



## ICIW10 - List of Abstracts

Presenting Author	Title	Presentation
Agterhuis, Tobias	South Atlantic Deep Ocean Temperature Evolution across the Eocene–Oligocene Transition from Clumped Isotope Thermometry	Poster 1
Alam, Md Samrat	Determining Natural Abundance Isotope Ratios of Polycyclic Aromatic Hydrocarbons in Complex Environmental Samples using GC–Orbitrap	Poster 2
Anstey, Fiona	Unlocking Cambrian Climate: Clumped Isotope Thermometry in Phosphatic Fossils	Poster 3
Bahniuk, Anelize	Clumped Isotope Constraints in Lower Cretaceous Pre-Salt Carbonates, Santos Basin, Brazil	Poster 4
Bajnai, David	Cryogenian Interglacial Climate Revealed by Dolomite Triple Oxygen Isotopes	Poster 5
Bernasconi, Stefano	A 20 Year Journey in Clumped Isotope Geochemistry at ETH	Keynote
Bernecker, Miguel	D <sub>4</sub> Xgui: A tool for baseline correction and standardization of carbonate clumped isotope raw data	Poster 6
Bondzie-Selby, Isaac	A Continuous Empirical Calibration from 0 to 250 °C for Dual Carbonate Clumped Isotopes ( $\Delta_{47}$ and $\Delta_{48}$ ) in Experimentally Synthesised Dolomites	Poster 7
Brown, Adriana	Using $\Delta_{47}$ to characterize water mass properties and distributions in the Cretaceous Western Interior Seaway	Poster 8
Chaudhuri, Swagata	From Greenhouse to Icehouse: Tropical Climate Insights from Larger Benthic Foraminifera of Kutch (Kachchh) Basin, Western India	Poster 9
Chiari, Andrea	The Palaeo-Adriatic Basin during the Mid-Piacenzian Warm Period: Clumped isotope-based seasonality reconstruction from Bivalve shells	Poster 10
Clark, Alexander	Applying coccolith clumped isotope thermometry to the past: a case study from the middle Miocene Climatic Transition	Oral
Clog, Matthieu	Methane Isotopologues ( $\delta^{13}\text{C-CH}_4$ , $\delta^2\text{H-CH}_4$ , $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ ) from Arctic wetlands: Characterization of high latitude methane sources	Poster 11
Curley, Allison	What's in a Shell? Methods for Time-Resolved Sampling to Disentangle Climate and Physiological Signals in Bivalve Shells with Dual Clumped Isotopes	Oral
Cury, Leonardo	Paleothermometry of Brazilian Carbonates: A Multi-Proxy Approach Using Clumped Isotopes and Fluid Inclusions	Poster 12



Daëron, Mathieu	NeoCarb: Navigating the Transition to New Reference Materials	Oral
	D95thermo: a Python Library/CLI for Dual Clumped Isotope Thermometry	Poster 13
Dasgupta, Bibhasvata	Thermal Calibration of Methane Clumped Isotopologues: Methods and Multi-Dataset Results	Oral
Davies, Amelia	Using Dual Carbonate Clumped Isotopes to Assess Kinetic Effects in Foraminiferal Calcite	Oral
de Winter, Niels	Clumped isotope-based Reconstructions from Fossil Mollusc Shells: Constraining Seasonal Variations in Climate and Hydrology	Oral
Domínguez Valdés, Elena	More Ice in Warmer Worlds? Reassessing Plio-Pleistocene Climate Relationships	Poster 14
Donenfeld, Rotem	Carbonate Clumped Isotope Constraints on the Stabilization of a Neoproterozoic Continental Lithosphere	Poster 15
Eckhardt, Henrik	Semi-continuous automated $\Delta 47$ Measurements of Atmospheric CO <sub>2</sub>	Oral
Eyal, Itay	Reconstructing the Thermal History of the Sedom Formation: A Plausibility Test for H <sub>2</sub> Storage	Poster 16
Fang, Yunhan	Disequilibrium Precipitation in <i>Mercenaria mercenaria</i> Clams Detected when Growing at the Extremes of Their Temperature Tolerance	Poster 17
Fernandez, Álvaro	Assessing the Influence of Dissolution and Recrystallization on Coccolith $\Delta 47$ -derived Temperatures Across a Depth Transect	Poster 18
Fiebig, Jens	Mass Spectrometric $\Delta 48$ Precision Insufficient to Resolve the Subtle Negative $\Delta 47$ Bias that is Recorded along the Growth Axis of Most Stalagmites	Poster 19
Germeau, Hailey	Disequilibrium of Water Column and Sediment Carbonates in the Dual Clumped Isotope Record of Fayetteville Green Lake, NY	Oral
Gomes, Lucas	Testing Climate-Driven Extinction Hypotheses on the Plio-Pleistocene Florida Platform with High-Resolution $\Delta 47$ -Sclerochronology	Poster 20
Goudsmit, Barbara	Clumped Isotope Analysis on Cultured Aragonite Bivalve Shells evaluates Applicability of Calcite Calibrations	Oral
Guilfoyle, Stephen	A novel dual inlet large radius IRMS for isotopologue measurement	Oral
Guo, Jingjing	75,000 Years of Hydroclimate and Temperature Variations in East Asia Derived from Snail Shell Clumped Isotopes	Poster 21



Guo, Yangrui	Clumped Isotope Constraints on Seawater Temperature and Isotopic Variability Across the Hirnantian Glaciation	Ora
Hayhow, Claire	Assessing CO <sub>2</sub> Absorption and Clumped Isotope Disequilibrium in Carbon Mineralization Products	Poster 22
Hofmann, Amy	The Rise of Orbitrap-IRMS for Clumped Isotope Geochemistry	Keynote
Hong, Jungpyo	Experimental Constraints of Equilibrium Triple Oxygen Isotope Fractionation in the Dissolved Inorganic Carbon System	Poster 23
Huntington, Kate	Repeat Until Precise: Small Carbonate Samples, High-Precision $\Delta_{48}$ on the Nu Perspective IRMS	Poster 24
Jautzy, Josué	How to kill with a FrankenKiel a MAT253+ (and bring it back from its ashes)	Poster 25
Kaiser, Jan	Seasonal, diel and interhemispheric variability of polyisotopic carbon dioxide on land and at sea	Poster 26
Kelson, Julia	A Progress Report on Paired Measurements of $\Delta_{47}$ and $\Delta^{17}O$ in CO <sub>2</sub> derived from a Single Aliquot of Carbonate	Poster 27
	TICTOC: Traceable Inter-Comparison of Triple Oxygen isotopes in Carbonates	Poster 28
Kim, Erin	Tracking Changes in Ocean Currents along the Miocene-Pliocene U.S. Mid-Atlantic Coastal Plain Using $\Delta_{47}$	Poster 29
Kozikowska, Emilia	Relatively warm deep-water formation in the Last Glacial Maximum: new constraints from clumped isotope thermometry	Poster 30
Kueter, Nico	Performance of cryogenic adsorbents for use in methane bulk and clumped isotope analysis	Poster 31
	Precise Kinetic Parameters for Thermal Resetting of Clumped Isotope Signatures in Biogenic and Abiogenic Calcites	Oral
Kuzmenko, Alona	Clumped Isotope Derived Temperatures, $\delta^{18}O$ , and $\delta^{13}C$ Values in Alluvial Carbonates Suggest a Wetter Environment Relative to Modern Conditions in the Hyper Arid Southern Negev During the Middle Pleistocene	Poster 32
Lee, Elena	Evaluating Miocene Temperature, Water Stress, and Hydrological Variability in the Atacama Desert with Carbonate Clumped and Triple Oxygen Isotopes	Poster 33
Leusch, Maja	Paired Coccolith and Foraminifera $\Delta_{47}$ Temperatures suggest tropical Upper-Ocean Thermal Stratification in the late Miocene	Poster 34



Loveall, Zachary	Facies-Specific Dual-Clumped Isotope Disequilibrium in Eocene Terrestrial Carbonates	Poster 35
Lu, Chaojin	Dual clumped isotopes indicate the control of diagenetic systems on the formation of cold seep carbonates	Poster 36
Magyar, Paul	Constraining Nitrous Oxide Sources and Sinks with Clumped Isotopes	Oral
Meckler, Nele	Constraining the Extent of Reordering in Biogenic Carbonates From Heat Exposure	Poster 37
Meijer, Niels	Terrestrial Cooling during the Middle Miocene Climate Transition in Spain	Poster 38
Mejía, Luz	Coccolith Clumped Isotopes Unveil Coccolithophores' Ecology, Challenge Miocene High-Latitude Warmth and Decipher Euphotic Zone Temperatures during the Cenozoic	Poster 39
Mengesha, Million	Clumped and Triple Oxygen Isotope Constraints on Vegetation and Water-stress across Rift landscapes of the Mid-Pliocene Lower Awash Valley, Ethiopia	Oral
Modestou, Sevi	A new low temperature reference material for clumped isotope analysis	Poster 40
Müller, Inigo	The clumped isotope signatures of acid resistant carbonates reacted at 120 °C with the new 'Nu React'	Oral
Nascimento, Ayrton	Establishing Methane Clumped Isotope Measurements on a High-Resolution IRMS: Methodological Challenges and Practical Insights	Poster 41
Nasri, Nesrinde	Isotopic Characterization of the Bargou-Sodga-Bous Sadia Karst Aquifer (northwestern, Tunisia)	Poster 42
Nelson, David	Recent Progress in Isotope Ratio Laser Spectroscopy of Clumped CO <sub>2</sub> and Triple Oxygen CO <sub>2</sub>	Poster 43
Nishida, Kozue	Micro-Sample and High-Temperature Capable, Custom-Built System for Diverse Carbonate Clumped Isotope Analysis	Poster 44
Olsen, Ellen	Dual Clumped Isotopes of Alkaline, Saline Lake Carbonates from the Cariboo Plateau and Atlin Playa, British Columbia, Canada	Poster 45
Pack, Andreas	Why caring about precise notations and accurate triple oxygen isotope data?	Oral
Peral, Marion	Assessing the Influence of Seawater pH on Clumped Isotope Thermometry ( $\Delta_{47}$ ) in Cultured Large Benthic Foraminifera	Poster 46
Pesnin, Marie	Quantification of <sup>17</sup> O Fractionation during Phosphoric Acid Digestion of Carbonate between 25° and 110°C	Oral



Pinto, Vittoria	Combining Triple-oxygen and Clumped isotopes analyses of carbonate sedimentary successions to shade light on diagenetic processes	Poster 47
Quizon, Alex	Assessing vital effects and paleoclimate reconstructions in turritellid gastropods with clumped isotopes ( $\Delta_{47}$ )	Poster 48
Rice, Addison	Exploring Long-term Oligocene to mid Miocene Temperature Change in the Tasmanian Sea: How do Clumped Isotopes in Coccoliths Compare?	Poster 49
Rinyu, László	Climate Chamber Calibration of Earthworm Biospheroids for Quantitative Paleothermometry	Poster 50
Rodrigues, Luiz Frederico	Clumped isotope constraints on the origin of methane hydrate from the Amazon Cone	Poster 51
Ryb, Uri	Simulating Solid State Isotope Reordering of C-O Bonds in the Framework of Trigonal Carbonate Mineral: A Probabilistic Approach	Oral
Santos, Madaleine	Atlantic upper-ocean temperature reconstructions from coccolith and foraminiferal clumped isotopes ( $\Delta_{47}$ ) across the Late Miocene	Poster 52
Staudigel, Philip	Mass-dependent diffusion in corals is resolvable with triple-oxygen isotopes, but further constraint is needed	Poster 53
Sun, Zeyang	Submarine Groundwater Discharge into the Plio-Pleistocene Florida Platform Suggested by Clumped Isotope Sclerochronology	Poster 54
Swart, Peter	Investigation of Dual Clumped Isotope Fractionation Using Farmed Calcite precipitated on Curved Glass Plates	Oral
Taylor, Victoria	Revisiting the Clumped Isotope to Temperature Calibration for Foraminifera	Oral
	Testing for Species-Specific Offsets in Benthic Foraminiferal Clumped Isotopes	Poster 55
Wilcots, Julia	Modern, Low-Temperature Dolomite from the Coorong Region, South Australia	Poster 56
Zahnw, Fabian	Unified Automated Triple Oxygen and Hydrogen Isotope Analysis of Water, Organics, and Non-Silicates on the VSMOW-SLAP Scale	Poster 57
Zhang, Naizhong	Towards improved inter-laboratory compatibility of clumped-isotope measurements for low- $\delta D$ biogenic methane	Oral
Zhao, Xianye	Dual Clumped Isotope Signature in Impactites: The Haughton Case Study	Poster 58



# South Atlantic Deep Ocean Temperature Evolution across the Eocene–Oligocene Transition from Clumped Isotope Thermometry

Tobias Agterhuis<sup>a,b</sup>, Martin Ziegler<sup>a</sup>, Maarten T. Bosman<sup>a</sup>, Arielle van Dusseldorp<sup>a</sup>, Dario Spina<sup>a</sup>, Maartje Bosman<sup>a</sup>, Clay Kelly<sup>c</sup> & Lucas J. Lourens<sup>a</sup>

<sup>a</sup> Department of Earth Sciences, Utrecht University, Utrecht, the Netherlands

<sup>b</sup> School of Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton, Southampton, United Kingdom

<sup>c</sup> Department of Geoscience, University of Wisconsin-Madison, Madison, WI, USA

The Eocene–Oligocene Transition (EOT; ~34 Ma) marks a period of major reorganization of Earth's global climate and rapid formation of a permanent ice sheet on Antarctica [1]. In the deep ocean, this transition is recorded as a two-step positive shift (1.2–1.5 ‰) in benthic foraminiferal oxygen isotopes ( $\delta^{18}\text{O}_b$ ), commonly interpreted to reflect a combination of deep-ocean cooling and an increase in seawater isotopic composition ( $\delta^{18}\text{O}_{sw}$ ) associated with Antarctic ice sheet expansion [2]. Clumped isotope thermometry ( $\Delta_{47}$ ) provides an independent temperature proxy that enables the separation of temperature and  $\delta^{18}\text{O}_{sw}$  signals from the  $\delta^{18}\text{O}_b$  record [3]. Here we apply  $\Delta_{47}$  to reconstruct bottom water temperatures (BWT) in the South Atlantic Ocean (ODP Site 1263) across the EOT, with particular focus on the Earliest Oligocene Oxygen Isotope Step (EOIS). The  $\Delta_{47}$  record indicates gradual deep ocean cooling from the relatively warm latest Eocene (~10 °C) towards the EOIS (~7 °C). However, these cooler conditions did not continue into the early Oligocene, as BWTs rebounded (~9 °C) after the EOIS at ~33.6 Ma. This long-term evolution of South Atlantic BWTs broadly agrees with  $\Delta_{47}$ -based reconstructions from the deep eastern Pacific and parallels trends in atmospheric CO<sub>2</sub> reconstructions [4]. This suggests that the observed BWT evolution reflects a global temperature signal driven by atmospheric CO<sub>2</sub> changes. The return to warmer conditions in the earliest Oligocene, despite continued Antarctic glaciation, implies a non-linear relationship between global temperature and ice volume, in which stabilizing feedbacks within the early Antarctic ice sheet were strong enough to prevent net ice melting [5]. Superimposed on the deep ocean cooling trend towards the EOIS, we identify a short-lived cold excursion (~3 °C) in the South Atlantic that is absent from Pacific  $\Delta_{47}$  records. We speculate that this transient deep cooling reflects temporary shifts in deep-water formation within the Atlantic sector of the Southern Ocean, linked to potentially unstable climatic conditions preceding the onset of major Antarctic glaciation.

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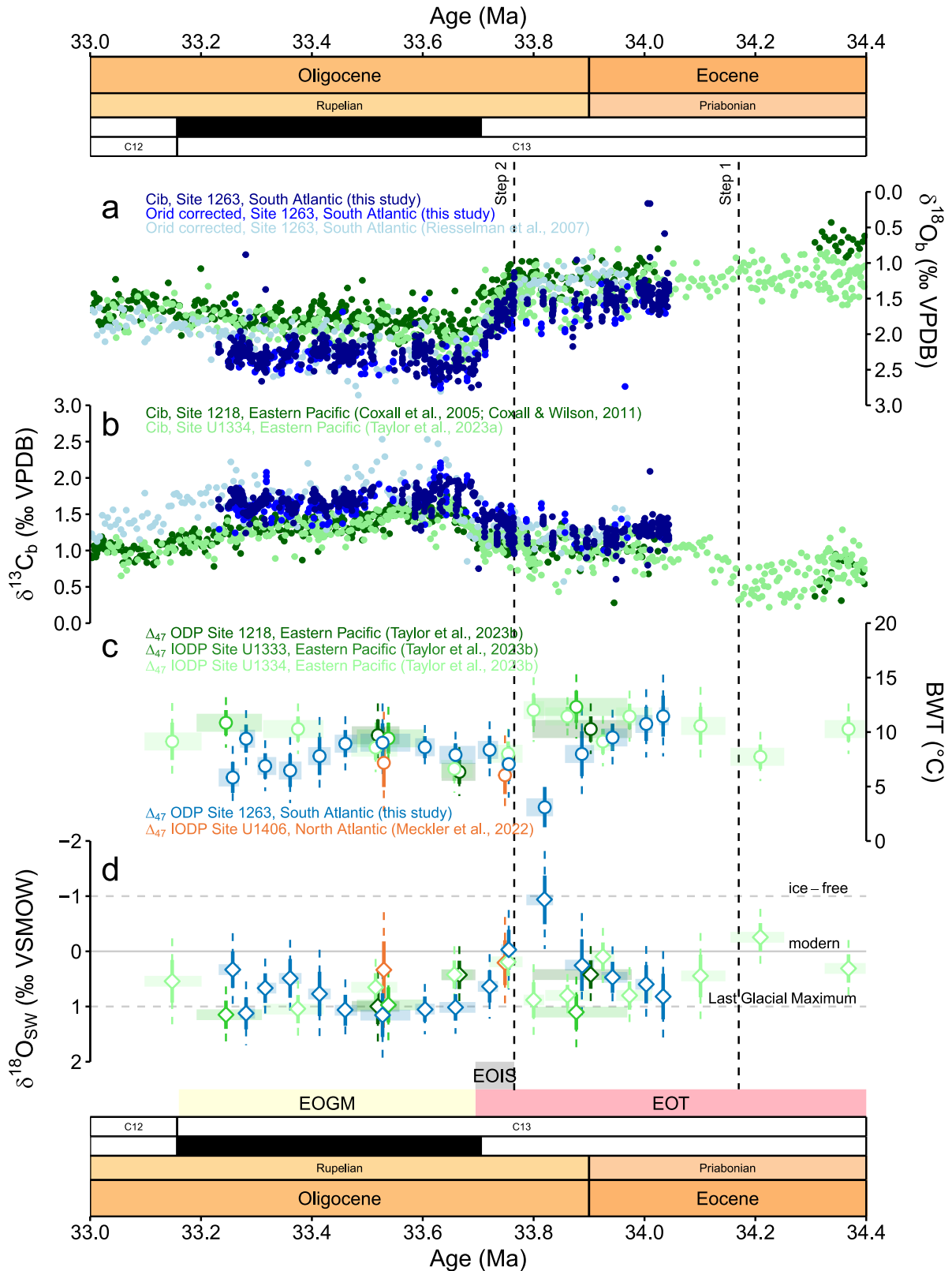


Figure 1: Comparison of high-resolution  $\delta^{18}\text{O}_b$  and  $\delta^{13}\text{C}_b$  records,  $\Delta_{47}$ -based BWT and inferred  $\delta^{18}\text{O}_{\text{sw}}$  composition across the EOT. Coloured bars and dashed lines indicate the timing and duration of the Eocene–Oligocene Transition (EOT), Earliest Oligocene Glacial Maximum (EOGM), Earliest Oligocene Isotope Shift (EOIS), Step 1, and Step 2.



## Determining Natural Abundance Isotope Ratios of Polycyclic Aromatic Hydrocarbons in Complex Environmental Samples using GC-Orbitrap

Md Samrat Alam<sup>a</sup>, Jason M. E. Ahad<sup>a</sup>, Leah Mindorff<sup>a</sup>, Benjamin R. Fosu<sup>a</sup> Josué J. Jautzy<sup>a</sup>

<sup>a</sup> Geological Survey of Canada, Natural Resources Canada, Québec, Canada

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and important molecular tracers of biomass burning, fossil fuel combustion, and geological processes. Their isotopic compositions provide valuable insights into source apportionment and formation pathways. Orbitrap mass spectrometry has sufficient mass resolving power to detect and measure the abundance of rare PAH isotopologues and distinguish isobaric interferences with mass accuracies down to the sub-1 ppm level. This enables both multi-substituted isotopologue and position-specific isotope analyses that are not achievable with conventional isotope ratio mass spectrometry (IRMS) approaches. Here, we report method development for molecular-average isotope ratios of PAHs using an Orbitrap platform applying direct elution measurements. Commercial isotopic standards (phenanthrene and pyrene) and mixed <sup>13</sup>C-labeled analogs were introduced into the Orbitrap MS through electron ionization (EI) and analyzed for calibration and to evaluate analytical performance. For each PAH, the Mo (all-<sup>12</sup>C) isotopologue and the singly <sup>13</sup>C-substituted isotopologue were quantified concurrently in the Orbitrap mass spectrum, and isotope ratios were calculated from the intensities of each mass peak. We further measured  $\delta^{13}\text{C}$  values for phenanthrene, pyrene and retene extracted from complex environmental matrices including petcoke, bitumen, ash, and atmospheric particulates. Analytical precisions and accuracy of  $\sim 1.0\text{‰}$  for  $\delta^{13}\text{C}$  were achieved. We aim to advance this methodology toward accurate quantification of clumped and position-specific isotope signatures in PAHs to gain insight into historical boreal fire severity.



