope Signatures in Dissolved Inorganic Carbon Species and the Influence of Solution Chemistry on Carbonate Mineral Composition.” *Geochimica et Cosmochimica Acta* 166

(October): 344–71. <https://doi.org/10.1016/j.gca.2015.06.021>.

Urey, H. C. 1947. “The Thermodynamic Properties of Isotopic Substances.” *Journal of the Chemical Society*, April, 562–81. <https://doi.org/10.1039/jr9470000562>.