# Unlocking Cambrian Climate: Clumped Isotope Thermometry in Phosphatic Fossils

Fiona Anstey<sup>a</sup>, Kristin D. Bergmann<sup>a</sup>

<sup>a</sup> Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, USA

The Cambrian Period (~540–485 Mya) was a pivotal moment in Earth’s history, marked by the emergence of complex marine organisms. Yet seawater temperature estimates based on low  $\delta^{18}\text{O}$  values from marine carbonates suggest ocean temperatures  $\geq 60^\circ\text{C}$ , significantly higher than the thermal tolerance of most modern marine invertebrates. These low  $\delta^{18}\text{O}$  values, anomalous in the geologic record, may reflect: (1) preferential diagenetic alteration of Cambrian rocks, perhaps linked to their original mineralogy; (2) a lower  $\delta^{18}\text{O}$  composition of seawater during the early Paleozoic; (3) elevated seawater temperatures; or a combination of these three end-member scenarios. Apatite-derived  $\delta^{18}\text{O}$  values suggest more moderate sea surface temperatures, but the data remain sparse [1]. To evaluate these uncertainties, we compare the existing  $\delta^{18}\text{O}$  record to clumped isotope-derived temperatures from apatite and co-occurring carbonate across a range of burial histories from 12 globally distributed localities.

Clumped isotope thermometry offers a means to independently assess the fidelity of the oxygen isotope record, though the Cambrian remains a critical gap in the global clumped isotope record [2]. Estimating primary temperatures in deep time from  $\Delta_{47}$  values comes with a suite of challenges, including assessing geologic indicators of diagenetic alteration, characterizing the point during burial history at which the target mineral stabilized, and evaluating the susceptibility of carbonate groups to solid-state reordering of C—O bonds. To address these challenges we target apatite, a mineral less soluble than calcite or dolomite and possibly more resistant to diagenetic overprinting, as a candidate for testing end-member scenarios. To evaluate thermal resetting, we model solid-state reordering across the burial histories of sampled localities. Preliminary clumped isotope data from Cambrian apatite fossils yield reasonable sea surface temperatures (26–38°C), supporting the potential of this proxy to preserve seawater signals [3]. This work will offer new insights into the environmental conditions that accompanied the early diversification of life and contribute to our understanding of clumped isotopes in phosphatic fossils as a tool for probing seawater conditions in deep time.

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## Clumped Isotope Constraints in Lower Cretaceous Pre-Salt Carbonates, Santos Basin, Brazil

Anelize Bahniuk Rumbelsperger<sup>a</sup>, Felipe Farias<sup>b</sup>, Leonardo Cury<sup>a</sup>

<sup>a</sup> Lamir Institute, Federal University of Paraná, Curitiba (PR), Brazil

<sup>b</sup> Petrobras Research Center, Rio de Janeiro, Brazil

Clumped isotope thermometry ( $\Delta_{47}$ ) is an important proxy for reconstructing carbonate formation temperatures and evaluating the thermal evolution of sedimentary basins. In this study,  $\Delta_{47}$  analyses were applied to Lower Cretaceous Pre-Salt carbonates of the Barra Velha Formation, Santos Basin, Brazil, to investigate the paleothermal history of these globally significant lacustrine reservoirs. The analyzed carbonates include Shrubstones and Spherulitstones facies, and diagenetic calcite and dolomite cements affected by multiple post-depositional processes. Representative samples from distinct paragenetic stages were measured using IRMS at the LAMIR Institute (UFPR). Results indicate clumped isotope temperatures significantly higher than present-day reservoir conditions, with values ranging from approximately 112 to 130°C in several diagenetic phases. These temperatures exceed current formation temperatures of about 80°C, suggesting carbonate precipitation under hydrothermal conditions rather than simple burial heating. The  $\Delta_{47}$  dataset indicates that high-temperature fluids circulated repeatedly through the reservoir during its diagenetic evolution, promoting recrystallization, cementation, silicification, and dissolution events. Calculated  $\delta^{18}\text{O}$  values of parent waters indicate interaction with isotopically evolved saline fluids, compatible with closed-basin lacustrine brines and deeper hydrothermal waters. Distinct  $\Delta_{47}$  temperatures among carbonate phases also allow discrimination between early diagenetic products and later hydrothermal overprints, helping to establish the relative timing of thermal events. The results demonstrate the strong potential of clumped isotope thermometry for resolving complex thermal histories in Pre-Salt carbonate reservoirs. In the Santos Basin,  $\Delta_{47}$  data expand the application of clumped isotopes to South American petroleum systems and provide a valuable framework for predicting reservoir heterogeneity, porosity evolution, diagenetic pathways, and fluid-flow processes in deeply buried carbonate systems.



## Cryogenian Interglacial Climate Revealed by Dolomite Triple Oxygen Isotopes

David Bajnai<sup>a</sup>, Jack Stacey<sup>b</sup>, Marie Pesnin<sup>a</sup>, Malcolm W. Wallace<sup>b</sup>, Andreas Pack<sup>a</sup>,  
Daniel Herwartz<sup>c</sup>, Uri Ryb<sup>d</sup>, Ashleigh van Smeerdijk Hood<sup>b</sup>

<sup>a</sup> Geoscience Center, University of Göttingen, Germany

<sup>b</sup> School of Geography, Earth and Atmospheric Sciences, University of Melbourne, Australia

<sup>c</sup> Institute for Geology, Mineralogy and Geophysics, Ruhr University Bochum, Germany

<sup>d</sup> The Fredy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Israel

Quantitative paleotemperature estimates for the Precambrian remain scarce, largely due to the limited availability of well-preserved material and the inherent constraints of traditional temperature proxies. Conventional oxygen isotope thermometry is hindered by the poorly constrained isotopic composition of ancient seawater, whereas clumped isotope thermometry can be compromised by solid-state reordering. In both cases, it is often difficult to verify whether the analyzed phases retain a primary seawater signature. Carbonate triple oxygen isotope measurements, integrating  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , offer a way to address these challenges by constraining carbonate formation and alteration pathways, thereby enabling insights into deep-time climate conditions even from non-pristine material.

In this study, we investigated interglacial carbonates deposited between the Sturtian and Marinoan Snowball Earth events, including dolomitized reef sediments from the Oodnaminta Reef Complex in Australia, the Gauss Formation in Namibia, and the Mt. Profeit Formation in Canada. Petrographic and sedimentological evidence indicates that dolomitization of originally aragonitic reef components occurred shortly after deposition, accompanied by precipitation of primary dolomite cements. In contrast, limestone samples, particularly those from deeper basin settings, show clear evidence of extensive reworking.

Samples were analyzed using laser spectroscopy following automated acid digestion at 90 °C. Across the studied localities, dolomite samples exhibit broadly consistent isotope compositions. Dolomite samples with the highest  $\delta^{18}\text{O}$  and lowest  $\Delta^{17}\text{O}$  values are consistent with growth at approximately 20 °C from a fluid with  $\delta^{18}\text{O}$  values of -3 to -4 ‰ and  $\Delta^{17}\text{O}$  values comparable to modern seawater, around -11 ppm. The observed variability within the dolomite dataset can be attributed to isotope exchange at elevated temperatures under relatively low water-rock ratios. Limestone samples, by comparison, show lower  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values, consistent with low-temperature alteration under high water-rock ratios, likely driven by meteoric fluids.

In summary, our results further demonstrate that triple oxygen isotopes can distinguish primary marine signals from diagenetic overprints and provide quantitative paleotemperature constraints for deep time. The Cryogenian interglacial was characterized by temperate climate conditions, in contrast to hypotheses invoking a generally warm Precambrian climate or an extreme greenhouse state between Snowball Earth glaciations.



## A 20 Year Journey in Clumped Isotope Geochemistry at ETH

Stefano M. Bernasconi<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zürich, Zürich, Switzerland

Clumped isotope geochemistry is arguably one of the most exciting developments in geochemistry of the last 25 years. During this time, it has transformed from an experimental methodology implemented in only few laboratories, to a mature and increasingly popular and broadly applied technique with many applications in earth sciences. With ever improving technology, the methodology initially focused on CO<sub>2</sub> and carbonates, is continuously and rapidly expanding to other molecules and isotopic systems. In this contribution, I will review some key experiences and lessons we learned in the past 20 years, that were key to transform the nascent field of clumped isotope geochemistry into a mature field.

As with any novel method, the comparability of measurements across laboratories is key to develop the scientific field and to produce robust results to tackle new scientific questions. Collaborative efforts and a healthy competition among groups, including workshops with animated and controversial discussions, are fundamental to improve the methodology and transform it into a technique that is recognized by the broader science community. The InterCarb exercise<sup>1</sup> is a prime example of how a community effort greatly improved interlaboratory reproducibility and the applicability of the method [1]. With new development towards new molecules, and the necessity to further reduce analytical uncertainty, similar efforts must continue in the future to further establish clumped isotope geochemistry as a key methodology that is contributing key information to better understand geological processes and improve our understanding of climate change through the geological past.

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## D4Xgui: A tool for baseline correction and standardization of carbonate clumped isotope raw data

Miguel Bernecker<sup>a</sup>, Mathieu Daëron<sup>b</sup>, Philip T. Staudigel<sup>a</sup>, Sven Hofmann<sup>a</sup>, Jens Fiebig<sup>a</sup>

<sup>a</sup> Institute of Geosciences, Goethe-University Frankfurt, Germany

<sup>b</sup> Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, France

The carbonate clumped isotope community has harmonized sample preparation, analysis, and standardization protocols, largely resolving the interlaboratory discrepancies that characterized the field's early years. Today, identically processed raw datasets from common reference materials are statistically indistinguishable across laboratories. However, this reproducibility is only guaranteed when analytical and standardization-derived uncertainties are fully propagated throughout the entire data-processing pipeline.

Daëron (2021) laid the mathematical groundwork for this with D47crunch, a framework that optimizes standardization parameters through variance minimization algorithms while ensuring complete error propagation. Fiebig et al. (2021) introduced a half-cup-based pressure baseline (PBL) correction, addressing the well-known dependency of  $\Delta_i$  values on bulk isotopic composition (*heated gas line*, [3]). PBL correction is particularly important for accurate and precise  $\Delta_{48}$  measurements on modern high-sensitivity gas source mass spectrometers, where the magnitude of PBL-induced bias is comparable to that historically observed for  $\Delta_{47}$  on earlier configurations [4].

After extensive development and internal validation, we present D4Xgui: a cross-platform application that unifies PBL correction and standardization within an intuitive graphical interface [5]. The tool accepts cycle- and replicate-level raw intensity data ( $m/z$  44–49 and  $m/z$  47.5) as well as pre-calculated replicate  $\delta^{45}$ – $\delta^{49}$  values as inputs. PBL scaling factors for  $m/z$  47–49 can either be determined from equilibrated gases or from carbonate standards. Standardization is performed via the integrated D47crunch module, applying full error propagation. Results are presented in interactive plots and spreadsheets, enabling intuitive exploration of replicate- and sample-level data. As open-source project, it allows community-driven implementation, and is intended to benefit from end-user feedback and suggestions.

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# A Continuous Empirical Calibration from 0 to 250 °C for Dual Carbonate Clumped Isotopes ( $\Delta_{47}$ and $\Delta_{48}$ ) in Experimentally Synthesised Dolomites

Isaac Bondzie-Selby<sup>a</sup>, Cole A. McCormick<sup>b</sup>, Peter K. Swart<sup>c</sup>, and Chelsea L. Pederson<sup>a</sup>

<sup>a</sup> Department of Geology and Geological Engineering, South Dakota School of Mines and Technology, Rapid City, United States

<sup>b</sup> Department of Geosciences, The Pennsylvania State University, State College, United States

<sup>c</sup> Rosenstiel School of Marine, Atmospheric, and Earth Science, University of Miami, Miami, United States

The dual carbonate clumped isotope proxies ( $\Delta_{47}$  and  $\Delta_{48}$ ) have emerged as powerful tools for reconstructing palaeotemperature, investigating diagenetic processes, and assessing isotopic equilibrium in modern and ancient carbonates. While empirical  $\Delta_{47}$  calibrations for dolomite exist across a broad range of temperatures, some scepticism remains over whether the  $\Delta_{47}$ -T relationship in dolomite is equivalent to that of calcite, thus introducing uncertainty in reconstructed dolomite temperatures – and, by extension, the oxygen-isotopic composition of the diagenetic fluid ( $\delta^{18}\text{O}_{\text{FLUID}}$ ) – in ancient carbonate rocks. Such uncertainty extends to  $\Delta_{48}$  values, which have received significantly less research. To address this gap, high-temperature experiments were conducted to dolomitise aragonite at 150–250 °C. Reaction products were characterised using X-ray diffraction (XRD), and only samples containing >98% dolomite were selected for dual clumped isotope ( $\Delta_{47}$  and  $\Delta_{48}$ ) analysis. The  $\Delta_{47}$  and  $\Delta_{48}$  values were measured on a Thermo 253-plus and evaluated against published empirical calibrations and the theoretical equilibrium trajectory of Hill et al. (2014). Both  $\Delta_{47}$  and  $\Delta_{48}$  values show a systematic negative dependence on synthesis temperature, across the 150–250 °C interval, broadly consistent with thermodynamic signatures. In the  $\Delta_{47}$ - $\Delta_{48}$  space, the dolomites plot close to the theoretical trajectory of Hill et al. (2014) and the empirical line of Fiebig et al. (2021). Combined with published low-temperature calcite data from the same laboratory (Swart et al., 2021; 5–65 °C), our dataset provides a basis for a continuous empirical calibration spanning 0–250 °C. This study provides the first experimental  $\Delta_{48}$  constraints for dolomite at elevated temperatures and lays the groundwork for a continuous empirical calibration of  $\Delta_{47}$ - $\Delta_{48}$  spanning 0–250 °C from a single laboratory. The findings have direct relevance to the application of dual clumped isotope thermometry in primary and diagenetically altered carbonate systems.

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## Using $\Delta_{47}$ to characterize water mass properties and distributions in the Cretaceous Western Interior Seaway

Adriana J. Brown<sup>a</sup>, Sierra V. Petersen<sup>a</sup>, Matthew M. Jones<sup>b</sup>

<sup>a</sup> Department of Earth and Environmental Science, University of Michigan, Ann Arbor, MI 40109, USA

<sup>b</sup> U.S. Geological Survey, Geology, Energy & Minerals Science Center, Reston, VA 20192, USA

The Western Interior Seaway (WIS) was a vast and shallow inland sea that spanned the North American continent during the middle to Late Cretaceous (~121–66 Ma). Conditions in the WIS were dynamic and complex, influenced by regional tectonic forces, global climate and eustatic sea level changes, and basin-scale circulation patterns. In this study, we report 117 new estimates of temperature and seawater oxygen isotope composition ( $\delta^{18}\text{O}_w$ ) from carbonate clumped isotope paleothermometry of well-preserved marine mollusks (mostly oyster specimens) from the United States (U.S.) and Canadian WIS. Our samples span the Albian to Maastrichtian stages (~113–66 Ma) across latitudes of 25–57 °N.

This dataset provides a long-term spatiotemporal record of reconstructed water temperature and  $\delta^{18}\text{O}_w$  values in the WIS. We find evidence for two distinct water mass end-members: warm (23–37 °C) and relatively enriched (0.0–1.1‰) gulf-sourced waters in latitudes below 48 °N and a cooler (16–24 °C) and isotopically lighter (–4.3 to –2.5‰) Arctic-sourced water mass at Canadian latitudes. Across all time periods, latitudinal temperature variation was minimal in the U.S. portion of the seaway, suggesting prevailing northward heat transport from a Gulf Coast-sourced water mass.  $\delta^{18}\text{O}_w$  depletion in the northern U.S. latitudes is interpreted as evidence for freshwater runoff into the basin from surrounding highlands.

The resulting insights into seawater temperature and circulation provide a framework for interpreting the paleontological records and climate-sensitive sedimentary facies of the WIS, as well as how paleoclimatic conditions in North America evolved during the Cretaceous greenhouse climate interval relative to other regions around the globe.



## From Greenhouse to Icehouse: Tropical Climate Insights from Larger Benthic Foraminifera of Kutch (Kachchh) Basin, Western India

Swagata Chaudhuri<sup>a</sup>, Aniket Mitra<sup>a,b</sup>, André Navin Paul<sup>c</sup>, Deepak Binu Beena<sup>a</sup>, Xianye Zhao<sup>a</sup>, Béatrice A. Ledéser<sup>b</sup>, Axel Gerdes<sup>c</sup>, Philippe Claeys<sup>a,d</sup>, Inigo A. Müller<sup>a</sup>

<sup>a</sup> Archaeology, Environmental Changes & Geo-Chemistry (AMGC), Vrije Universiteit Brussel, Brussels, Belgium

<sup>b</sup> Institut des Sciences de la Terre de Paris (ISTeP), CY Cergy Paris Université, Neuville-sur-Oise, France

<sup>c</sup> Frankfurt Isotope and Element Research Center (FIERCE), Goethe University Frankfurt, Frankfurt am Main, Germany

<sup>d</sup> Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, BC, Canada

Tropical Eocene and Oligocene records assesses how low-latitude systems responded to major global climate shifts from hothouse to icehouse condition. Kutch (or Kachchh), a western Indian pericratonic rift Basin with paleotropical positioning in late Paleogene preserves thick Eocene to Oligocene sedimentary successions along with well-preserved larger benthic foraminifera (LBF), providing a valuable archive for paleoclimate reconstruction. The pristinity of LBF like *Nummulites* from the different units of Eocene to Oligocene epoch were evaluated by major and trace element concentration through micro-XRF prior to stable isotope analyses on foraminiferal samples using a NuCarb–Perspective instrumental setup. Then, U–Pb laser ablation ICP–MS dating was performed on multiple shell chambers and inner-wall domains of selected samples to distinguish different recrystallization phases to better estimate the depositional age of the fossil material. Mean annual sea surface temperatures (SST) were estimated from clumped isotopes ( $\Delta_{47}$ ),  $\delta^{13}\text{C}_{\text{cc}}$  and  $\delta^{18}\text{O}_{\text{cc}}$  data, from powdered calcite shell material to track hydroclimate and biogenic carbonate-factory changes across the tropical carbonate platform during the Bartonian and Rupelian time. Stratigraphically upward, mean annual SST shift from peak warmth in the early Bartonian (38 °C) to slightly milder mid Bartonian values (~ 35 °C), then become more variable with a general cooling trend in the late Bartonian. Before transitioning to cooler Rupelian conditions (~25.2°C) the fossil record shows a brief heat surge up to ~35.5 C. Over the same interval, periodic variability in  $\delta^{13}\text{C}_{\text{cc}}$ ,  $\delta^{18}\text{O}_{\text{cc}}$ , and  $\delta^{18}\text{O}_{\text{sw}}$  provides evidence for variations in the evaporation–precipitation budget due to variations in the climate and/or the basin structure. Finally the new tropical climate record is compared to the global climate of the late Eocene to early Oligocene to disentangle local from global climate signals.



# The Palaeo-Adriatic Basin during the Mid-Piacenzian Warm Period: Clumped isotope-based seasonality reconstruction from Bivalve shells

Andrea Chiari<sup>a</sup>, Niels de Winter<sup>b</sup>, Gaia Crippa<sup>a</sup>, Giulio Pavia<sup>c</sup>, Martin Ziegler<sup>d</sup>

<sup>a</sup> Department of Earth Sciences 'A. Desio', University of Milan, Milan, Italy

<sup>b</sup> Department of Earth Sciences, Vrije Universiteit Amsterdam, Amsterdam, Netherlands

<sup>c</sup> Department of Earth Sciences, University of Turin, Turin, Italy

<sup>d</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

Bivalve shells represent one of the most important biotic archives of geochemical proxies for high-resolution palaeoclimatic and palaeoenvironmental reconstructions. In particular, sclerochronological and sclerochemical analyses of calcium carbonate shells allow seasonal investigations of environmental variability (e.g. seawater temperature,  $\delta^{18}\text{O}_{\text{sw}}$ , pH and nutrient supply) and comparisons across modern, historical or deep-time settings. The Mid-Piacenzian Warm Period (3.3–3.0 Ma) is a Pliocene climate warming event, recognised as the most recent example of prolonged global warming in the geological past and regarded as a possible analogue for the future climate conditions [1]. The Rio Vaccaruzza section, Villalvernia (Piedmont, Italy) deposited in the Palaeo-Adriatic Basin, continuously covers this time interval and has rich mollusc assemblages [2]. It represents a key section in which to study the seasonal palaeotemperature variation recorded by its excellently preserved bivalve shells using clumped isotope thermometry ( $\Delta_{47}$ ) through a sclerochronological approach. Here, we analyse four pristine bivalve specimens belonging to two families characterised by different growth rates: two *Glycymeris bimaculata* (Poli, 1795) having slow growth rates, and two pectinids: one *Aequipecten opercularis* (Linnaeus, 1758) and one *Perapecten scabrellus* (Lamarck, 1819) having fast growth rates. The use of species with different growth rates enables the reconstruction of the seasonality at different temporal resolutions, from 2–3 years (Pectinidae) to more than 10–15 years ranges (Glycymerididae). Specimens were collected from Bed 3 of the Rio Vaccaruzza section, which is characterised by a muddy sand lithology belonging to the Sabbie di Asti Formation. The depositional environment is interpreted as an infralittoral setting influenced by hyperpycnal flows that produce bottom water instability and salinity fluctuations. Due to this depositional setting, the application of clumped isotope analyses is crucial as it allows an independent reconstruction of seasonal seawater temperatures and  $\delta^{18}\text{O}_{\text{sw}}$  variability recorded by bivalve shells. The preliminary  $\Delta_{47}$  and  $\delta^{18}\text{O}$  values of bivalve shells suggest a higher annual mean water temperature than in the modern Northern Adriatic Sea and seasonal fluctuations in  $\delta^{18}\text{O}_{\text{sw}}$  consistent with a shallow-marine environment characterised by seasonally varying freshwater input.

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## Applying coccolith clumped isotope thermometry to the past: a case study from the middle Miocene Climatic Transition

Alexander J. Clark<sup>a</sup>, Andrea Karen<sup>a</sup>, Madalina Jaggi<sup>a</sup>, Stefano M. Bernasconi<sup>a</sup>, Heather M. Stoll<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zürich, Zürich, Switzerland

Coccoliths are the calcite plates of coccolithophores, unicellular photosynthesizing algae that live in all ocean basins. Coccoliths are a significant contributor to the global carbonate deposition in the deep ocean and have been found throughout the Meso- and Cenozoic periods. However, despite the widespread usage of the coccolithophore-derived alkenone Uk'<sub>37</sub> temperature proxy, coccoliths as a proxy carrier for temperature are generally understudied. Deciphering potential overgrowth, uncertain calcification depths, and obtaining a relatively pure coccolith size fraction are among the commonly occurring difficulties. A few studies have shown the potential of coccoliths as a temperature proxy carrier, specifically for clumped isotopes ( $\Delta_{47}$ ) but were measured before the introduction of the I-CDES carbonate standardization [1,2]. Recently, coccoliths from cultures and sediment traps were used to generate a coccolith-specific clumped isotope calibration, which showed a consistent relationship between  $\Delta_{47}$  and calcification temperatures, distinct from foraminifera by  $\sim 1-2^\circ\text{C}$  [3].

Here we present some of the difficulties and successes in applying coccolith clumped isotope thermometry to the past, focusing on the late middle Miocene Climatic Transition (MMCT; here taken as  $\sim 13.90 - 13.6$  Ma). This was a period of change between a relatively warm and dynamic Miocene Climatic Optimum to a colder and more stable post-MMCT world. Previously measured Mg/Ca, Uk'<sub>37</sub>,  $\delta^{18}\text{O}$ , and  $\Delta_{47}$  temperature proxies show both stable and decreasing surface or bottom water temperature changes across the MMCT [4,5]. To disentangle these inter-proxy differences, we apply coccolith clumped isotope thermometry to a globally distributed set of sites. In-depth quantitative preservation analysis was performed using circular polarized light and scanning electron microscopy and elemental analysis, to screen and judge samples suitable for clumped isotope analysis. No systematic change in coccolith calcification temperatures were found across the MMCT, and a direct regional comparison to modern core tops and sediment traps reveal little coccolith calcification temperature change between the MMCT and the Holocene. Thus, with the correct preservation screening, coccoliths show great potential for future palaeothermometry applications.

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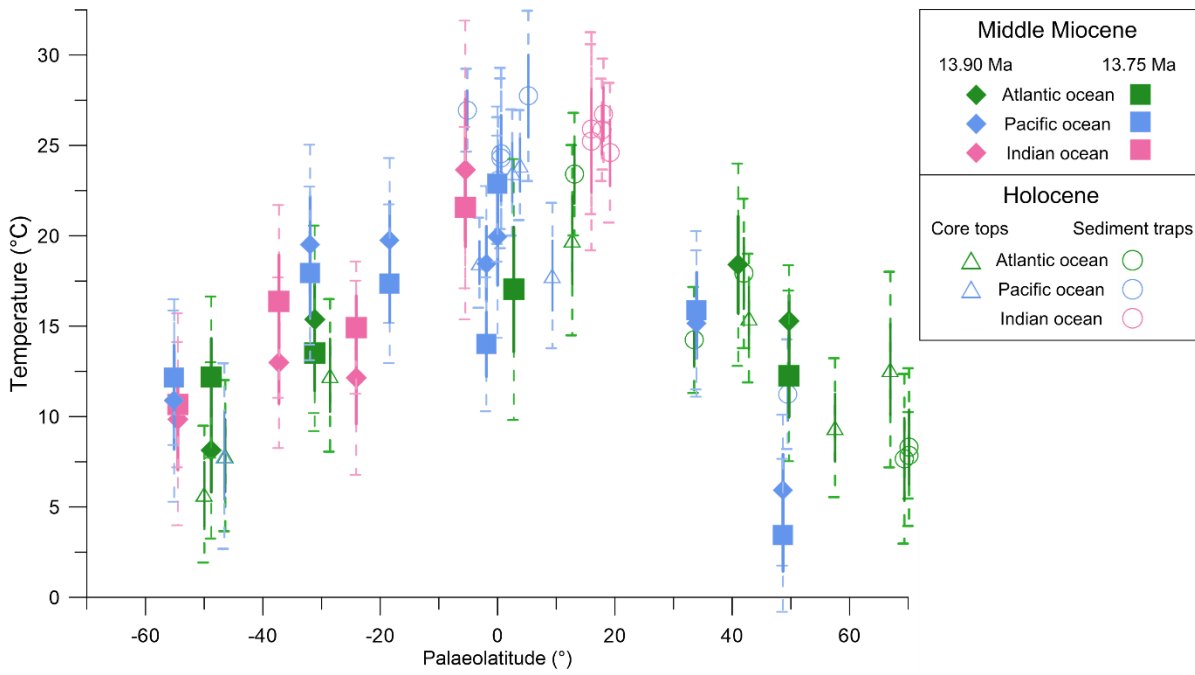


Figure 1: Coccolith clumped isotope temperatures against the (paleo-)latitude for two timeslices during the middle Miocene, Holocene core tops, and modern sediment traps. Each time period is colour coded using ocean basins; Atlantic (green), Pacific (blue), and Indian (pink) oceans, and using symbols; 13.90 Ma (diamonds), 13.75 Ma (squares), core tops (empty triangles), and sediment traps (empty circles).



## Methane Isotopologues ( $\delta^{13}\text{C}-\text{CH}_4$ , $\delta^2\text{H}-\text{CH}_4$ , $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ ) from Arctic wetlands: Characterization of high latitude methane sources

Matthieu Clog<sup>a</sup>, Sara Defratyka<sup>b</sup>, Matilda Lundström<sup>c</sup>, Chris Rennick<sup>d</sup>, Freya Wilson<sup>d</sup>, Alex McDonald<sup>a</sup> and Tim Arnold<sup>c,e</sup>

<sup>a</sup> SUERC – Centre for the Isotope Sciences, University of Glasgow, Glasgow, United Kingdom

<sup>b</sup> Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL) CEA-CNRS-UVSQ Université Paris Saclay, Gif-sur-Yvette, France

<sup>c</sup> Department of Earth and Environmental Sciences, Lund University, Lund, Sweden

<sup>d</sup> National Physical Laboratory, Teddington, United Kingdom

<sup>e</sup> School of GeoSciences, University of Edinburgh, Edinburgh, UK

Clumped isotopes have the potential to provide insight into the global atmospheric methane budget and measuring the major methane isotopic source signatures is critical in that effort. Arctic wetlands are of major interest as their methane emissions are expected to increase with higher temperatures, resulting in a positive climate feedback, however, to-date no clumped isotope measurements exist.

We report the results from a week-long sampling campaign conducted in the Abisko-Stordalen Palsa Bog (68°21' N, 19°03'E), a sporadic permafrost zone in northern Sweden during the summer of 2025. To ensure that sufficient volumes of air samples could be gathered over several hours for clumped isotope measurements a 1000 L chamber was used for accumulation, followed by collection in sealed, gas-tight bags. Three different locations were chosen with different vegetation covers, with diurnal and nocturnal emissions collected separately. Samples were processed to remove all gases other than methane using a preconcentrator developed at NPL, followed by cryostatic and gas chromatography methods at SUERC. The pure methane samples were then measured using a TFS Ultra high-resolution isotope ratio mass spectrometer. Duplicate sampling allowed us to evaluate the robustness of the processing workflow – from collection at the remote field site to the final measurement in the laboratory – with the results providing the first direct measurement constraints on clumped methane from Arctic wetlands.



# What's in a Shell? Methods for Time-Resolved Sampling to Disentangle Climate and Physiological Signals in Bivalve Shells with Dual Clumped Isotopes

Allison N. Curley<sup>a</sup>, Sruthi Sreenivasan<sup>b</sup>, Thomas Steuber<sup>b</sup>, Niels J. de Winter<sup>c</sup>, Brendan Oerlemans<sup>c</sup>, Melita Peharda<sup>d</sup>, and Jens Fiebig<sup>a</sup>,

<sup>a</sup> Institute for Geosciences, Goethe Universität–Frankfurt, Frankfurt am Main, Germany

<sup>b</sup> Department of Earth Science, Khalifa University, Abu Dhabi, United Arab Emirates

<sup>c</sup> Department of Earth Sciences, Vrije Universiteit Amsterdam, Amsterdam, Netherlands

<sup>d</sup> Institute of Oceanography and Fisheries, Split, Croatia

Dual clumped isotopes are a powerful tool for investigating paleotemperature and kinetic effects tied to mineralization processes. Bivalves often precipitate at least their outer shell layer in equilibrium with seawater, although  $\Delta_{47}$  disequilibrium localized to specific sectors of the shell has been observed<sup>1</sup>. Schlidt et al. (2025) showed that homogenized whole-shell measurements yield equilibrium  $\Delta_{47}$ - $\Delta_{48}$  temperatures in many bivalves<sup>2</sup>, but this is an uncommon sampling strategy as archival preservation and time-resolved sampling are often important considerations. The present work aims to (1) evaluate whether high-resolution drilling techniques alter  $\Delta_{47}$ -temperatures, (2) assess the fidelity of outer and inner layer shell measurements to known growth temperature, and (3) apply high-resolution sampling techniques to understudied periods in the Pleistocene Persian/Arabian Gulf.

We found no measurable difference in  $\Delta_{47}$ ,  $\Delta_{48}$ ,  $\delta^{18}\text{O}$ , or  $\delta^{13}\text{C}$  when time-synchronous samples from a giant clam shell were milled at different drill speeds or crushed by mortar and pestle. Although high-speed drilling was found to thermally reset  $\Delta_{47}$  in some archives<sup>3</sup>, it seems that frequent breaks, constant slow motion, and light pressure are sufficient to avoid frictional resetting. Drilling at low speed, we made time-synchronous measurements between the outer and inner layers of four modern bivalve species: *Arctica islandica*, *Glycymeris bimaculata*, *Senilia senilis*, and *Geloina erosa*. We found equilibrium behavior in all species, with excellent agreement between  $\Delta_{47}$ -temperature and environmental growth temperature in both layers. However, bulk  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  differed between layers, likely indicating a “source effect”, i.e. a difference inherited from the isotopic composition of the physiologically regulated calcifying fluid. Although  $\Delta_{47}$ -temperatures are accurate, this is problematic for  $\delta^{18}\text{O}_{\text{water}}$  reconstruction,  $\delta^{18}\text{O}_{\text{carb}}$  thermometry, and forward-modelling of  $\delta^{18}\text{O}_{\text{carb}}$ .

Finally, we sampled giant clams at sub-annual resolution to fill major time gaps in the paleotemperature record of the Persian/Arabian Gulf: MIS 7 and MIS 3. Hypersaline conditions persisted in both periods, and Gulf temperatures were on par with global ocean models ( $\sim 32^\circ\text{C}$  and  $\sim 25^\circ\text{C}$ , respectively). The MIS 3 observations additionally resolve controversial palaeoshoreline reconstructions for this relatively cool period, which may be the last occurrence of giant clams in the Gulf before their conspicuous failure to recolonize modern reefs.

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## Paleothermometry of Brazilian Carbonates: A Multi-Proxy Approach Using Clumped Isotopes and Fluid Inclusions

Adelita Rodrigues<sup>a</sup>, André Pestilho<sup>b</sup>, **Leonardo Cury<sup>a</sup>**, Anelize Bahniuk Rumbelsperger<sup>a</sup>

<sup>a</sup> Lamir Institute, Federal University of Paraná, Curitiba (PR), Brazil

<sup>b</sup> Geofluid Laboratory, Geosciences Institute, University of São Paulo, (SP), Brazil

Carbonate minerals are valuable archives of paleoenvironmental and diagenetic conditions, preserving geochemical signatures related to temperature, fluid composition, water chemistry, and depositional processes through geological time. This study explores the combined application of Clumped Isotope Thermometry ( $\Delta_{47}$  CDES-90 | T°C), stable carbon and oxygen isotopes (‰ VPDB) measured by IRMS, and Fluid Inclusion Microthermometry (FI) to carbonate materials from distinct Brazilian geological settings. Complementary petrographic, mineralogical, and chemical analyses, including optical microscopy, scanning electron microscopy, X-ray diffraction, and X-ray fluorescence, support lithological characterization and evaluation of diagenetic alteration. Preliminary results include samples from the Cretaceous, Quaternary, and Holocene. Aptian microbial carbonates of the Codó Formation, Parnaíba Basin, yielded  $\delta^{13}\text{C} = -7.55\text{‰}$ ,  $\delta^{18}\text{O} = -6.59\text{‰}$ , and  $T = 39^\circ\text{C}$ . These deposits formed in restricted lacustrine to evaporitic environments associated with syn-rift tectonics. Quaternary tufas from Serra da Bodoquena, central-western Brazil, linked to karstification of the Corumbá Group, presented  $\delta^{13}\text{C} = -6.50\text{‰}$ ,  $\delta^{18}\text{O} = -6.48\text{‰}$ , and  $T = 14^\circ\text{C}$ , recording meteoric waters and continental hydrological processes. Holocene stromatolites and microbial mats from the hypersaline Fluminense Lagoons, Rio de Janeiro coast, formed during sea-level fluctuations, yielded  $\delta^{13}\text{C} = +18.70\text{‰}$ ,  $\delta^{18}\text{O} = -1.29\text{‰}$ , and  $T = 32^\circ\text{C}$ . These values reflect strong evaporation, elevated alkalinity, and active microbial mediation. The preliminary dataset demonstrates the potential of Brazilian carbonate archives to preserve meaningful thermal and environmental information across contrasting depositional and tectonic settings. Comparison between clumped isotope temperatures and FI data provides an important framework for evaluating thermal reliability and refining paleotemperature interpretations. This contribution expands the calibration and application of clumped isotope thermometry to Southern Hemisphere materials, still underrepresented in global datasets, and offers new insights into paleoclimate evolution, fluid-rock interaction, and diagenetic pathways recorded in carbonate systems.



## NeoCarb: Navigating the Transition to New Reference Materials

Mathieu Daëron<sup>a</sup>, Magali Bonifacie<sup>b</sup>, Alexis Licht<sup>c</sup>

<sup>a</sup> Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France

<sup>b</sup> Institut de Physique du Globe de Paris, France

<sup>c</sup> Centre de Recherche et d'Enseignement des Géosciences de l'Environnement, France

The establishment of the InterCarb - Carbon Dioxide Equilibrium Scale (I-CDES) marked a key milestone for carbonate  $\Delta_{47}$  metrology, effectively solving long-standing issues regarding inter-laboratory comparisons [1] and also, arguably, the calibration of equilibrium  $\Delta_{47}$  values in calcite [2]. The I-CDES is anchored to a set of four international reference materials (IRMs) prepared at ETH Zürich almost a decade ago [3]. Today, available stocks of some of these IRMs are nearing exhaustion, and some laboratories have found that trace contaminants [4] potentially affect analyses of ETH-3, a key IRM for paleoclimatology and paleoceanography because it acts as a metrological anchor for marine carbonates formed at Earth-surface temperatures. Beyond  $\Delta_{47}$ , there is an emerging but equally crucial need for additional IRMs that would be well-suited for standardizing  $\Delta_{48}$  and/or  $\Delta^{17}\text{O}$  measurements. Thus the identification, preparation, characterization, and distribution of new carbonate reference materials is widely regarded as a high priority for the clumped-isotope and clump-adjacent communities.

As a focus for open discussion, we will attempt to summarize the challenges we are facing, the practical constraints we have to work within, potential strategies to move forward, and discuss some of the ways in which we could self-organize, as a community, to navigate this critical transition to new IRMs. We will also outline our ongoing efforts to fund and set up NeoCarb, an integrated facility dedicated to supporting future community efforts to process, package and distribute suitable carbonate standards.

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# D95thermo: a Python Library/CLI for Dual Clumped Isotope Thermometry

Timothy Pollard<sup>a</sup>, Mathieu Daëron<sup>b</sup>

<sup>a</sup> School of Geography, Earth & Atmospheric Sciences, University of Melbourne, Australia

<sup>b</sup> Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France

Dual clumped isotope compositions ( $\Delta_{47} + \Delta_{48}$ ) can be used to test whether carbonates formed in clumped isotope equilibrium, and to identify and/or characterize processes associated with clumped isotope disequilibrium in natural carbonates [1–2]. However, these measurements come with large, potentially correlated analytical uncertainties [3]. What's more, the  $\Delta_{47}$  and  $\Delta_{48}$  calibrations we use to parameterize isotopic equilibrium in ( $\Delta_{47}$ ,  $\Delta_{48}$ ) space also come with quantifiable uncertainties [4]. We present a mathematical framework accounting for these sources of uncertainty and aiming to (a) provide a quantitative statistical test of the null-hypothesis that any given ( $\Delta_{47}$ ,  $\Delta_{48}$ ) measurement is consistent with isotopic equilibrium; (b) for observations statistically indistinguishable from equilibrium, compute the “best-fitting” equilibration temperature, expressed as a Gaussian distribution and/or a non-Gaussian probability distribution function (PDF); (c) for observations statistically incompatible with equilibrium, project ( $\Delta_{47}$ ,  $\Delta_{48}$ ) back onto the equilibrium curve according to an independently constrained isotopic fractionation vector to yield “disequilibrium-corrected” temperature estimates expressed as above. We also provide an open-source, calibration-agnostic, fully-documented Python implementation of this framework. The D95thermo library features computation, plotting, and reporting methods, along with a built-in command-line interface for Python-averse users.

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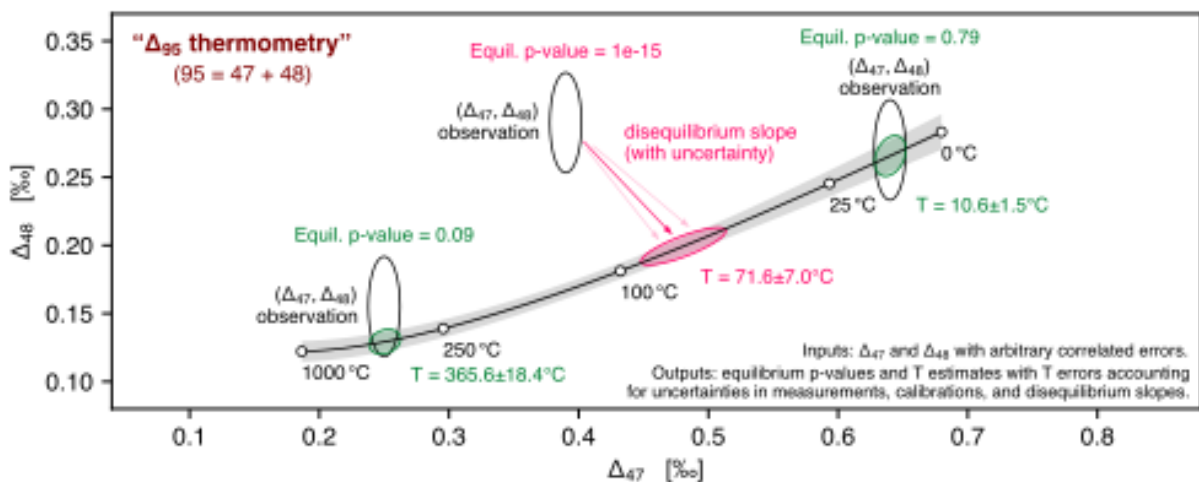


Figure 1: An example of the features provided by D95thermo



## Thermal Calibration of Methane Clumped Isotopologues: Methods and Multi-Dataset Results

Bibhasvata Dasgupta<sup>a</sup>, Henrik Eckhardt<sup>a</sup>, Malavika Sivan<sup>b</sup>, Alexis Gilbert<sup>a</sup>, Thomas Röckmann<sup>a</sup>

<sup>a</sup> Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht University, Utrecht, the Netherlands

<sup>b</sup> Royal Netherlands Meteorological Institute (KNMI), De Bilt, The Netherlands

Accurate thermal calibration of methane clumped isotopologues ( $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$ ) is essential for converting instrument-measured values into reliable formation temperatures. Previous calibrations were limited in temperature range and typically performed on a single working gas, leaving the low-temperature ( $<0^\circ\text{C}$ ) regime poorly constrained. Here we present thermal calibration experiments for two working gases (AP613 and CAL1549) spanning the widest range reported to date:  $-20$  to  $+550^\circ\text{C}$ . The  $-20^\circ\text{C}$  point required months of equilibration using  $\gamma\text{-Al}_2\text{O}_3$  catalyst, but extending the calibration range to sub-ambient temperatures improves the precision of the linear regression slope. For  $\Delta^{12}\text{CH}_2\text{D}_2$ , the theoretical range covered increases from  $\sim 15\text{‰}$  (Sivan 2021<sup>[1]</sup>,  $50\text{--}400^\circ\text{C}$ ) to  $\sim 27\text{‰}$  (this work,  $-20$  to  $550^\circ\text{C}$ ), reducing the  $2\sigma$  uncertainty on the regression slope from  $\pm 0.22$  to  $\pm 0.09$ . This means scale compression can be detected at a level of  $\sim 0.1$  instead of  $\sim 0.2$ , which matters given the observed slopes of  $0.79\text{--}0.94$  across datasets.

We apply two calibration methods: Method 1, a weighted-mean  $\Delta\text{--}T$  fit (Monte Carlo) yielding a single working-gas offset; and Method 2, a York regression<sup>[2]</sup> of  $\Delta_{\text{experimental}}$  vs  $\Delta_{\text{theoretical}}$ , which yields both slope and intercept. We recommend reporting both, as the slope is a diagnostic for scale compression and measurement biases that the intercept alone cannot reveal. Method 1 offsets are  $-2.26 \pm 0.11\text{‰}$  (AP613) and  $-5.96 \pm 0.11\text{‰}$  (CAL1549) for  $\Delta^{13}\text{CH}_3\text{D}$ . York slopes for  $\Delta^{12}\text{CH}_2\text{D}_2$  are persistently sub-unity ( $0.79\text{--}0.94$ ), while  $\Delta^{13}\text{CH}_3\text{D}$  slopes are near unity. AP613 shows no drift between the 2021 and 2025 campaigns. Conversion of all datasets to the absolute thermodynamic frame confirms convergence at  $\sim 0.2\text{‰}$  for  $\Delta^{13}\text{CH}_3\text{D}$ , supporting cross-laboratory comparisons.

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## Using Dual Carbonate Clumped Isotopes to Assess Kinetic Effects in Foraminiferal Calcite

Amelia J. Davies<sup>a,b</sup>, Marion Peral<sup>c</sup>, Jonathan Erez<sup>d</sup>, Adam Levi<sup>d</sup>, David Evans<sup>e</sup>, Oliver Friedrich<sup>f</sup>, Thibaut Caley<sup>c</sup>, Romi Nambiar<sup>a,e</sup>, Douglas Coenen<sup>a</sup>, Philip T. Staudigel<sup>a</sup>, Mattia Tagliavento<sup>a</sup>, Miguel Bernecker<sup>a</sup>, Jens Fiebig<sup>a</sup>

<sup>a</sup> Institut für Geowissenschaften, Goethe Universität Frankfurt, Frankfurt am Main, Germany

<sup>b</sup> Institut für Geologie und Mineralogie, Universität zu Köln, Köln, Germany

<sup>c</sup> Université de Bordeaux, CNRS, Bordeaux INP, EPOC, UMR 5805, Pessac, France

<sup>d</sup> Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem, Israel

<sup>e</sup> School of Ocean and Earth Science, University of Southampton, Southampton, UK

<sup>f</sup> Institute of Earth Sciences, Heidelberg University, Heidelberg, Germany

Measurement of the clumped isotope ( $\Delta_{47}$ ) composition of foraminiferal archives provides a powerful means to reconstruct upper and bottom water temperatures. However, uncertainty persists regarding whether foraminiferal calcite precipitates in clumped isotope equilibrium. Here, we address this question using dual clumped isotope ( $\Delta_{47}-\Delta_{48}$ ) analyses of foraminiferal calcite [1,2].

We present the dual clumped isotope data from both cultured and field-collected high-Mg large benthic foraminifera (LBF) (*O. ammonoides* and *A. lobifera*). We show a statistically significant offset in the dual clumped isotope composition of LBF from empirical equilibrium, suggesting the influence of kinetic processes such as CO<sub>2</sub> absorption or a combination of ion attachment/detachment effects at the solution-crystal interface and slight DIC disequilibrium. Dual clumped isotope measurements provide a valuable means of identifying kinetic effects that bias  $\Delta_{47}$ -derived growth temperatures in LBF, where sample size permits. Our results indicate that equilibrium  $\Delta_{47}$ -temperature relationships cannot be reliably applied to LBF samples that deviate significantly from empirical dual clumped isotope equilibrium (95% CI). These samples therefore require empirical calibration.

We also present dual clumped isotope data for low-Mg core top foraminifera, consisting of three planktic samples from two species (*G. ruber* and *Neogloboquadrina pachyderma*) and one deep-ocean benthic sample (*L. wuellerstorfi*). These data show no clear indication of significant kinetic bias in clumped isotope composition, though sample size (n=4) limits definitive conclusions.

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# Clumped isotope-based Reconstructions from Fossil Mollusc Shells: Constraining Seasonal Variations in Climate and Hydrology

Niels J. de Winter<sup>a</sup>, Barbara Goudsmit-Harzevoort<sup>b</sup>, Johan Vellekoop<sup>c</sup>, Nick van Horebeek, Tobias Agterhuis<sup>d</sup>, Jingjing Guo<sup>e</sup>, Xiulan Zong<sup>f</sup>, Martin Ziegler<sup>b</sup>

<sup>a</sup> Department of Earth Sciences, VU Amsterdam, Amsterdam, Netherlands

<sup>b</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

<sup>c</sup> Department of Earth and Environmental Sciences, KU Leuven, Leuven, Belgium

<sup>d</sup> School of Ocean and Earth Science, National Oceanography Centre Southampton, University of 9 Southampton, Southampton, United Kingdom

<sup>e</sup> GFZ Helmholtz Centre for Geosciences, Germany

<sup>f</sup> State Key Laboratory of Loess Science, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

The shells of molluscs (e.g., clams, snails and oysters) are grown incrementally and mineralize on timescales of hours to decades, making fossil shells excellent archives of short-term variability in past (hydro)climates [1]. Capitalizing on this, recent studies have employed clumped isotope ( $\Delta_{47}$ ) records of incrementally microsampled shells to accurately reconstruct seasonal temperature and hydrological conditions during various climate states in Earth's geological past [2–3].

However, the comparatively large sample sizes required for clumped isotope analysis create a trade-off between measurement precision and temporal resolution of the record in paleoclimate reconstructions [4]. In addition, while many mollusc shells record annual, daily or even tidal-scale growth increments, in many fossil specimens these markers may be challenging to interpret due to the lack of close living relatives, or obscured by the fossilization process. Seasonal cyclicity in the oxygen isotopic composition of mollusc shells may serve as alternative means to internally date chemical records in shells [5], but can be hard to interpret due to changes in growth rate and the interplay of (sea)water chemistry and temperature seasonality in the animal's micro-environment.

In this contribution, we discuss ways to deal with the challenge of aligning high-resolution clumped isotope data relative to the annual cycle and discuss how to treat sources of uncertainty in this alignment. To contextualize the problem of (sub-)seasonal data analysis, we present a selection of recent studies of modern and fossil shell records which highlight specific challenges related to the diverse environments in which these animals lived and built their shells.

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## More Ice in Warmer Worlds? Reassessing Plio–Pleistocene Climate Relationships

Elena Domínguez Valdés <sup>a</sup>, Ilja J. Kocken <sup>b</sup>, Tobias Agterhuis <sup>c</sup>, Inigo A. Müller <sup>d</sup>,  
Renée M. van der Kloos <sup>a</sup>, Pien Hendriks <sup>a</sup>, Noa J. Bode <sup>e</sup>, Melanie M. Broos <sup>e</sup>, Lucas J.  
Lourens <sup>a</sup> and Martin Ziegler <sup>a</sup>

<sup>a</sup> Faculty of Geosciences, Utrecht University, The Netherlands

<sup>b</sup> School of Ocean and Earth Science and Technology, University of Hawaii, Manoa

<sup>c</sup> National Oceanography Centre, University of Southampton, United Kingdom

<sup>d</sup> Archaeology, Environmental Changes and Geo–Chemistry Group, Vrije Universiteit Brussels, Brussels

<sup>e</sup> Unknown

Paleoproxy records of bottom water temperature (BWT) have been used to investigate past reconfigurations of ocean circulation, infer changes in global ice volume following deconvolution of benthic oxygen isotopes, and extract information about average surface climate in warm, equilibrated states. Despite the wealth of BWT data available for the past 5 million years, persisting uncertainties in the proxy systems and methods most widely used to derive BWT have led to different, at times conflicting, views of climate and sea level variability across key Plio–Pleistocene transitions. Here we present ongoing work to constrain the long-term evolution of Plio–Pleistocene BWTs using clumped isotopes from benthic foraminifera, including a reassessment of foraminifera–based clumped isotope calibrations. Our results question previous definitions of the relationship between mean ocean BWTs and global ice volume, with puzzling implications for the so-called onset and intensification of Northern Hemisphere glaciations after the mid–Piazzencian Warm Period and the expected influence of ice-sheets on global climate. Moreover, these new records support the tentative use of mean ocean BWT as a reflection of average surface climate beyond the Miocene, thereby showing great potential to inform the development of new paleo-informed climate models.



# Carbonate Clumped Isotope Constraints on the Stabilization of a Neoproterozoic Continental Lithosphere

Rotem Donenfeld<sup>a</sup>, Hagit Affek<sup>a</sup> and Uri Ryb<sup>a</sup>

<sup>a</sup> Department of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem, Israel

The buoyancy of continental lithospheres controls the extent of vertical motions they experience in response to sediment loading and unloading, regulating sedimentation and erosion fluxes to and from continental crusts. Over geological timescales, these fluxes affect the global carbon cycle, influencing Earth's climate and the evolution of life. Yet, the evolution of lithospheric buoyancy through geological history remains poorly understood. Thermal histories of sedimentary basins that evolved on continental lithospheres record sedimentation and erosion cycles that respond to buoyancy changes and thereby approximate the schedule of continental lithosphere stabilization.

Here we use carbonate clumped isotope thermometry to constrain the stabilization schedule of the Neoproterozoic Arabian Nubian Shield (ANS). We collected 39 carbonate samples from Cambrian, Cretaceous, and Eocene units exposed in Eilat Mts. (southern Israel), deposited since the Neoproterozoic over several cycles of sedimentation separated by regional unconformities. We identified and drilled specific mineral fabrics (matrix, fossils, cements) resulting in 44 sub-samples containing >93% calcite or dolomite. We then measured their oxygen ( $\delta^{18}\text{O}$ ) and carbon ( $\delta^{13}\text{C}$ ) isotope compositions, and clumped isotope temperatures ( $T\Delta_{47}$ ). Preliminary results from the Cambrian Timna Fm. show calcite  $T\Delta_{47}$  values ranging from ~37–66 °C. To constrain the peak burial temperatures required to preserve such values, we consider the alteration of  $T\Delta_{47}$  signals through recrystallization and solid-state reordering in a Monte-Carlo simulation across a wide range of possible thermal histories. The modeled results indicate peak burial temperatures between 60–130 °C. Assuming a geothermal gradient of 25 °C km<sup>-1</sup> and a surface temperature of 20 °C these results suggest that the Timna Fm. was buried to a maximum depth of ~1.6–4.4 km.

Previous thermochronological studies from across the ANS, including southern Israel, consistently record significantly higher Devonian temperatures in the crust and overlying Paleozoic sediments. This may be interpreted as an episode of deep (>8 km) reburial, implying a complex stabilization schedule for the ANS. Our results reject this scenario, favoring a simple, early stabilization schedule for the ANS, in which Devonian heating can be viewed as a local hydrothermal event, rather than a regional burial signal.



## Semi-continuous automated $\Delta_{47}$ Measurements of Atmospheric $\text{CO}_2$

Henrik Eckhardt<sup>a,b</sup>, Martina Schmidt<sup>a</sup>, Thomas Röckmann<sup>b</sup>, Norbert Frank<sup>a</sup>

<sup>a</sup> Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany

<sup>b</sup> Institute for Marine and Atmospheric research Utrecht, Utrecht University, Utrecht, The Netherlands

Stable isotope measurements of atmospheric  $\text{CO}_2$  are a powerful tool for partitioning contributions of different  $\text{CO}_2$  sources and sinks. In addition to the conventional tracers  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , the “clumped isotope” tracer  $\Delta_{47}$  can improve the distinction between high- and low-temperature sources of atmospheric  $\text{CO}_2$  in urban studies. Despite its potential,  $\Delta_{47}$  measurements of atmospheric  $\text{CO}_2$  remain sparse, particularly from long-term observations. One reason for this may be the high effort of manually processing samples for the measurement of  $\Delta_{47}$  in atmospheric  $\text{CO}_2$ , with high precision analysis typically require several hours per sample. Here, we present an automated preparation line coupled with a dual inlet isotope ratio mass spectrometer (MAT253+). This setup enables automated extraction and purification of atmospheric  $\text{CO}_2$  and measurement of approximately five atmospheric  $\text{CO}_2$  samples per day with sample preparation time of about 90 minutes. Over a 10-month period, the system achieved a reproducibility of  $\sim 0.005$  ‰ for  $\delta^{13}\text{C}$ ,  $\sim 0.01$  ‰ for  $\delta^{18}\text{O}$ , and  $\sim 0.011$  ‰ for  $\Delta_{47}$ .

Regular measurements using this setup provided insight into the temporal change in atmospheric  $\Delta_{47}$  in the semi-urban area of Heidelberg (Germany). In addition to the technical challenges, also the scientific interpretation of atmospheric  $\Delta_{47}$  data is not straightforward, because this “clumped isotope” tracer exhibits nonlinear behavior during air-mass mixing. Consequently, linear extrapolation approaches such as the traditional Keeling plots can yield biased source signature estimates. We therefore present a thorough correction procedure applicable to cases where  $\text{CO}_2$  enhancements are too small to allow for a direct nonlinear fit.



## Reconstructing the Thermal History of the Sedom Formation: A Plausibility Test for H<sub>2</sub> Storage

Itay Eyal<sup>a,b</sup>, Ran Issachar<sup>b</sup>, Ram Weinberger<sup>b</sup>, Hagit Affek<sup>a</sup>, Uri Ryb<sup>a</sup>

<sup>a</sup> Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem, Israel

<sup>b</sup> Geological Survey of Israel, Jerusalem, Israel

Hydrogen gas (H<sub>2</sub>) is a promising carbon-free energy source, but its large-scale deployment requires storage in large, impermeable reservoirs. A promising solution for H<sub>2</sub> storage lies in man-made caverns within underground rock salt formations, which are impermeable and leak-proof. Under sufficient pressure, rock salt flows in solid-state and can therefore self-heal fractures. However, high flow rates may compromise potential reservoirs integrity.

The Sedom Fm. in the southern Dead Sea Basin is mainly composed of halite and may be suitable for H<sub>2</sub> storage. Although largely buried, the formation crops out at Mt. Sedom, the surface expression of the Sedom diapir. Some previous studies hypothesized that the diapir is fed exclusively from a deep basin east of Mt. Sedom, where the Sedom Fm. is buried at a depth of 3.7–5.7 km. In contrast, other studies suggested that the western part of the Karbolet Mbr., at the western flank of the diapir, rises from the Ami'az Plain to the west of Mt. Sedom, where the Sedom Fm. is buried at a depth of 1.7–2.6 km. If correct, the latter interpretation implies high flow rates beneath the Ami'az Plain, possibly rendering it unsuitable for H<sub>2</sub> storage.

Here we use carbonate clumped isotope thermometry to reconstruct the thermal history of the exposed diapir and to constrain peak burial temperatures of interbedded carbonates within it. We collected 24 rock samples from across Mt. Sedom, drilled calcite and dolomite components and measured their oxygen ( $\delta^{18}\text{O}$ ), carbon ( $\delta^{13}\text{C}$ ) and clumped isotopes ( $\Delta_{47}$ ) values. We then calculated their observed apparent temperatures ( $T\Delta_{47}$ ).  $T\Delta_{47}$  values range from 27 to 101 °C, reflecting recrystallization and possibly alteration by solid state reordering at a wide range of burial depths.  $T\Delta_{47}$  values increase towards the mountain's western flank, reaching temperatures of up to  $101 \pm 12$  °C in the Karbolet Mbr., corresponding to burial depths of at least  $3.3 \pm 0.5$  km. These results support a single eastern source for the diapir and suggest that the Sedom Fm. beneath the Ami'az Plain does not flow at high rates, making it a suitable potential location for H<sub>2</sub> storage.



## **Disequilibrium Precipitation in *Mercenaria mercenaria* Clams Detected when Growing at the Extremes of Their Temperature Tolerance**

**Yunhan Fang<sup>a</sup>, Sierra V. Petersen<sup>a,b</sup>, Lucas D. Gomes<sup>a</sup>**

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA

<sup>b</sup> Museum of Paleontology, University of Michigan, Ann Arbor, MI 48109, USA

Oxygen isotope ( $\delta^{18}\text{O}_{\text{carb}}$ ) sclerochronology in bivalve shells is a widely used proxy for reconstructing paleoseasonality in the deep past; however, its quantitative ability is limited by the unknown oxygen isotope composition of the ambient water ( $\delta^{18}\text{O}_{\text{w}}$ ) during carbonate precipitation. Carbonate clumped isotope paleothermometry ( $\Delta_{47}$ ) has the potential to resolve this limitation by providing  $\delta^{18}\text{O}_{\text{w}}$ -independent temperatures, which allows for the subsequent derivation of  $\delta^{18}\text{O}_{\text{w}}$ . However, applying  $\Delta_{47}$  at high resolution has been hindered by large sample-size requirements and time-intensive analysis. In addition, regardless of the isotope proxy used, sclerochronological paleothermometry is inherently complicated by temperature-dependent preferential growth in bivalves, including complete growth shutoffs. Reconstructed profiles may not capture full annual cycles. Species-specific differences in growth temperature tolerances and preferences further complicate this limitation. Therefore, accurate interpretation of these profiles requires prior, species-specific knowledge of the interplay between bivalve physiology and isotope thermometry from modern calibration studies.

In this study, we present high-resolution  $\Delta_{47}$ -derived sclerochronological profiles of temperature and  $\delta^{18}\text{O}_{\text{w}}$  from the bivalve *Mercenaria mercenaria*, collected from sites with monitored growth conditions in Maine, Massachusetts, and Florida. We compare (i)  $\Delta_{47}$ -derived temperatures with instrumental seawater temperatures, and (ii)  $\Delta_{47}$ -derived  $\delta^{18}\text{O}_{\text{w}}$  values with empirically derived  $\delta^{18}\text{O}_{\text{w}}$  estimates based on instrumental salinity. Our results highlight potential biases in paleoclimate records derived from *M. mercenaria*. Specifically, we confirm (i) the inability of *M. mercenaria* to capture wintertime temperature minima due to growth shutoffs and (ii) good matches between  $\Delta_{47}$ -derived temperatures and instrumental records when growth occurs in an optimal temperature range of 20–30°C. However, surprisingly, when growth continues to occur outside of the optimal range,  $\Delta_{47}$  “overshoots” and records temperatures 5–10°C too hot. These vital effects lead to approximately the same mean annual temperature (MAT) at all sites, whereas the real latitudinal range of MAT is 10–25°C. We also discuss the potential of dual-clumped isotope ( $\Delta_{48}$ ) analysis as a physiological proxy, given its sensitivity to disequilibrium during carbonate formation. Our study reminds the community of the role of biological factors in  $\Delta_{47}$  sclerochronology and highlights the need for species-specific, high-resolution  $\Delta_{47}$  calibrations before applying these methods to fossil shells.



## Assessing the Influence of Dissolution and Recrystallization on Coccolith $\Delta_{47}$ -derived Temperatures Across a Depth Transect

Raquel López Ortiz<sup>a</sup>, Marta Marchegiano<sup>b</sup>, Victoria E. Taylor<sup>c</sup>, Nele Meckler<sup>c</sup>, Blanca Ausín Gonzalez<sup>d</sup>, Luz Maria Mejia Ramirez<sup>e</sup>, Mariem Saavedra-Pellitero<sup>f</sup>, Isabel Sanchez Almazo<sup>b</sup>, Jose Mesa Fernandez<sup>b</sup>, and **Álvaro Fernandez Bremer<sup>a</sup>**

<sup>a</sup> Instituto Andaluz de Ciencias de la Tierra, Granada, Spain

<sup>b</sup> University of Granada, Granada, Spain

<sup>c</sup> Department of Earth Science and Bjerknes Centre for Climate Research, University of Bergen, Bergen, Norway

<sup>d</sup> Instituto de Recursos Naturales y Agrobiología de Salamanca, Spanish National Research Council (CSIC), Salamanca, Spain

<sup>e</sup> Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

<sup>f</sup> University of Portsmouth, Portsmouth, England

Paleoclimate reconstructions of past warm intervals provide key constraints on the behavior of Earth's climate system, offering a means to evaluate climate sensitivity and to test model performance under boundary conditions that differ markedly from the present. Among the available approaches, coccolith clumped isotope ( $\Delta_{47}$ ) thermometry is particularly attractive because it directly reflects calcification temperatures, is largely insensitive to variations in seawater chemistry, and presents clear advantages over traditional proxies, especially in deep-time sedimentary archives. However, the extent to which post-burial processes such as dissolution and recrystallization modify coccolith  $\Delta_{47}$  signatures remains insufficiently constrained, limiting confident application of this proxy.

In this study, we examine the impact of post-depositional alteration on  $\Delta_{47}$  signals in coccolith-rich sediments recovered along a paleo-water depth transect in the eastern equatorial Pacific. We target three well-constrained and contemporaneous intervals (33.90 Ma, 33.60 Ma, and 33.30 Ma) from a closely spaced set of sites spanning a gradient in depth relative to the lysocline. This framework enables us to isolate the role of burial conditions on coccolith preservation while assuming broadly comparable initial ocean temperatures across the transect. Preservation states were assessed using scanning electron microscopy (SEM) to identify textural indicators of dissolution and recrystallization. In parallel, clumped isotope thermometry was applied to purified coccolith size fractions to evaluate potential modification of primary temperature signals. By combining microstructural observations with isotopic analyses, this study seeks to clarify how diagenetic processes influence the integrity of coccolith  $\Delta_{47}$  signals and to guide their application in deep-time climate reconstructions.



## Mass Spectrometric $\Delta_{48}$ Precision Insufficient to Resolve the Subtle Negative $\Delta_{47}$ Bias that is Recorded along the Growth Axis of Most Stalagmites

Jens Fiebig<sup>a</sup>, Christoph Spötl<sup>b</sup>, Ana Moreno<sup>c</sup>, Haiwei Zhang<sup>d</sup>, Miguel Bernecker<sup>a</sup>, Philip Staudigel<sup>a</sup>, Allison Curley<sup>a</sup>, Nele Meckler<sup>e</sup>, Monika Markowska<sup>f,g</sup>, Julian Schröder<sup>g</sup>, Hubert Vonhof<sup>g</sup>

<sup>a</sup> Institute of Geosciences, Goethe University, Frankfurt, Germany

<sup>b</sup> Institute of Geology, University of Innsbruck, Innsbruck, Austria

<sup>c</sup> Department of Geoenvironmental Processes and Global Change, IPE-CSIC, Zaragoza, Spain

<sup>d</sup> Institute of Global Environmental Change, Jiaotong University, Xi'an, China

<sup>e</sup> Department of Earth Sciences, University of Bergen, Bergen, Norway

<sup>f</sup> Department of Geography and Environmental Sciences, Northumbria University, Newcastle upon Tyne, UK

<sup>g</sup> Department of Climate Geochemistry, Max Planck Institute for Chemistry, Mainz, Germany

Speleothems are important archives for the reconstruction of terrestrial paleoenvironmental conditions. Unfortunately, it is challenging to resolve between the temperature, hydrological and kinetic information that is recorded in the bulk stable isotopic composition of these carbonates. It has been demonstrated that dual clumped isotope thermometry, i.e. analysis of  $\Delta_{48}$  alongside  $\Delta_{47}$  in  $\text{CO}_2$  evolved from phosphoric acid digestion of carbonate [1], holds the potential to identify, quantify and correct for kinetic bias in carbonate formation temperatures without having to know the oxygen isotope composition of the water from which the carbonate precipitated [2]. A recent publication implied that dual clumped isotope thermometry allows identification of isotopic equilibria in stalagmites, thereby making these archives accessible for robust paleoclimate reconstructions [3].

We performed paired  $\Delta_{47}$ - $\Delta_{48}$  measurements on speleothems to investigate to what extent isotopic disequilibrium is recorded in these archives, considering propagation of standardization errors onto analytical uncertainties for the interpretation of our results.

No significant disequilibrium bias seems to be recorded in slowly grown pool carbonates and cryogenic carbonates, suggesting that the temperature and hydrological information that is recorded in these carbonates can be accurately reconstructed through the analysis of  $\Delta_{47}$  along with  $\delta^{18}\text{O}$ .

Stalagmites sampled closest to their growth axis where disequilibrium should be least pronounced also plot indistinguishably from dual clumped isotope equilibrium. However, unlike the investigated cryogenic and pool carbonates, most stalagmites record a subtle, but significant  $-\Delta_{47}$  disequilibrium bias with respect to known formation temperatures. The observed bias predominantly originates from rapid dehydration/dehydroxylation of dissolved bicarbonate. A contribution from diffusion-driven degassing of  $\text{CO}_2$  cannot be excluded, but is below current analytical resolution. Due to mass spectrometric shot noise limit constraints on  $\Delta_{48}$ , it is challenging to resolve the  $\Delta_{47}$  disequilibrium bias that can occur along the growth axis of stalagmites. Unless kinetic bias can be ruled out independently,  $\Delta_{47}$  values of stalagmites should, therefore, only be considered as upper limits of cave temperature. Correction of kinetic bias in stalagmite  $\Delta_{47}$ - $\Delta_{48}$  pairs and, hence, accurate cave temperature reconstruction seems possible, but is at the expense of precision relative to kinetically unbiased archives such as bivalve mollusks [4].

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## Disequilibrium of Water Column and Sediment Carbonates in the Dual Clumped Isotope Record of Fayetteville Green Lake, NY

Hailey E. Germeau<sup>a</sup>, Andrew J. Schauer<sup>a</sup>, Tyler Kukla<sup>a</sup>, Gregory D. Hoke<sup>b</sup>, Casey Saenger<sup>c</sup>, Katharine W. Huntington<sup>a</sup>

<sup>a</sup> Department of Earth and Space Sciences, University of Washington, Seattle, United States

<sup>b</sup> Department of Earth Sciences, Syracuse University, Syracuse, United States

<sup>c</sup> Geology Department, Western Washington University, Bellingham, United States

Lake sediments are widely used as archives of past terrestrial climate, with lacustrine carbonates commonly interpreted to record mean summer surface-water temperatures during equilibrium “whiting events.” However, growing evidence suggests microbial mediation and authigenic processes can drive disequilibrium fractionation, obscuring primary temperature signals.

Dual carbonate clumped isotope thermometry ( $\Delta_{47}$ ,  $\Delta_{48}$ ) enables reconstruction of mineral formation temperatures independent of water isotopes. Deviations from the  $\Delta_{47}$ – $\Delta_{48}$  equilibrium relationship quantitatively diagnose disequilibrium and may constrain carbonate formation pathways. Here, we evaluate how these deviations vary with depth and microbial activity in the water column and sediments of Fayetteville Green Lake (FGL), NY, USA. We analyze carbonate particles filtered from 6 discrete depths in the upper 15 m of the water-column during a summer whiting event and 3 shallow sediment core segments from the center of the lake. All samples ( $n=9$ ) received 15 to 28 replicate measurements (NuCarb–Nu Perspective, 500–530  $\mu\text{g}$  carbonate per replicate, 7.5–15 g per sample), achieving fully propagated analytical precision of  $\pm 0.009\text{‰}$  for  $\Delta_{47}$  and  $\pm 0.027\text{‰}$  for  $\Delta_{48}$  (95% confidence).

Water-column carbonates yield anomalously high apparent equilibrium temperatures ( $T_{\text{ac}}$ ; 30–40 °C) and  $-\Delta_{47}/+\Delta_{48}$  deviations indicative of isotopic disequilibrium. The  $\Delta_{47}$ – $\Delta_{48}$  signature is consistent with microbially mediated carbonate formation linked to autotrophic metabolisms, suggesting FGL whiting events are driven by photosynthetic activity. In contrast, shallow sediment carbonates record near-equilibrium  $T_{\text{ac}}$  values of 20–21 °C, consistent with mean summer surface-water temperatures. This result is paradoxical, as whiting events in FGL are thought to be the primary source of carbonate, deposited as annual sediment laminations or true varves in the unmixed bottom waters with no evidence of bioturbation; thus, an additional carbonate formation or alteration pathway must be present.

These results challenge the assumption that sedimentary carbonates reliably record lake surface temperatures, particularly in microbially active systems. Sediment  $\Delta_{47}$ – $\Delta_{48}$  values likely reflect a physical mixture of two (or more) carbonate endmembers, potentially linked to heterotrophically influenced carbonate formation at depth. In lakes like FGL, carbonate-based paleotemperature reconstructions may therefore be biased toward microbial processes rather than ambient conditions, requiring disequilibrium fractionation and formation pathways to be explicitly constrained.

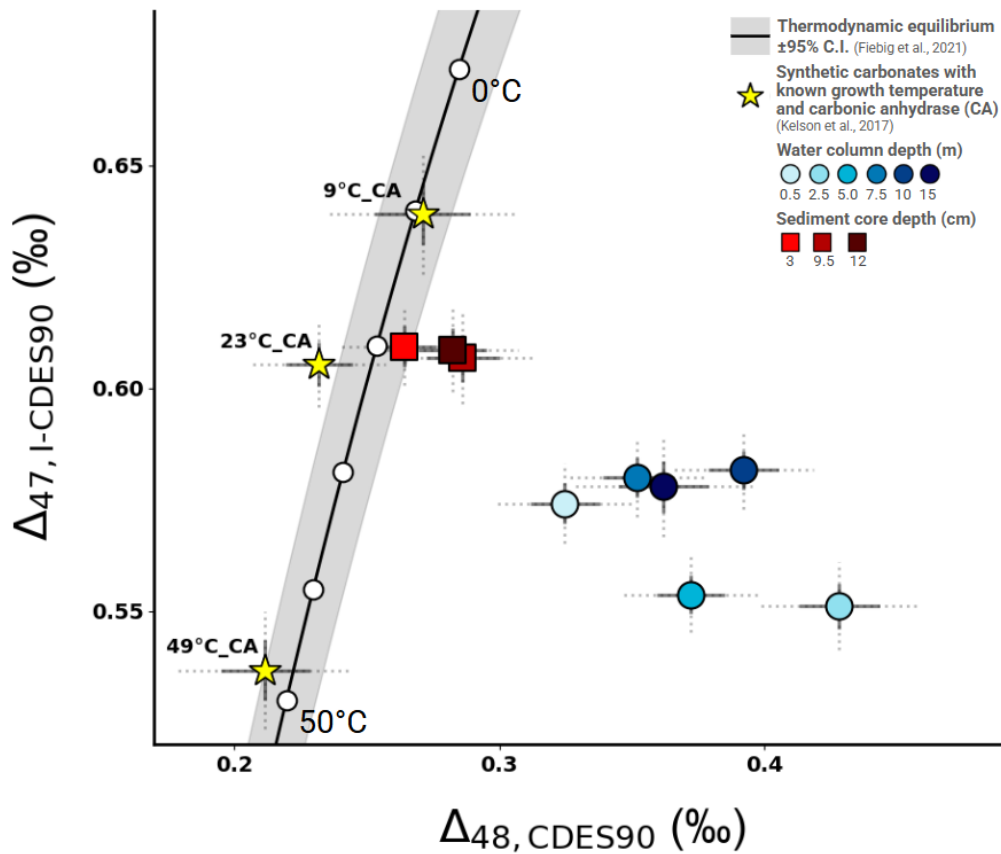


Figure 1: Dual clumped isotopic disequilibrium in water column and shallow sediment core carbonates from Fayetteville Green Lake, NY, USA. Propagated errors are shown as 1 standard error (solid line) and 95% (dashed line) confidence intervals.



# Testing Climate-Driven Extinction Hypotheses on the Plio-Pleistocene Florida Platform with High-Resolution $\Delta_{47}$ -Sclerochronology

Lucas D. Gomes<sup>a,b</sup>, Sierra V. Petersen<sup>a,b</sup>, Eric R. Waters<sup>a,b</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan, United States

<sup>b</sup> Museum of Paleontology, University of Michigan, Ann Arbor, Michigan, United States

Shallow marine ecosystems on the Florida Platform underwent a dramatic transformation over the past ~4 million years, part of a “regional mass extinction” documented broadly around the Plio-Pleistocene West Atlantic. A longstanding hypothesis to explain this event invokes cooling marine temperatures as the primary extinction driver, yet previous  $\delta^{18}\text{O}_{\text{carb}}$ -based efforts to constrain marine temperature variability have been stifled by poorly known and seasonally-variable  $\delta^{18}\text{O}_{\text{water}}$  compositions on the ancient Florida Platform [2]. In this study, we resolve this issue and test the cooling-driven extinction hypothesis by applying  $\Delta_{47}$ -thermometry to fossil bivalves from six Plio-Pleistocene formations from Florida. We report >500  $\Delta_{47}$ -temperatures from 68 individual shells, following a multi-taxonomic sampling approach (>20 genera) to account for species-specific growth biases. A subset of shells (n=13) from large, fast-growing taxa were sampled in a profile along the shell growth axis (high-resolution  $\Delta_{47}$ -sclerochronology) to reconstruct subannual temperature extremes and  $\delta^{18}\text{O}_{\text{water}}$  variability. We show that marine temperatures throughout the Tamiami Fm. (Late Pliocene) were remarkably cool, with temperature seasonality (~13–26°C) more closely resembling the present-day coast of North Carolina. Marine climates warmed rapidly during the Early Pleistocene, with warmer-than-present conditions during deposition of the Caloosahatchee Fm. (Early Pleistocene) and climates similar to the present-day through subsequent highstand intervals. These findings challenge the longstanding refrigeration hypothesis for regional marine extinction, conversely suggesting that climatic warming in the Early Pleistocene triggered turnover of shallow marine ecosystems. Reconstructed unit-average  $\delta^{18}\text{O}_{\text{water}}$  compositions in Florida are typically more enriched than previously assumed, and our high-resolution  $\Delta_{47}$  profiles indicate a remarkable degree of subannual  $\delta^{18}\text{O}_{\text{water}}$  variability that likely reflects seasonal freshwater inputs and evaporative effects along ancient coastal margins. These findings further highlight the utility of high-resolution  $\Delta_{47}$ -sclerochronology for absolute seasonal temperature reconstruction in coastal settings where  $\delta^{18}\text{O}_{\text{water}}$  may vary dramatically in space and time.

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## Clumped Isotope Analysis on Cultured Aragonite Bivalve Shells evaluates Applicability of Calcite Calibrations

Barbara Goudsmit-Harzevoort<sup>a,b</sup>, Rob Witbaard<sup>a</sup>, Annelou Hulsker<sup>b</sup>, Brendan Oerlemans<sup>c</sup>, Niels J. de Winter<sup>c</sup>, Martin Ziegler<sup>b</sup>

<sup>a</sup> Department of Estuarine and Delta Systems, Royal Netherlands Institute for Sea Research (NIOZ), Netherlands

<sup>b</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

<sup>c</sup> Department of Earth Sciences, VU Amsterdam, Amsterdam, Netherlands

Due to their incremental growth bands, fossil mollusk shells can serve as climate archives of seasonal temperature when micro-sampled for clumped isotope analysis ( $\Delta_{47}$ ) [1]. Most mollusk shells are formed of aragonitic carbonate. Yet, current calibrations of the relationship between  $\Delta_{47}$  and formation temperature rely on predominantly calcite samples [2,3,4]. Since theoretical models show that equilibrium  $\Delta_{47}$  values slightly differ per carbonate mineralogy [5], application of these calibration equations on aragonitic  $\Delta_{47}$  data needs to be justified to avoid biased temperature records.

This study involves clumped isotope analysis on aragonitic shells of the bivalve species *Venerupis philippinarum* that were grown under known temperature conditions for nine consecutive months in 2024 in the NIOZ harbor on the island of Texel in the Netherlands. The individually tagged bivalve specimens were exposed to outdoor water temperature conditions that were recorded every 20 minutes. Individual shell growth was monitored on an approximately monthly basis, allowing precise allocation of growth increments to calendar date.

Clumped isotope analysis was performed on micro-samples from the experimentally grown aragonite of ten specimens, resulting in a dataset of over 500  $\Delta_{47}$  measurements. The combination of monthly mean  $\Delta_{47}$  values and known monthly mean temperatures allows for an evaluation of the applicability of existing temperature calibrations on aragonite samples in the temperature range 8 – 20°C. The results indicate that the foraminifera-based calibration of Meinicke et al. (2021) overestimates the formation temperature by on average  $2.5 \pm 2.4^\circ\text{C}$  (95% confidence interval), while the wide-temperature range calibrations of Anderson et al. (2021) and OGLS23 [4] both show a comparably good fit with a mean difference with the formation temperature of  $1 \pm 2.4^\circ\text{C}$  (95% confidence interval). In this contribution, we will discuss the implications for the use of calcite-based temperature calibrations on  $\Delta_{47}$  data from aragonite samples.

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## **A novel dual inlet large radius IRMS for isotopologue measurement**

**Garry Armstrong<sup>a</sup>, Damian Tootell<sup>b</sup>, Stephen Guilfoyle<sup>b</sup>**

<sup>a</sup> Sercon Ltd, Crewe, UK

<sup>b</sup> Isotopx Ltd, Middlewich, UK

The challenges with the measurement of the isotopologues of carbon dioxide using IRMS are well documented. In particular, achieving the required measurement precision for the heavier isotopologues ( $m/z$  48 and 49) has proved difficult.

Measurement precision can be improved by using a much larger radius IRMS instrument. Several such instrument are commercially available, although they can be expensive to buy and difficult to operate.

Sercon and Isotopx have co-developed a dual inlet large radius IRMS that is based on the ion optical configuration of the Isotopx Phoenix TIMS. This offers very wide flat top peaks and excellent stability, as well as being very easy to use.

The proven, automated Sercon dual inlet system ensures low ppm precision for most of the CO<sub>2</sub> isotopologues. Baselines are clean, and the Isotopx ATONA Faraday system offers ultra-low background noise coupled with excellent gain stability. ATONA also allows extremely large beam sizes where there is sufficient sample.

We present isotope ratio data for CO<sub>2</sub> standards and samples, highlighting the analytical possibilities of this new platform.



# 75,000 Years of Hydroclimate and Temperature Variations in East Asia Derived from Snail Shell Clumped Isotopes

Jingjing Guo<sup>a</sup>, Martin Ziegler<sup>a</sup>, Jibao Dong<sup>b</sup>, Youbin Sun<sup>b</sup>, Francien Peterse<sup>a</sup>

<sup>a</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

<sup>b</sup> State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

Records of relative changes in past East Asian climate and monsoon intensity have been obtained from a wide variety of paleoclimate archives. However, quantitative reconstructions of land surface temperatures in East Asia remain sparse. Here we present a 75-kyr temperature record derived from the carbonate clumped isotope composition ( $\Delta_{47}$ ) of land snail shells from a loess-paleosol sequence at Yuanbao, on western edge of the Chinese Loess Plateau (CLP). Modern growing season (mid-April to September) temperature based on  $\Delta_{47}$  is  $21.2 \pm 1.2$  °C. The  $\Delta_{47}$  record reveals that there are certain periods where land surface temperatures were lower: the last glacial maximum (LGM) was  $\sim 7$  °C colder, Marine Isotope Stage 3 (MIS3)  $\sim 5$  °C and MIS4  $\sim 6$  °C, but also the mid-Holocene was  $\sim 9$  °C colder than present day. Temperatures similar to present day occurred during Northern Hemisphere Summer Insolation (NHSI) minima within MIS3 and the Bølling-Allerød (BA). The magnetic susceptibility record of the same loess-paleosol section indicates that these warm periods are characterized by relatively dry conditions. This is further supported by the relative enrichment in the temperature-independent oxygen isotope composition of snail body water ( $\delta^{18}\text{O}_{\text{bw}}$ ) during these time intervals, reflecting a negative moisture balance. In contrast, the unexpected low  $T_{47}$  for the mid-Holocene could be the result of wet conditions. Our record thus suggests that soil moisture availability exerts a strong influence on land surface temperatures recorded by snails stored in loess archives.



## Clumped Isotope Constraints on Seawater Temperature and Isotopic Variability Across the Hirnantian Glaciation

Yangrui Guo<sup>a</sup>, Jianfang Hu<sup>a</sup>

<sup>a</sup> State Key Laboratory of Deep Earth Processes and Resources, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

The Hirnantian Glaciation represents the only major icehouse event of the Early Paleozoic, yet debates persist regarding its global climate impacts and ice volume dynamics. Here, we present a high-resolution carbonate clumped isotope ( $\Delta_{47}$ ) record from well-preserved micritic carbonate rocks of the Baltic Basin (Estonia), which was situated at a paleolatitude of  $\sim 20\text{--}30^\circ\text{S}$  during the Late Ordovician. Our results reveal stable tropical-to-subtropical sea surface temperatures of  $\sim 43^\circ\text{C}$  throughout the entire Hirnantian Carbon Isotope Excursion (HICE) interval. Notably, no significant temperature fluctuations are observed corresponding to the prominent positive-to-negative shift in carbonate  $\delta^{13}\text{C}$ . While the relatively high temperature values may imply a minor diagenetic overprint, the relative temperature variability is considered robust. Building on this constraint, reconstructed seawater oxygen isotope compositions ( $\delta^{18}\text{O}_{\text{sw}}$ ) exhibit a  $\sim 2\text{‰}$  negative shift during deglaciation, coupled to the negative excursion of the HICE. This  $\delta^{18}\text{O}_{\text{sw}}$  variability is interpreted to reflect near-complete melting of the Gondwanan ice sheet, with no temperature contribution, eliminating the long-standing circular reasoning in traditional oxygen isotope thermometry. Our findings confirm that Hirnantian cooling was confined to high latitudes, while mid-low latitudes maintained stable warm conditions. This pattern supports extreme polar amplification and suggests sea-level change and carbon cycle perturbations, rather than global cooling, were the primary drivers of the Late Ordovician mass extinction. These data provide critical isotopic constraints on Early Paleozoic icehouse dynamics and ocean-atmosphere system behavior.



## Assessing CO<sub>2</sub> Absorption and Clumped Isotope Disequilibrium in Carbon Mineralization Products

Claire M. Hayhow<sup>a</sup>, Kristin D. Bergmann<sup>a</sup>

<sup>a</sup> Department of Earth Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, USA

Avoiding the most deleterious effects of climate change necessitates reducing emissions and developing geoengineering solutions to reduce atmospheric CO<sub>2</sub> concentrations. A wide range of carbon capture and storage technologies (CCS) have emerged to meet this need; however, most carbon mineralization technologies rely on modeling CO<sub>2</sub> fluxes or using stoichiometric calculations to estimate CO<sub>2</sub> absorption. Conditions that promote rapid and efficient CO<sub>2</sub> absorption into carbonate minerals are poorly constrained, as are their isotopic consequences. Clumped isotopes, particularly  $\Delta_{47}$ - $\Delta_{48}$  dual clumped isotope analysis can constrain the mechanisms of kinetic isotope effects [1]. This may be a tool for standardizing methods of verifying sequestered CO<sub>2</sub>, which remains a critical gap in the CCS field.

We test the utility of clumped isotopes with a series of carbonate precipitation experiments. We have generated precipitates using two methods: CaO hydrolysis and from dissolved CO<sub>2</sub> at a range of temperatures, pHs, and fluid volumes. To estimate CO<sub>2</sub> fluxes, we monitored changes in mineral phase, mass, and  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$ , and  $\Delta_{48}$ . In these experimental carbonates, we observe significant kinetic fractionation associated with CO<sub>2</sub> absorption, characterized by enriched  $\Delta_{47}$  and depleted  $\Delta_{48}$  relative to equilibrium with the largest KIEs ( $\Delta\Delta_{47} = 0.277$ ,  $\Delta\Delta_{48} = -0.695$ ) in samples simulating direct air capture technologies. We compare these experimental carbonates with other known CO<sub>2</sub> absorbing-systems, including alkaline travertines associated with basalt weathering and archeological concrete.

We compare these results from experimental and natural samples with modelled kinetic isotope effects associated with exchange reactions in the DIC-H<sub>2</sub>O system and crystal growth reactions in the CaCO<sub>3</sub>-DIC system using the IsoDIC model.

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## The Rise of Orbitrap-IRMS for Clumped Isotope Geochemistry

Amy E. Hofmann<sup>a,b</sup>

<sup>a</sup> Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

<sup>b</sup> Geological & Planetary Sciences Division, California Institute of Technology, Pasadena, CA, USA

The advent of Orbitrap-based Fourier-transform mass spectrometry for isotope ratio analysis at natural abundances can be traced back to roughly 2016 and the publication of two geochemistry abstracts and two nuclear forensics manuscripts. The seminal 2017 paper by Eiler and colleagues [1] demonstrating precise and accurate quantification of molecular isotopic contents and structures by Orbitrap-IRMS was published soon thereafter, arguably launching a new subfield of stable isotope geochemistry.

By eliminating the need to convert analytes into simple gases, Orbitrap-IRMS bypasses a major limitation of traditional magnetic sector instruments, enabling the direct isotopic analysis of intact molecules and/or specifically targeted molecular fragments. Orbitrap-IRMS thus enables us to constrain not only an analyte's molecular-average (i.e., compound-specific) isotopic composition but also the proportions of multiply substituted species within a given analyte population and, for certain compounds, the differences in isotopic compositions between symmetrically inequivalent sites within the molecule itself.

Major enabling technical features of the Orbitrap mass analyzer include: (1) its ultrahigh mass-resolving power, which facilitates baseline separation of near-isobaric species such as <sup>13</sup>C- and D-bearing isotopologues; (2) its high sensitivity, which facilitates analysis of extremely low concentration analytes; and (3) its extraordinary mass accuracy and wide range of analyzable masses and, hence, the number of ion beams that can be observed simultaneously. Different sample introduction and ionization techniques incorporated on various Orbitrap-bearing platforms have further expanded the array of analytes accessible to isotopic interrogation.

Over the past ~10 years, the number of Orbitrap-IRMS-based publications has increased exponentially, reflecting the rapidly growing international userbase and the expanding array of scientific applications. In this presentation, I will discuss the implementation of Orbitrap-IRMS in clumped isotope geochemistry: the scientific landscape, current best practices and known limitations, emerging opportunities, and means for joining this burgeoning community.

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## Experimental Constraints of Equilibrium Triple Oxygen Isotope Fractionation in the Dissolved Inorganic Carbon System

Jungpyo Hong<sup>a</sup>, Benjamin H. Passey<sup>a</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, United States of America

Triple oxygen isotope systematics of carbonate minerals are emerging as valuable tools for reconstructing Earth's past hydroclimate. However, it requires a quantitative understanding of the isotope fractionations between carbonate minerals and their parent water, which remains poorly constrained. In addition, carbonate isotopic compositions are influenced by the isotopic compositions of the dissolved inorganic carbon (DIC) species that are reactants in carbonate precipitation reactions. As such, isotopic disequilibrium among these species may be recorded as disequilibrium signatures in precipitated carbonate. Therefore, it is necessary to investigate the isotope fractionations ( $\alpha$ ) not only in mineral-water systems but also among DIC species ( $\text{CO}_2(\text{aq})$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) and water. Previous studies have explored the equilibrium and kinetic triple oxygen isotope fractionations in the DIC- $\text{CO}_2$ - $\text{H}_2\text{O}$  system theoretically [1,2]. However, to date, there are no experimental constraints on equilibrium isotope fractionation factors that can verify theoretical calculations. Here, we present experimentally determined equilibrium triple oxygen isotope fractionation exponents ( $\theta_{\text{eq}} = \ln(^{17}\alpha)/\ln(^{18}\alpha)$ ) between  $\text{HCO}_3^-(\text{aq}) / \text{CO}_3^{2-}(\text{aq})$  and water. Witherite ( $\text{BaCO}_3$ ) precipitation experiments were conducted at different temperatures (15, 25, and 40 °C) and pH range (from 8 to 12), enabling the capture of the isotopic compositions of DIC species following rapid introduction of  $\text{BaCl}_2(\text{aq})$  to equilibrated DIC solutions [3]. Our results yield  $\theta_{\text{eq}} = 0.5253$ – $0.5254$  for  $\text{HCO}_3^-$ - $\text{H}_2\text{O}$ , and  $0.5246$  for  $\text{CO}_3^{2-}$ - $\text{H}_2\text{O}$ , both of which are lower than the theoretical predictions ( $\theta_{\text{eq}} = 0.5259$ – $0.5262$  and  $0.5251$ – $0.5254$ , respectively, over a 15–40 °C range) [2]. The reasons for these discrepancies remain unclear, but they may reflect uncertainties in theoretical calculations or experimental factors, such as the acid fractionation factor. Our study provides new experimental constraints on equilibrium triple oxygen isotope fractionation and contributes to a more robust understanding of the triple oxygen isotope system itself.

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## Repeat Until Precise: Small Carbonate Samples, High-Precision $\Delta_{48}$ on the Nu Perspective IRMS

Katharine W. Huntington<sup>a</sup>, Hailey Germeau<sup>a</sup>, Andrew J. Schauer<sup>a</sup>, Jillian Ruby<sup>a</sup>, Sophia Robillard<sup>a</sup>

<sup>a</sup> Department of Earth & Space Sciences and IsoLab, University of Washington (UW), Seattle, Washington, USA

Dual-clumped isotope ( $\Delta_{47}$ – $\Delta_{48}$ ) analysis constrains carbonate formation conditions but is limited by large sample sizes typically required for high-precision  $\Delta_{48}$  measurements. We evaluate  $\Delta_{47}$  and  $\Delta_{48}$  precision and accuracy on a NuCarb–Nu Perspective system using equilibrated gases, carbonate standards, and unknowns, and show that with sufficient replication, small-sample analyses are accurate with external precision comparable to the highest-precision published datasets.

We present 522 dual-clumped analyses collected over four months using cold-finger small-sample mode (500–530  $\mu\text{g}$  carbonate per replicate). The dataset includes all seven InterCarb standards (15–34 replicates each,  $\mu=20$ ), GU1, and  $\text{CO}_2$  gases equilibrated at 4 °C and 1000 °C spanning  $\delta^{47}$  and  $\delta^{48}$  ranges of 80 and 120 ‰. Twelve unknowns (10–28 replicates each,  $\mu=20$ ) include challenging low-carbonate (~3%) lacustrine samples embedded in silica filters, requiring pretreatment to remove sulfur and organic contaminants; and three synthetic carbonates [1] grown at known temperatures in the presence of carbonic anhydrase.

Analyses used Nu Stable software with UW-modified scripts enabling controlled timing and trap temperature. Capillary crimps were optimized for balanced sample-working gas signal decay (90 to 40 nA over 60 comparisons; 1200 s integration). Quality control used cycle-level diagnostics for sample-working gas mismatch and contamination. Data were processed using D47crunch [2] pooled-session standardization.

$\Delta_{47}$  CDES (gas-only calibrated) values for carbonate standards digested at 70°C are consistent with the published acid fractionation factor ( $\text{AFF}_{90-70}$ ) [3].  $\Delta_{48}$  CDES results indicate  $\text{AFF}_{90-70}$  is indistinguishable from theoretical predictions [4] and yield consistent GU1 values [5].

Repeatabilities for unknowns are 18 ppm ( $\Delta_{47}$  I-CDES90) and 49 ppm ( $\Delta_{48}$  CDES90, anchored to gases and published 90°C-acid carbonate values). Withholding one carbonate anchor at a time,  $\Delta_{47}$  (I-CDES90) values for InterCarb standards agree with accepted values, including Merck, despite use of a batch (lot-B1774559010) with  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions distinct from InterCarb Merck (lot-B1164559515) [3].

Synthetic calcite  $\Delta_{47}$  (I-CDES90,  $\pm 0.0096$ – $0.0136$ ‰, 95% CL) and  $\Delta_{48}$  (CDES90,  $\pm 0.0244$ – $0.0345$ ‰, 95% CL) values match expected growth temperatures. Lacustrine carbonates achieve average 95% CL precision of 0.0095‰ ( $\Delta_{47}$ ) and 0.0262‰ ( $\Delta_{48}$ ) from 7.5–15 mg total carbonate equivalent per sample. These results demonstrate accurate, high-precision dual-clumped analyses on small carbonate samples using this system.

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## How to kill with a FrankenKiel a MAT253+ (and bring it back from its ashes)

Josué J. Jautzy<sup>a</sup>, Benjamin R. Fosu<sup>a</sup>, Guillaume Barré<sup>a</sup>

<sup>a</sup> Geological Survey of Canada, Natural Resources Canada, Québec, Canada

Isobaric interferences at  $m/z$  47–49 present a significant analytical challenge for accurately quantifying clumped-isotope abundances in CO<sub>2</sub>, and these interferences may originate from a wide range of known and unknown sources. While a few specific interference sources have now been systematically identified, many potential isobaric generation pathways remain largely unexplored, leaving significant gaps in our understanding of their formation and behavior in inlet systems. Since converting our Kiel device into the “Frankenkiel,” we have progressively increased our operating temperature and have experienced some isobaric interference on  $m/z$  47–49. These ranged from sporadic episodes – triggered when certain samples saturated the Porapak and Ag cleaning traps – to persistent, long-lived (months) backgrounds on the  $m/z$  48 and/or 49 collectors.

Initial analyses conducted at 90 °C produced stable results; however, we observed a slow but continuous rise in the  $m/z$  48 background. Although  $m/z$  47 initially remained unaffected, a subsequent source vent for filament replacement marked a turning point: interference began showing increasing correlation with the  $m/z$  49 parameter, accompanied by progressive deterioration in standard  $\Delta_{47}$  reproducibility. Additionally, background decay after closing the changeover valve became unusually slow, often requiring nearly 10 hours to approach baseline levels. These effects did not depend on the type of gas introduced into the ion source – CO<sub>2</sub>, N<sub>2</sub>, and Ar each induced comparable background behavior on  $m/z$  48 and 49 – but instead appeared correlated to the amount of time gas was injected in the source.

Repeated full-instrument bakeouts failed to restore optimal baseline conditions and frequently amplified the  $m/z$  48 background. Only a comprehensive bakeout of the entire inlet system, carried out with all valves open, successfully re-established acceptable working conditions and standard deviation on  $\Delta_{47}$  standards, but without fully removing the background remaining in the cup collecting the  $m/z$  48 beam.

Throughout this investigation, we encountered diverse contamination scenarios, including inadvertent introduction of monosulfide-bearing materials (e.g., PbS) and systematic testing of O-ring materials – Kalrez, Aflas, and Viton – each displaying distinct contamination signatures. In this contribution, by presenting these contamination behaviors, we underscore not only how subtle contamination in inlet systems can propagate into long-term analytical drift, but also how insufficiently characterized are isobaric sources in carbonate clumped isotopic analyses. This highlights the critical need for rigorous, comprehensive isobaric investigations and improved trap and gas purification design.



## Seasonal, diel and interhemispheric variability of polyisotopic carbon dioxide on land and at sea

Jan Kaiser<sup>a</sup>, Penelope A. Pickers<sup>a,b</sup>, Grant L. Forster<sup>a,b</sup>, Alina Marca<sup>a</sup>, Richmal B. Paxton<sup>a</sup>

<sup>a</sup> Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK

<sup>b</sup> National Centre for Atmospheric Science, University of East Anglia, Norwich, UK

Polyisotopic elements, such as oxygen with its stable isotopes  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ , enable advanced tracing of biogeochemical processes through polyisotopologue analysis. The UK NERC-funded POLYGRAM project investigates polyisotopologues of greenhouse gases, including ‘clumped isotopes’, to improve estimates of gross primary productivity (GPP) and atmospheric exchange. Simultaneous measurements of  $\delta(^{18}\text{O})$  and  $\delta(^{17}\text{O})$  in  $\text{CO}_2$ , and their deviation from mass-dependent fractionation (expressed as ‘triple oxygen isotope excess’  $\Delta(^{17}\text{O})$ ), simplify GPP estimation by reducing dependence on soil and leaf water isotope ratios.

A 2.5-year dataset (2021–2024) from Weybourne Atmospheric Observatory on the north Norfolk coast (UK) using Aerodyne TILDAS laser spectrometry demonstrates high reproducibility in  $\delta(^{13}\text{C})$ ,  $\delta(^{18}\text{O})$ ,  $\delta(^{17}\text{O})$  and  $\text{CO}_2$  amount fractions and clearly resolved seasonal and diurnal cycles.

Complementary shipboard measurements during the AMT31 cruise (Southampton to Montevideo, November–December 2024) used similar instrumentation to sample marine air. Despite reduced precision due to ship motion, hourly averages achieved  $<0.05 \mu\text{mol mol}^{-1}$  for  $\text{CO}_2$  amount fraction and  $<0.03 \text{‰}$  for isotope ratios.  $\Delta(^{17}\text{O})$  precision was typically  $<10 \text{ ppm}$ , though target tanks showed unexplained day-to-day variability ( $\pm 35 \text{ ppm}$ ).

Preliminary corrections suggest southern hemisphere marine air has  $\delta(^{18}\text{O})$ , values 1.2–1.8 ‰ higher and  $\Delta(^{17}\text{O})$  values ( $70 \pm 22 \text{ ppm}$ ) greater than northern hemisphere background levels. This interhemispheric gradient exceeds model predictions and may reflect enhanced stratospheric return flux in austral spring or stronger biospheric exchange in boreal autumn.

Finally, we will present results from a 7-day deployment of the instrument in Alice Holt Forest (Hampshire, UK).

Together, these land and ocean observations advance the use of polyisotopologues in global carbon cycle research.



## A Progress Report on Paired Measurements of $\Delta_{47}$ and $\Delta^{17}\text{O}$ in $\text{CO}_2$ derived from a Single Aliquot of Carbonate

Julia R. Kelson<sup>a</sup>, Molly E. Karnes<sup>a</sup>, Annika A. Jorgenson<sup>a</sup>, Amelia J. Davies<sup>b</sup>, Simon Davis<sup>b</sup>, Mattia Tagliaento<sup>b</sup>, Richard Wehr<sup>c</sup>

<sup>a</sup> Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, Indiana, USA

<sup>b</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

<sup>c</sup> Aerodyne Research, Inc., Billerica, Massachusetts, USA

Clumped isotopes ( $\Delta_{47}$ ) and triple oxygen isotopes ( $\Delta^{17}\text{O}$ ) in carbonate give complimentary information about (paleo-)temperatures and (paleo-) hydrologic processes from a single mineral phase [1,2]. Measuring these two isotope parameters from a single aliquot of carbonate (i.e., one acid digestion) would greatly enhance paleoclimate reconstructions by reducing sample size requirements and user effort. At Indiana University, we are linking three commercially available instruments to achieve this goal: 1) an IBEX (Protium MS) to digest and purify carbonate-derived  $\text{CO}_2$ , 2) a MAT 253 Plus (Thermo Fisher) optimized for  $\Delta_{47}$ , and 3) a  $^{17}\text{O}\text{-CO}_2$  TILDAS (Aerodyne) [3]. We will present an update on advances and challenges in setting up this system, including splitting and freezing  $\text{CO}_2$  into two cold fingers (i.e., chilled by liquid nitrogen), measuring isotope values simultaneously vs. in series, and managing differing sample size and time requirements for the mass spectrometer and the laser spectroscope. While setup is ongoing at the time of writing, we plan to present an initial assessment of our success by comparing  $\delta^{18}\text{O}$  values measured in aliquots of carbonate reference materials measured via mass spectrometry and laser spectroscopy, and by comparing measured  $\Delta^{17}\text{O}$  and  $\Delta_{47}$  values to community-accepted values. We will present preliminary sample data from the Early Eocene Climatic Optimum in floodplain paleosols of the Green River Basin (Wyoming, USA) to demonstrate the how paired  $\Delta_{47}/\Delta^{17}\text{O}$  can be used to detect simultaneous changes in temperature, evaporative effects, and the origin of paleo-meteoric waters in ancient terrestrial environments.

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## TICTOC: Traceable Inter-Comparison of Triple Oxygen isotopes in Carbonates

Julia Kelson<sup>a</sup>, David Bajnai<sup>b</sup>, Vincent Hare<sup>c</sup>, Mathieu Daëron<sup>d</sup>

<sup>a</sup> University of Indiana, USA

<sup>b</sup> University of Göttingen, Germany

<sup>c</sup> University of Cape Town, South Africa

<sup>d</sup> LSCE-CNRS, France

Work on  $\Delta^{17}\text{O}$  in carbonates is expanding rapidly, with a growing number of laboratories and an increasingly diverse range of analytical approaches coming online. Given this momentum, we feel this is an ideal moment for the community to come together and undertake an inter-laboratory effort aimed at strengthening the metrological foundations of carbonate  $\Delta^{17}\text{O}$  measurements across different analytical techniques and improving the comparability of standardization approaches across laboratories. In this spirit, we invite you to participate in TICTOC (Traceable Inter-Comparison of Triple Oxygen isotopes in Carbonates).

We propose two interrelated and parallel exercises, termed “Calvin” and “Hobbes”, respectively:

The Hobbes exercise is designed to assess inter-laboratory reproducibility of carbonate  $\Delta^{17}\text{O}$  data when normalized using carbonate-based standardization. This effort aims to improve our understanding of the nature and sources of systematic errors in  $\text{CaCO}_3$  measurements, with particular emphasis on laser spectroscopy techniques. Participation in the Hobbes exercise involves measuring two unknown carbonate samples, two carbonate reference materials (NBS18 and IAEA603), and two IAEA  $\text{CO}_2$  reference materials provided in copper tubes. The unknown carbonates analyzed in this exercise are under consideration to become new reference materials certified by the IAEA.

The Calvin exercise aims to better constrain the relative  $\Delta^{17}\text{O}$  values of carbonate reference materials NBS18 and IAEA603 and improve their traceability to VSMOW–SLAP scale via  $\text{H}_2\text{O}$ – $\text{CO}_2$  equilibration. Participation is open to all analytical approaches, including  $\text{O}_2$ -analyte methods and techniques relying on isotope exchange. For this exercise, participation involves analyses of NBS18 and IAEA603, as well as  $\text{CO}_2$  ampoules generated by equilibration with VSMOW and SLAP or VSMOW2 and SLAP2 (ampoules may be prepared in each participating lab and/or provided by the organizers).

If you wish to participate, please sign up by emailing the TICTOC organizing committee at [tictoc-organizers@groupe.renater.fr](mailto:tictoc-organizers@groupe.renater.fr)



## Tracking Changes in Ocean Currents along the Miocene–Pliocene U.S. Mid-Atlantic Coastal Plain Using $\Delta_{47}$

Erin H. Kim<sup>a,b</sup>, Sierra V. Petersen<sup>a,b</sup>, Harry J. Dowsett<sup>c</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI

<sup>b</sup> Museum of Paleontology, University of Michigan, Ann Arbor, MI

<sup>c</sup> United States Geological Survey, Florence Bascom Geoscience Center, Reston, VA

Along the U.S. East Coast, climate is mainly influenced by the competing influences of two coastal currents: the warm, salty, northward flowing Gulf Stream Current and the cool, fresher, southward flowing Labrador Current. The Gulf Stream heavily controls the climate of the states south of North Carolina as well as Europe, and contributes to western European climate being temperate and moist. These current systems differ in temperature and salinity, both on average, seasonally, and with depth. However, using these parameters to reconstruct past current strength or position is difficult because identifying qualities are either not recorded (salinity) or not unique (temperature). Newly identified  $\sim 2$  ‰ differences in seawater  $\delta^{18}\text{O}_w$  between the two water masses can be leveraged towards this issue. In this study, we use clumped isotope paleothermometry ( $\Delta_{47}$ ) to reconstruct average ocean temperatures and  $\delta^{18}\text{O}_w$  values from the Late Miocene Eastover Formation and Pliocene Yorktown Formation and  $\delta^{18}\text{O}_c$  sclerochronology to track subannual variability.  $\Delta_{47}$  data obtained from scallops (*Chesapecten jeffersonius*, *Chesapecten madisonius*) and clams (*Glycymeris americana*, *Mulinia* sp., *Panopea* sp., and *Striarca centenaria*) show that bottom water temperatures in this region were warmer than present. Large shifts in  $\delta^{18}\text{O}_w$  values and the sinusoidicity of  $\delta^{18}\text{O}_c$  sclerochronology profiles are consistent with a northward shift in the position of the Gulf Stream Current break-off point, between the Miocene and Pliocene. Our new data quantitatively define U.S. East Coast oceanic conditions in the Miocene–Pliocene, key past greenhouse climate intervals. When linked with studies of faunal turnover in the region, quantitative estimates like these can help determine the sensitivity of molluscan life and other biota to climate change. This study also demonstrates how three lines of evidence (T,  $\delta^{18}\text{O}_w$ , seasonal  $\delta^{18}\text{O}_c$ ) can be combined to track the past position of coastal currents, a method that can be applied to other regions and times. Understanding coastal current behavior under past greenhouse periods like these can help predict how currents may behave under future warming and elevated sea levels.



## Relatively warm deep-water formation in the Last Glacial Maximum: new constraints from clumped isotope thermometry

Jack H. Wharton<sup>a</sup>, Emilia Kozikowska<sup>a,b</sup>, Lloyd D. Keigwin<sup>c</sup>, Thomas M. Marchitto<sup>d</sup>, Mark A. Maslin<sup>a</sup>, Martin Ziegler<sup>b</sup>, David J. R. Thornalley<sup>a,c</sup>

<sup>a</sup> Department of Geography, University College London, London, United Kingdom

<sup>b</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

<sup>c</sup> Woods Hole Oceanographic Institution, Woods Hole, USA

<sup>d</sup> Department of Geological Sciences and INSTAAR, University of Colorado, Boulder, CO, USA

Resolving the hydrographic structure of the deep North Atlantic during the Last Glacial Maximum (LGM; 19–23 ka BP) is critical for benchmarking the Earth system models used to project future climate change [1]. Prior pore-water estimates have suggested near-freezing glacial deep-water temperatures, implying haline rather than thermal stratification and a fundamentally different circulation structure to today [2]. However, these estimates carry methodological uncertainties, motivating the need for independent proxy constraints.

We apply benthic foraminiferal clumped isotope thermometry ( $\Delta_{47}$ ) alongside Mg/Ca and Mg/Li trace-metal ratios [3] to reconstruct bottom-water temperatures and seawater  $\delta^{18}\text{O}$  across a depth transect (1.5–5 km) of 13 Northwest Atlantic sediment cores, supplemented by 3 Northeast Atlantic cores south of Iceland. Reconstructions span the LGM and mid-to-late Holocene (2–6 ka BP) [3,4].  $\Delta_{47}$  serves as an independent cross-check on Mg/Ca, bypassing the carbonate-ion saturation biases that can affect trace-metal reconstructions in deep-sea settings.

$\Delta_{47}$ - and Mg/Ca-derived temperatures show strong cross-proxy agreement, with LGM cooling of  $-2.02 \pm 0.95$  °C and  $-1.63 \pm 0.44$  °C relative to modern, respectively (figure 1). No significant species-specific offsets are observed in  $\Delta_{47}$ , supporting its robustness across multiple benthic taxa. These results indicate that the deep Northwest Atlantic was only approximately 0–2 °C colder than today during the LGM, substantially warmer than prior pore-water estimates suggest [2]. The ice-volume-corrected  $\delta^{18}\text{O}_{\text{sw}}$  was  $0.3 \pm 0.1$ ‰ higher than modern values, pointing to relatively salty glacial NADW. Tracing this signal along the Gulf Stream to North Atlantic Current pathway implies sustained deep-water formation throughout the LGM, driven by continued northward transport of warm, saline surface waters.

These findings challenge the idea that glacial deep waters were near freezing and support sustained NADW production during the LGM [5], reconciling longstanding proxy uncertainties and providing updated benchmarks for glacial climate simulations.

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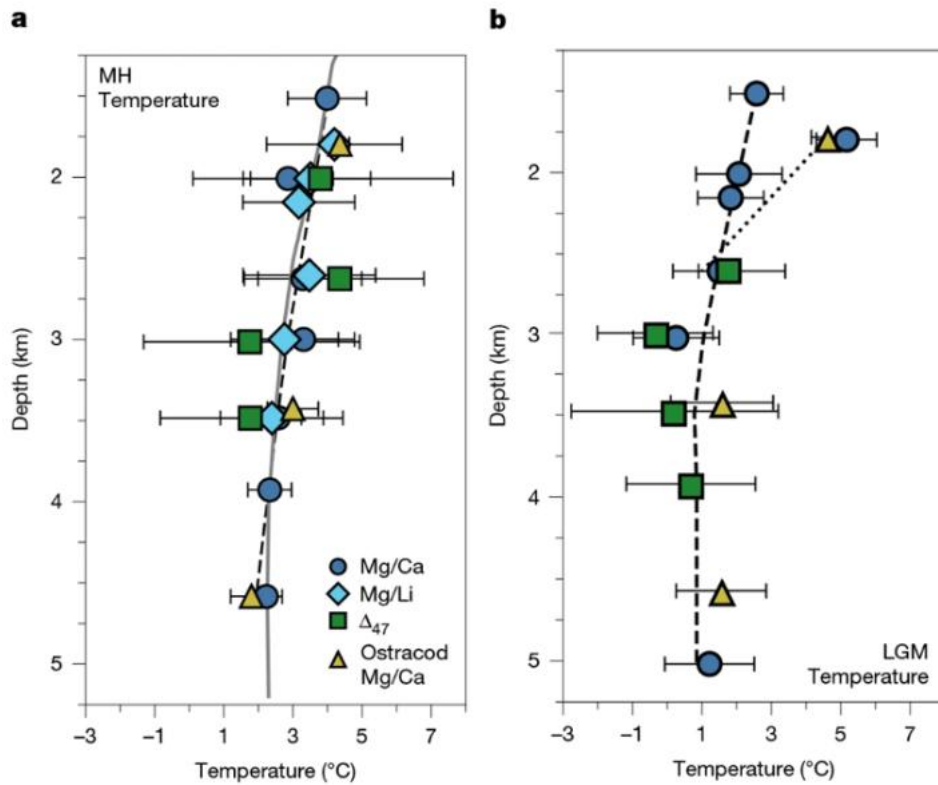


Figure 1: Vertical Deep Northwest Atlantic Temperature Structure During the Mid-to-Late Holocene and the Last Glacial Maximum. The filled colored symbols in a and b represent the mean value for each depth and associated errors bars of  $\pm 2$  s.e. The dashed black lines are locally weighted scatterplot smoothing lines through all foraminiferal temperature data from this study. The grey line and ribbon in a and b, respectively, denote the modern temperature from WOA23 and the  $\delta^{18}O_{sw}$  structure of the Northwest Atlantic and modern salinity- $\delta^{18}O_{sw}$  relationships.



## Performance of cryogenic adsorbents for use in methane bulk and clumped isotope analysis

Nico Kueter<sup>a,b</sup>, Naizhong Zhang<sup>c</sup>, Jan G.C. Meissner<sup>a,c</sup>, Léna Monnereau<sup>a</sup>, Paul M. Magyar<sup>b</sup>, Lukas Emmenegger<sup>b</sup>, Stefano M. Bernasconi<sup>a</sup>, Joachim Mohn<sup>c</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zurich, Zurich, Switzerland

<sup>b</sup> Geological Institute, RWTH Aachen, Aachen, Germany

<sup>c</sup> Laboratory for Air Pollution / Environmental Technology, Empa, Dübendorf, Switzerland

Cryogenic trapping of methane is essential for bulk and clumped isotope analyses, requiring adsorbent materials that enable efficient recovery and preserve isotopic signatures. We tested the performance (capacity, isotopic fractionation, and ease of use) of silica gels, zeolite molecular sieves, and activated carbon under various trapping and desorption conditions. A focus is set on the preservation of methane clumped isotope signatures.

A well-characterized methane reference gas (40 mL) was cryofocused at 77 K in containers filled with silica gels, zeolite molecular sieves (5A and 13X), or activated carbon alongside non-loaded containers. After loading, the containers were warmed in a water bath (21 to 95 °C) for various dwell times. The bulk ( $\delta\text{D}-\text{CH}_4$  and  $\delta^{13}\text{C}-\text{CH}_4$ ) and clumped ( $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$ ) isotopic composition of the desorbed methane were measured against the untreated reference gas using novel quantum cascade laser absorption spectroscopy (QCLAS).

Among the tested adsorbents, silica gels demonstrated superior performance, preserving  $\delta^{13}\text{C}-\text{CH}_4$ ,  $\delta\text{D}-\text{CH}_4$ ,  $\Delta^{13}\text{CH}_3\text{D}$ , and  $\Delta^{12}\text{CH}_2\text{D}_2$  values close to or within performance targets while offering high adsorption capacity, reproducibility, and ease of regeneration. Although effective for gas trapping, zeolite molecular sieves, and activated carbon introduced significant bulk and clumped isotopic shifts possibly due to catalytic effects and chromatographic isotopologue separation. Adsorbent-free cryotrapping is a viable alternative for sufficiently large methane volumes, where vapor pressure isotope effects (VPIEs) become negligible. However, cryogenic adsorbents remain indispensable for ensuring isotopic accuracy for small sample volumes and high-precision applications.



# Precise Kinetic Parameters for Thermal Resetting of Clumped Isotope Signatures in Biogenic and Abiogenic Calcites

Nico Kueter<sup>a,b</sup>, Nathan Looser<sup>a</sup>, Jordon D. Hemingway<sup>a</sup>, Nils B. Gies<sup>c</sup>, Gregory D. Price<sup>d</sup>, Alberto Perez-Huerta<sup>e</sup>, Stefano M. Bernasconi<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zurich, Zurich, Switzerland

<sup>b</sup> Geological Institute, RWTH Aachen, Aachen, Germany

<sup>c</sup> Institute of Geological Sciences, University of Bern, Bern, Switzerland

<sup>d</sup> School of Geography, Earth & Environmental Sciences, University of Plymouth, Plymouth, United Kingdom

<sup>e</sup> Department of Geological Sciences, The University of Alabama, Tuscaloosa, USA

The reordering kinetics of biogenic and abiogenic calcites have long been suspected to differ [1-3]. However, previous heating experiments aimed at deriving Arrhenius kinetic parameters have yielded inconclusive results [2,3]. To address this uncertainty, we performed high-resolution heating experiments on optical (abiogenic) and belemnite (biogenic) calcite. By capturing early signals and conducting experiments at lower temperatures than in previous studies, we derive new, precise disordered kinetic parameters for both materials (Table 1) [4].

In addition, a series of snapshot experiments conducted at 420 °C for 2 hours on a diverse suite of calcite materials reveals systematic differences in the thermal resetting behavior between biogenic and abiogenic calcites, emphasizing the importance of structural and compositional material properties (Fig. 1). These simple snapshot experiments provide a practical way to select the appropriate kinetic parameters for the thermal modelling of different calcites.

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Table 1: Averaged disordered Arrhenius kinetic parameters

Material	$\mu_E$ (kJ mol <sup>-1</sup> )	$v_0$ (min <sup>-1</sup> )	$\sigma_E$ (kJ mol <sup>-1</sup> )
Optical Calcite	216.5 ± 7.0	28.6 ± 1.1	14.5 ± 1.2
Belemnite Calcite	180.2 ± 8.0	27.8 ± 1.4	22.2 ± 2.6

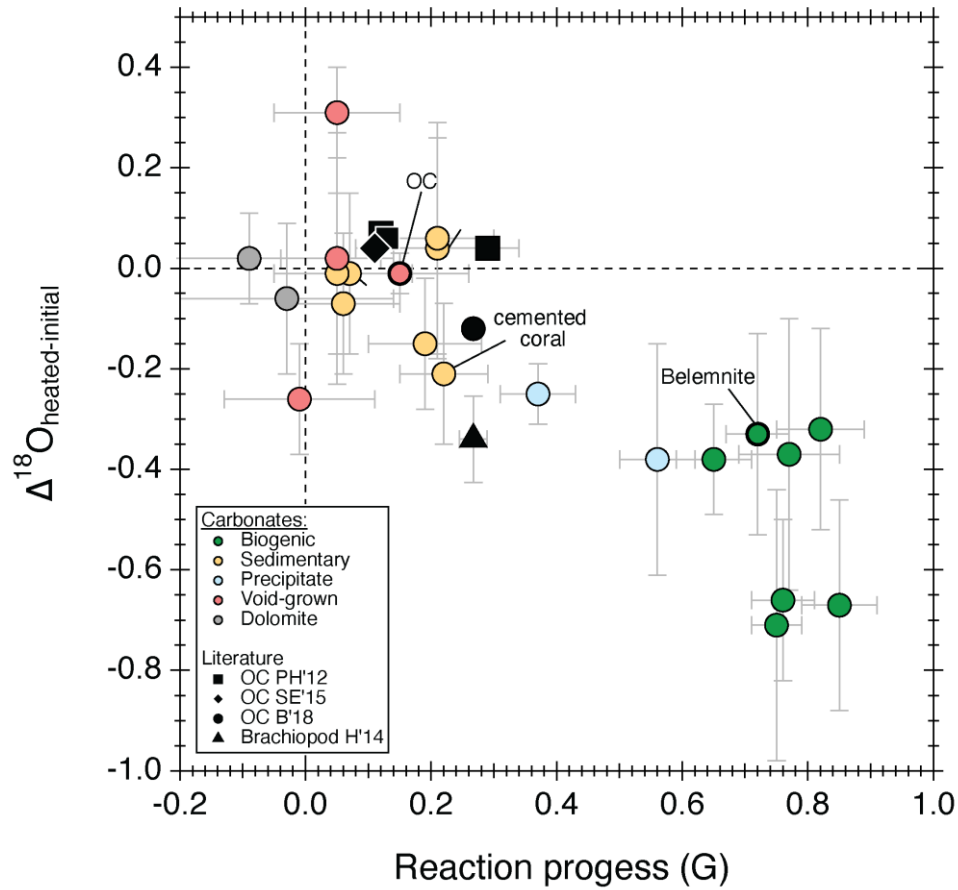


Figure 1: Results of snapshot experiments on a range of calcite and dolomite materials. Biogenic calcites exhibit significantly faster reordering and a stronger decrease in bulk  $\delta^{18}\text{O}$  than abiogenic calcite and dolomite. OC = Optical Calcite.



# Clumped Isotope Derived Temperatures, $\delta^{18}\text{O}$ , and $\delta^{13}\text{C}$ Values in Alluvial Carbonates Suggest a Wetter Environment Relative to Modern Conditions in the Hyper Arid Southern Negev During the Middle Pleistocene

Alyona Kuzmenko<sup>a</sup>, Zhennan Wang<sup>b</sup>, Paul Kapp<sup>b</sup>, Jay Quade<sup>b</sup>, Ari Matmon<sup>a</sup>

<sup>a</sup> Institute of Earth Sciences, the Hebrew University of Jerusalem, Jerusalem, Israel

<sup>b</sup> Department of Geosciences, The University of Arizona, Tucson, AZ, USA

Paleoclimatic interpretation of the stable isotope composition of  $\text{CaCO}_3$  deposits in the alluvial channels of the hyper-arid southern Negev has been held back by uncertain formation temperatures. Here, we measured  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and clumped isotope composition ( $\Delta_{638}$ ) in laminated carbonate that cements Middle-Pleistocene (~200–550 ka) [1] alluvial terrace sediment in the Shehoret catchment. Clumped isotope derived cementation temperatures were used to calculate precipitating water  $\delta^{18}\text{O}$ . Samples present the most depleted stable isotopic values observed in the southern Negev, with  $\delta^{13}\text{C}$  values of  $-3.4\text{‰}$  to  $-2.1\text{‰}$  and  $\delta^{18}\text{O}$  values of  $-10.5\text{‰}$  to  $-8.1\text{‰}$  (Fig. 1). Depleted  $\delta^{13}\text{C}$  values suggest enhanced soil respiration relative to modern conditions, and a possible increased dominance of  $\text{C}_3$  plants. Clumped isotope derived cementation temperatures ( $23.6 \pm 4.9^\circ\text{C}$  to  $31.0 \pm 5.5^\circ\text{C}$ , Fig. 1) fall within the range of modern temperatures at the carbonate formation depths. Calculated  $\delta^{18}\text{O}$  values of precipitating water range from  $-7.4\text{‰}$  to  $-5.5\text{‰}$  (Fig. 1), more depleted than modern southern Negev precipitation ( $-3.1\text{‰}$  to  $+3.3\text{‰}$ ) [2,3], and well within the northern and central Negev ranges ( $-9.5\text{‰}$  to  $-1.8\text{‰}$ ) [4]. These results indicate decreased aridity in the Mid-Pleistocene southern Negev, where increased rainfall from sources different from modern ones support higher biogenic activity in alluvial channels at warm surface temperatures.

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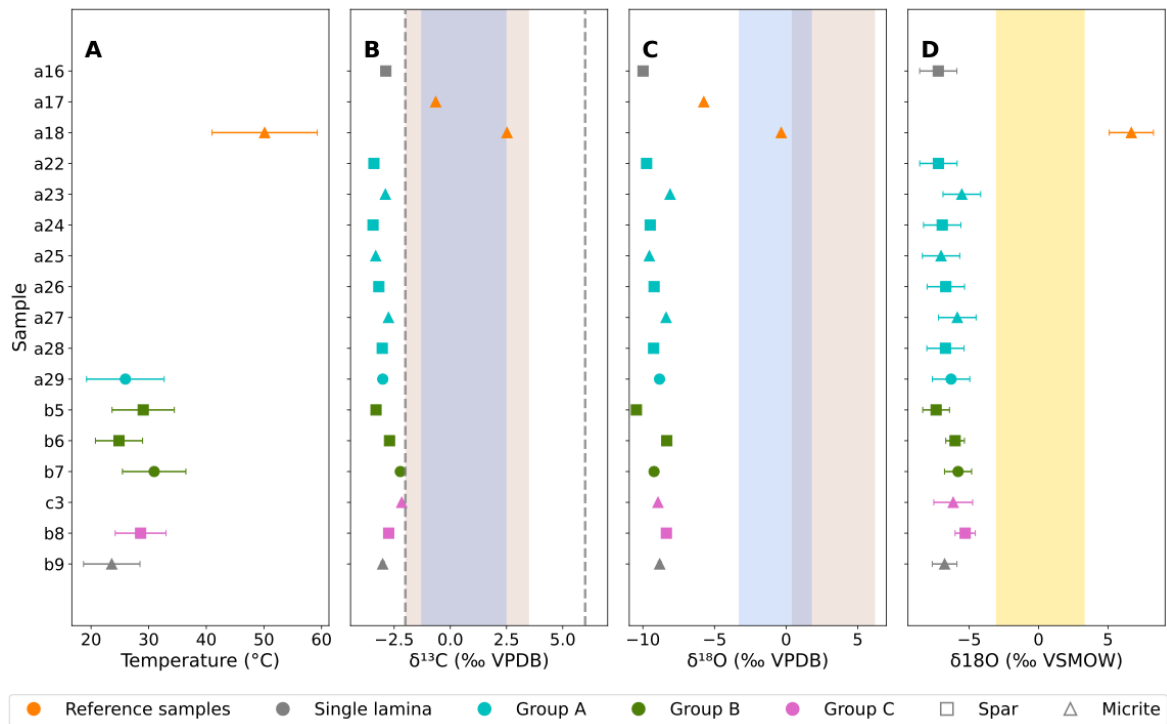


Figure 1: (A) Clumped isotope derived cementation temperature ( $T\Delta_{638}$ ). (B)  $\delta^{13}\text{C}$  values including expected Cretaceous and Cenozoic marine carbonate values (dashed grey lines), local modern (blue), and Late Pleistocene (beige) alluvial carbonate values [4]. (C) measured  $\delta^{18}\text{O}$  values. (D) Calculated precipitating water  $\delta^{18}\text{O}$  values, including modern local rainfall composition (yellow shaded zone) [1,2].



# Evaluating Miocene Temperature, Water Stress, and Hydrological Variability in the Atacama Desert with Carbonate Clumped and Triple Oxygen Isotopes

Elena Y. Lee<sup>a</sup>, Naomi E. Levin<sup>a</sup>, Jason A. Rech<sup>b</sup>, Erik Oerter<sup>c</sup>, Ronald Amundson<sup>d</sup>, Jay Quade<sup>e\*</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI, United States

<sup>b</sup> Department of Geology, Miami University, Oxford, OH, United States

<sup>c</sup> Lawrence Livermore National Laboratory, Livermore, CA, United States

<sup>d</sup> Department of Environmental Science, Policy, and Management, University of California, Berkeley, United States

<sup>e</sup> Department of Geosciences and the Desert Lab, University of Arizona, Tucson, AZ, United States,

\*Deceased

The Atacama Desert in northern Chile, spanning over 8° of latitude and 6000 meters of elevation, is one of Earth's driest places, yet we do not fully understand the drivers or timing of its aridification. Previous studies of authigenic carbonates (pedogenic, palustrine, travertine) in the Atacama have attributed an increase in carbonate  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{CO}_3}$ ) values 15–10 Ma to greater evaporation associated with the development of the Andean rain shadow [1–3]. However, increasing  $\delta^{18}\text{O}_{\text{CO}_3}$  values could also indicate a decrease in temperature or an increase in precipitation  $\delta^{18}\text{O}$  composition. Here we use the clumped and triple oxygen isotopic composition of pedogenic, palustrine and travertine carbonates from the Atacama spanning 23–2.1 Ma to evaluate how temperature and evaporation have influenced  $\delta^{18}\text{O}_{\text{CO}_3}$  values [1–5].  $\Delta^{17}\text{O}$  values of carbonate formation waters ( $\Delta^{17}\text{O}_{\text{rfw}}$ ) range from  $-58 \pm 14$  per meg to  $20 \pm 20$  per meg (VSMOW-SLAP), consistent with the range observed for South American precipitation and surface waters.  $\Delta_{47}$  temperatures range from  $5 \pm 3$  to  $31 \pm 4^\circ\text{C}$  and allow us to reconstruct carbonate formation water  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{rfw}}$ ) values, which range from  $-6.3 \pm 1.0\text{‰}$  to  $1.5 \pm 0.8\text{‰}$ .  $\Delta^{17}\text{O}$  values,  $\Delta_{47}$  temperatures, and  $\delta^{18}\text{O}_{\text{rfw}}$  values do not show clear temporal trends, such that neither an increase in evaporative stress nor a decrease in temperature explains the observed increase in  $\delta^{18}\text{O}_{\text{CO}_3}$  values. Instead, we find a combination of factors influences the  $\delta^{18}\text{O}_{\text{CO}_3}$  record, with both facies and site location (e.g. elevation, latitude) proving important in explaining the observed variation. For example,  $\Delta_{47}$ -derived temperatures average  $28 \pm 3^\circ\text{C}$  for palustrine carbonates versus  $9 \pm 6^\circ\text{C}$  for travertines, and pedogenic carbonates yield temperatures of  $11 \pm 4^\circ\text{C}$  at 2290 masl versus  $26 \pm 4^\circ\text{C}$  at 750 masl. We observe strong relationships between  $\Delta^{17}\text{O}_{\text{rfw}}$  and  $\delta^{18}\text{O}_{\text{rfw}}$  values across sample locations, indicating that both evaporation and local variation in precipitation  $\delta^{18}\text{O}$  values influence inter-site variation in  $\delta^{18}\text{O}_{\text{rfw}}$  and  $\Delta^{17}\text{O}_{\text{rfw}}$  values. Our results suggest the observed mid-Miocene increase in  $\delta^{18}\text{O}_{\text{CO}_3}$  values from the Atacama may be the amalgamated signal of heterogeneity in temperature, hydrology, and evaporation across the landscape rather than a story of aridification alone.

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## Paired Coccolith and Foraminifera $\Delta_{47}$ Temperatures suggest tropical Upper-Ocean Thermal Stratification in the late Miocene

Maja Leusch<sup>a</sup>, Madalina Jaggi<sup>a</sup>, Stefano Bernasconi<sup>a</sup> and Heather Stoll<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zürich, Zürich, 8092, Switzerland

Coccolith clumped isotopes ( $\Delta_{47\text{cocco}}$ ) have recently emerged as a promising proxy for reconstructing past upper-ocean temperatures. Unlike established proxies such as  $U_{37}^k$  and  $\text{TEX}_{86}$ ,  $\Delta_{47\text{cocco}}$  reflects calcification temperatures rather than relying on empirical regressions to sea surface temperature. Thus, in tropical oceans characterized by steep vertical temperature gradients, temporal variation in  $\Delta_{47\text{cocco}}$  may not only reflect upper-ocean temperature variability but also be influenced by changes in coccolithophore habitat depth.

Upper-ocean stratification is a key factor governing coccolithophore depth habitat and, therefore, their calcification temperature. Here, we assess the upper-ocean thermal structure in the tropical Atlantic during the late Miocene (~7.5–5.3 Ma) by combining a new  $\Delta_{47\text{cocco}}$  temperature record with paired measurements from planktonic foraminifera *Globorotalia menardii* and *Trilobatus sacculifer*, which feature distinct upper-ocean habitats.

Our new  $\Delta_{47\text{cocco}}$  record indicates tropical upper-ocean temperatures of ~20–25 °C during this period. Preliminary  $\Delta_{47}$  temperatures derived from *G. menardii* are slightly colder but remain within ~2 °C of the paired  $\Delta_{47\text{cocco}}$  temperatures, whereas *T. sacculifer* yields warmer values. This offset is consistent with modern differences in habitat depth in this region, where *G. menardii* and coccolithophores record thermocline conditions, while *T. sacculifer* calcifies in the warmer mixed layer.

These initial results suggest modest thermal stratification between the habitats of the studied species in the western tropical Atlantic during the late Miocene. More broadly, this study explores the potential of paired coccolith–foraminifera clumped isotope thermometry to assess water column structure in regions with steep vertical temperature gradients.



# Facies-Specific Dual-Clumped Isotope Disequilibrium in Eocene Terrestrial Carbonates

Zachary C. Loveall<sup>a</sup>, Ellen K. Olsen<sup>a</sup>, Miquela K. Ingalls<sup>a</sup>

<sup>a</sup> Department of Geosciences, The Pennsylvania State University, University Park, PA, USA

Recent advances in the field of carbonate isotopic geochemistry have found that most Earth surface calcites — abiotic and biogenic — do not precipitate in isotopic equilibrium [1]. Dual-clumped isotopes ( $\Delta_{47}$ - $\Delta_{48}$ ) provide a powerful framework for identifying kinetic isotope effects during carbonate formation. In terrestrial environments, dissolved inorganic carbon (DIC) cycling — including CO<sub>2</sub> degassing, CO<sub>2</sub> absorption, and water mixing — can drive the DIC-H<sub>2</sub>O system out of isotopic equilibrium. Because isotopic equilibration during the rate limiting steps (CO<sub>2</sub> hydration and hydroxylation) for DIC interconversion occurs on timescales of hours to days [2], rapidly precipitating carbonates may preserve transient isotopic disequilibria that deviate from thermodynamic equilibrium [3].

We investigate these effects in terrestrial carbonates from different facies and lake stages of the Green River Formation, which records lacustrine, wetland, and shoreline environments during the Early Eocene Climatic Optimum. These deposits provide a natural laboratory for evaluating how carbonate facies and corresponding precipitation pathways influence clumped isotope signatures under greenhouse climate conditions. Petrographic screening and mineralogical analyses were conducted on samples to assess diagenetic overprinting prior to isotopic analysis. Preliminary  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\Delta_{47}$ - $\Delta_{48}$  isotope measurements are evaluated to characterize deviations from equilibrium relationships expected for temperature-controlled carbonate formation. Initial results indicate facies-dependent variability in dual-clumped signatures, with placements above, below, and on the thermodynamic equilibrium line within one lake system. Deviations from equilibrium likely reflect kinetic isotope effects associated with carbonate precipitation mechanisms rather than temperature alone.

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## Dual clumped isotopes indicate the control of diagenetic systems on the formation of cold seep carbonates

Chaojin Lu<sup>a,b,c</sup>, Antoine Crémière<sup>d</sup>, Fang Hao<sup>a,b</sup>, Fuyun Cong<sup>a,b</sup>, Peter K. Swart<sup>c</sup>

<sup>a</sup> State Key Laboratory of Deep Oil and Gas, China University of Petroleum (East China), Qingdao, China

<sup>b</sup> School of Geosciences, China University of Petroleum (East China), Qingdao, China

<sup>c</sup> Department of Marine Geosciences, Rosenstiel School of Marine, Atmospheric and Earth Sciences, University of Miami, Miami, USA

<sup>d</sup> dCNRS–Université de Brest, Plouzané, France

While methane-derived authigenic carbonates (MDACs) are widely used to reconstruct paleoclimate and biogeochemical cycles, such interpretation comes with a challenge in that the C and O isotopic values of MDACs may have experienced significant kinetic isotope effects induced by rapid precipitation and increased alkalinity during their formation. In order to further understand the non-equilibrium process during the formation of MDACs, we analyzed a suite of modern samples from North, Barent and Marmara Sea using the dual clumped isotope approach ( $\Delta_{47}$  and  $\Delta_{48}$ ), a novel proxy for investigating kinetic isotope effects. The four petrographic textures of our MDACs, that include aragonite matrix, cavity filling cements, Mg-calcite, and dolomite, show a range of  $\Delta_{47}$  and  $\Delta_{48}$  values. The aragonite matrix and cavity filling cements have more positive  $\Delta_{48}$  values and more negative  $\Delta_{47}$  values relative to expected equilibrium values, comparable to the samples in South China Sea, which was interpreted as a product of rate-limiting bicarbonate dehydration/dehydroxylation in an open-system environment [1]. In contrast, the  $\Delta_{48}$  values of the Mg-calcite and dolomite show negative  $\Delta_{48}$ -disequilibrium, generally recognized in the carbonate minerals mediated by microbial sulfate reduction [2,3]. Such a disequilibrium is mostly attributed to the elevated concentrations of dissolved inorganic carbon relating to CO<sub>2</sub> hydration/hydroxylation in a closed system in which the produced CO<sub>2</sub> slowly diffuses into ocean, rather than the rapidly degas. The differential disequilibrium of the dual clumped isotopes highlights the importance of diagenetic systems (open vs closed) in controlling the formation mechanism of MDACs and defining their geochemical signatures.

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## Constraining Nitrous Oxide Sources and Sinks with Clumped Isotopes

Paul M. Magyar<sup>a</sup>, Noémy Chénier<sup>a,b</sup>, Joachim Mohn<sup>a</sup>

<sup>a</sup> Empa, Laboratory for Air Pollution / Environmental Technology, Dübendorf, Switzerland

<sup>b</sup> University of Basel, Department of Environmental Sciences, Basel, Switzerland

Mitigating the anthropogenically-stimulated accumulation of nitrous oxide (N<sub>2</sub>O) in the atmosphere is of paramount importance for achieving climate and air quality goals. Clumped isotopes have potential to add to existing isotopic and biogeochemical tools to better constrain sources and sinks of N<sub>2</sub>O. We describe an optimized approach and workflow for measuring the clumped isotopologues <sup>14</sup>N<sup>15</sup>N<sup>18</sup>O, <sup>15</sup>N<sup>14</sup>N<sup>18</sup>O, and <sup>15</sup>N<sup>15</sup>N<sup>16</sup>O alongside  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ , and <sup>15</sup>N site preference (SP) using quantum cascade laser absorption spectroscopy. The selectivity and sensitivity enabled by this spectroscopic approach provides significant advantages over previously reported mass spectrometric methods. Equilibration of N<sub>2</sub>O over  $\gamma\text{-Al}_2\text{O}_3$  provides a robust absolute reference frame for <sup>14</sup>N<sup>15</sup>N<sup>18</sup>O, <sup>15</sup>N<sup>14</sup>N<sup>18</sup>O, and SP. We evaluate the utility of this set of singly and doubly substituted isotopologues for characterizing microbial N<sub>2</sub>O cycling, including the opposing effects of N<sub>2</sub>O production and reduction and the emerging variability associated with bacterial denitrification.



## Constraining the Extent of Reordering in Biogenic Carbonates From Heat Exposure

Ellie J. Pryor<sup>a,b</sup>, Victoria E. Taylor<sup>a</sup>, Jakub Seneš<sup>c</sup>, Carin Andersson<sup>b,d</sup>,  
Christopher Miller<sup>b,c</sup>, **A. Nele Meckler<sup>a,b</sup>**

<sup>a</sup> Department of Earth Sciences, University of Bergen, Bergen, Norway

<sup>b</sup> Centre for Early Sapiens Behaviour (SapienCE), University of Bergen, Norway

<sup>c</sup> Department of Geosciences, University of Tübingen, Germany

<sup>d</sup> Norwegian Research Center, Bergen, Norway

The temperature-dependent re-equilibration of clumped isotopes in carbonates presents an opportunity to reconstruct heat exposure in archeological deposits [1,2]. In these settings, shell remains often represent food waste, and reconstructions of heat exposure can provide new insights into cooking methods and hearth locations. However, the extent and speed of resetting may be material-specific, for example influenced by mineralogy and amount of organic matter in the biogenic carbonates.

Here we present a series of heating experiments conducted on modern aragonitic *Turbo sarmaticus* and *Bivalvia Mollusca* to constrain the extent of clumped isotope re-equilibration following heat exposure. Oven heating experiments were conducted on both archives at varying temperatures of between 100 to 550 °C and varying exposure times of between 5 to 300 minutes.

We find a clear relationship between heating temperature and the clumped isotope signature, which is similar for both archives and shows promise for reconstructing heat exposure in archeological samples. However, as heating times also affect the extent of resetting, the determination of precise heating temperatures remains challenging without additional constraints.

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## Terrestrial Cooling during the Middle Miocene Climate Transition in Spain

Niels Meijer<sup>a</sup>, Jens Fiebig<sup>b</sup>, Wout Krijgsman<sup>c</sup>, Iuliana Vasiliev<sup>a</sup>, Andreas Mulch<sup>a,b</sup>

<sup>a</sup> Senckenberg Biodiversity and Climate Research Centre (SBIK-F), Frankfurt am Main, Germany.

<sup>b</sup> Goethe University Frankfurt, Institute of Geosciences, Frankfurt am Main, Germany.

<sup>c</sup> Department of Earth Sciences, Utrecht University, Utrecht, Netherlands

The Middle Miocene Climate Transition (MMCT; 14.7–13.8 Ma) involved global cooling, growth of Antarctic ice sheets and changes in ocean circulation following peak warmth during the Miocene Climatic Optimum (MCO). However, the terrestrial impact remains unclear. Here we use dual clumped isotope thermometry ( $\Delta_{47}$  and  $\Delta_{48}$ ) on pedogenic carbonates from the Iberian Peninsula (Armantes section, Spain) to reconstruct soil temperatures across the MCO and MMCT. The Armantes section has been well-dated using magnetostratigraphy and spans from 16 to 13 Ma. The dual clumped isotope approach reveals that all pedogenic carbonate samples plot on the isotope equilibrium line once samples were bleached to remove  $\text{NO}_2$  contaminants. The reconstructed soil temperatures are relatively stable at  $23 \pm 3^\circ\text{C}$  (2SE) during the MCO, followed by a gradual cooling between 14.0 and 13.6 Ma to  $20 \pm 3^\circ\text{C}$  after the MMCT. Both, timing and magnitude of cooling correspond perfectly with sea surface temperature reconstructions in the North Atlantic Ocean. This suggests a strong coupling between land and ocean temperatures and highlights the use of dual clumped isotope thermometry on pedogenic carbonates for continental temperature reconstructions of unprecedented accuracy.



## Coccolith Clumped Isotopes Unveil Coccolithophores' Ecology, Challenge Miocene High-Latitude Warmth and Decipher Euphotic Zone Temperatures during the Cenozoic

Luz María Mejía<sup>a</sup>, Victoria Taylor<sup>b</sup>, Nele Meckler<sup>b</sup>, Heather Stoll<sup>c</sup>, Stefano M. Bernasconi<sup>c</sup>, Alvaro Fernandez<sup>d</sup>, Hongrui Zhang<sup>e</sup>, José Guitián<sup>f</sup>, Heiko Pälike<sup>a</sup>

<sup>a</sup> MARUM, Bremen University, Bremen, Germany

<sup>b</sup> Department of Earth Sciences, Bergen University, Bergen, Norway

<sup>c</sup> Department of Earth Sciences, ETH Zurich, Zurich, Switzerland

<sup>d</sup> Instituto Andaluz de Ciencias de la Tierra (CSIC), Granada, Spain

<sup>e</sup> School of Ocean and Earth Sciences, Tongji University, Shanghai, China

<sup>f</sup> Instituto de Investigaciones Mariñas (CSIC), Vigo, Spain

Understanding past ocean temperature response to high CO<sub>2</sub> is essential for improving model projections of future climate under anthropogenic forcing. However, widely-used temperature proxies are subject to limitations that may affect the reliability of absolute reconstructions (e.g. assumptions of seawater chemistry, or the insufficient comprehension of processes affecting proxies). Clumped isotope ( $\Delta_{47}$ ) thermometry offers a robust alternative, being independent of seawater composition and grounded on well-constrained thermodynamics.

Here, we apply  $\Delta_{47}$  thermometry to calcite produced by coccolithophores, providing a direct signal from the euphotic zone. Holocene coccolith  $\Delta_{47}$  temperatures from globally-distributed sediments suggest that coccolithophores can biomineralize at depth, particularly in tropical warm areas. This challenges the conventional assumption of unique surface production of widely-used alkenone calibrations, indicating that alkenone reconstructions, as traditionally interpreted, may show a warm bias.

An alkenone-coccolith  $\Delta_{47}$  temperature offset is also evident in the North Atlantic (ODP Site 982) since the Mid-Miocene, where  $\Delta_{47}$  temperatures are  $\sim 9$  °C colder than those derived from coeval alkenones. Alkenone-derived high-latitude records underpin the paradigm of extreme polar warmth during past warm intervals, like the Miocene, while our coccolith  $\Delta_{47}$  data indicate a more modest high-latitude amplification and is in better agreement with climate models.

We present the first low-resolution Cenozoic coccolith  $\Delta_{47}$  temperature record from low (Eastern Equatorial Pacific, PEAT transect) and high latitude (ODP Site 1170, South Tasman Rise; nearby IODP Site U1553) euphotic oceans. Both records reproduce the variability observed in foraminiferal  $\delta^{18}\text{O}$ , although tropical temperatures are systematically cooler than expected. Trace elements and SEM observations show no evidence of early recrystallization. Alternative controls include variations in upwelling intensity and production depth. Consistent with the North Atlantic record, the Southern Hemisphere coccolith  $\Delta_{47}$  temperatures suggests a rather modest polar amplification during the Mid-Miocene, with potentially impactful implications in our understanding high-latitude sensitivity to future CO<sub>2</sub> forcing.



## Clumped and Triple Oxygen Isotope Constraints on Vegetation and Water-stress across Rift landscapes of the Mid-Pliocene Lower Awash Valley, Ethiopia

Million A. Mengesha<sup>a,b</sup>, Naomi E. Levin<sup>a</sup>, Beverly Z. Saylor<sup>c</sup>, Christopher J. Campisano<sup>d,e</sup>, Benjamin H. Passey<sup>a</sup>, Daniel I. Hembree<sup>f</sup>, Takele M. Mihretie<sup>c</sup>, Will Newman<sup>a</sup>, Yasmina Zimmer<sup>a</sup>, Yohannes Haile-Selassie<sup>d,e</sup>

<sup>a</sup> Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI, USA

<sup>b</sup> School of Earth Sciences, Addis Ababa University, Addis Ababa, Ethiopia

<sup>c</sup> Earth, Environmental, and Planetary Sciences, Case Western Reserve University, Cleveland, OH, USA

<sup>d</sup> School of Human Evolution and Social Change, Arizona State University, Tempe, AZ, USA

<sup>e</sup> Institute of Human Origins, Arizona State University, Tempe, AZ, USA

<sup>f</sup> Department of Earth, Environmental, and Planetary Sciences, University of Tennessee Knoxville, Knoxville, TN, USA

In eastern Africa, carbon and oxygen isotopic compositions of pedogenic carbonates are widely used to infer C<sub>3</sub>-C<sub>4</sub> vegetation distributions, with increases in C<sub>4</sub> vegetation often linked to aridification. Although regional climate strongly influences vegetation, tectonically driven landscape heterogeneity in active rift settings can decouple local vegetation structure from regional climate trends. Here we report  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$  and  $\Delta^{17}\text{O}$  data from mid-Pliocene (3.5 – 3.2 Ma) pedogenic carbonates (n=125) sampled across multiple depositional settings in the Lower Awash Valley, from the Woranso-Mille (WM) and Hadar (HD) paleoanthropological sites, to evaluate the relationships between vegetation, temperature and water stress across rift landscapes.

We observe wide isotopic ranges ( $\delta^{13}\text{C}$  -13.9 to -2.5‰;  $\delta^{18}\text{O}$ : -10.9 to +1.3‰) indicating the presence of C<sub>3</sub>- and C<sub>4</sub>- dominated ecosystems along with mixed systems, across a range of hydroclimate conditions. When all samples are considered,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  show no clear covariance, however, some sites show inverse  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  relationships indicating depositional setting controls. These patterns challenge the simplified “C<sub>3</sub>-wet” and “C<sub>4</sub>-arid” frameworks commonly used to interpret  $\delta^{13}\text{C}$  records.

$\Delta_{47}$ -derived soil temperatures (n=29) range from 20 to 35°C. Mean temperatures are  $27 \pm 3^\circ\text{C}$  at WM and  $25 \pm 4^\circ\text{C}$  at HD (overall mean =  $26 \pm 4^\circ\text{C}$ ), which are slightly cooler than modern soil temperatures.  $\Delta_{47}$  shows no systematic relationship with  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , suggesting that relationships among soil temperature and C<sub>3</sub>-C<sub>4</sub> vegetation structure, and hydroclimate are not straightforward.

Reconstructed soil water  $\Delta^{17}\text{O}$  values (-55 to 24 per meg) indicates evaporative states consistent with those observed in modern semi-arid to arid settings in the Serengeti and Awash regions. We used  $\Delta^{17}\text{O}$  data to constrain the effects of evaporation, and  $\Delta_{47}$ -derived soil temperatures to reconstruct oxygen isotopic composition of soil water ( $\delta^{18}\text{O}_{\text{rsw}}$ ). The  $\delta^{18}\text{O}_{\text{rsw}}$  values span a wide range (-6.5 to +2.1‰; n=25) and vary with basin position, suggesting differences in input water that are likely linked to landscape position and, potentially, to distinct climatic regimes. The combination of  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $\Delta_{47}$  and  $\Delta^{17}\text{O}$  data from well contextualized settings highlight the importance of landscape position in governing the relationship between water availability and vegetation.



## A new low temperature reference material for clumped isotope analysis

Sebastian F.M. Breitenbach<sup>a</sup>, **Sevi Modestou**<sup>a</sup>, Stuart Umbo<sup>b</sup>, David Hodell<sup>c</sup>, Kit Baker<sup>c</sup>, Alexander Osinzev<sup>d</sup>, Hamish Cooper<sup>e</sup>, Gideon M. Henderson<sup>e</sup>, Jens Fiebig<sup>f</sup>

<sup>a</sup> Northumbria Isotope and Clumped geothermometry for Environmental Studies Laboratory, School of Geography and Natural Sciences, Northumbria University, Newcastle upon Tyne, UK

<sup>b</sup> Department of Natural Sciences, Manchester Metropolitan University, Manchester, UK

<sup>c</sup> Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, Cambridge, UK

<sup>d</sup> Speleoclub Arabika, St. Mamina-Sibiriyaka 6a, 664058 Irkutsk, RF

<sup>e</sup> Department of Earth Sciences, Oxford University, Oxford, OX1 3AN, UK

<sup>f</sup> Institute of Geosciences, Goethe University Frankfurt, Frankfurt am Main, D

Clumped isotope thermometry has become a highly versatile tool to quantify the temperature at which carbonates precipitated and the oxygen isotope signature of the water from which the carbonate formed. For robust inter-laboratory comparison of clumped isotope analyses in a common, accepted absolute reference frame (known as Carbon Dioxide Equilibration Scale, CDES), matrix-matched reference materials are required. Several international reference carbonate materials, representing different formation temperatures and isotopic compositions (most prominently ETH-1, ETH-2, ETH-3, ETH-4, and IAEA-C2), have been characterised for this purpose. However, the available reference materials all formed above ca. 13°C, which means that carbonates formed at lower temperatures fall outside the reference (temperature) calibration frame. This is especially relevant for low temperature applications, including palaeoceanography and palaeoclimatology.

Here we present the subaqueously-precipitated speleothem POL-2 as a promising candidate material. The U/Th age of this speleothem is  $457 \pm 33$  ka. POL-2 formed subaqueously as a rimstone of a cave lake in southern Siberia, with a modern cave air temperature of  $1.9 \pm 0.1$ °C. Given the geometry and location of the cave, the temperature is unlikely to have differed during the time of formation. The isotopic composition ( $d^{18}O_{cc}$ ,  $d^{13}C_{cc}$ ,  $D_{47}$ ,  $D_{48}$ ) has been determined in three laboratories. At Northumbria University, using a Nu Instruments Perspective,  $d^{18}O_{cc}$  is  $-9.23 \pm 0.08$  (1s) ‰ VPDB,  $d^{13}C_{cc}$  is  $-7.14 \pm 0.03$  (1s) ‰ VPDB, and  $D_{47}$  is  $0.6557 \pm 0.0046$  (1 SE, ‰ CDES, N = 70). At Cambridge University, also using a Nu Instruments Perspective,  $d^{18}O_{cc}$  is  $-9.22 \pm 0.05$  (1s) ‰ VPDB,  $d^{13}C_{cc}$  is  $-6.96 \pm 0.02$  (1s) ‰ VPDB, and  $D_{47}$  is  $0.674 \pm 0.0027$  (1 SE, ‰ CDES, N = 80). Dual clumped analysis at the Goethe University Frankfurt gives  $D_{47} = 0.6668 \pm 0.0014$  and  $D_{48} = 0.2727 \pm 0.0048$  ‰ (1 SE) (N = 43). Dual clumped analysis implies that this speleothem formed at  $1.4^{+1}_{-1.8}$ °C and under quasi-equilibrium conditions.

POL-2's formation under isotope equilibrium at near freezing temperature and its isotopic composition make it an excellent candidate as a reference material. A serious problem, however, is posed by the amount of raw material that can be prepared, due to the inaccessibility of the cave under today's political situation. Ca. 220 gr of POL-2 are currently available for critical applications.



## The clumped isotope signatures of acid resistant carbonates reacted at 120 °C with the new ‘Nu React’

**Inigo A. Müller<sup>a</sup>**, Martin Moore<sup>b</sup>, Peter Li<sup>b</sup>, Swagata Chaudhuri<sup>a</sup>, Anjana Shaju<sup>c</sup>, Xianye Zhao<sup>a</sup>, Aniket Mitra<sup>e,a</sup>, Olivier Namur<sup>c</sup>, Andreas Beinlich<sup>d</sup>, Steven Goderis<sup>a</sup>, Stephen Rablen<sup>b</sup> and Philippe Claeys<sup>a</sup>

<sup>a</sup> Archaeology, Environmental Changes & Geo-Chemistry, Vrije Universiteit Brussel, Brussels, Belgium

<sup>b</sup> Nu Instruments Ltd, Wrexham, United Kingdom

<sup>c</sup> Department of Earth and Environmental Sciences, KU Leuven, Leuven, Belgium

<sup>d</sup> Institute of Geological Sciences, Freie Universität Berlin, Berlin, Germany

<sup>e</sup> Institut des Sciences de la Terre de Paris (ISTeP), CY Cergy Paris Université, Neuville-sur-Oise, France

A set of carbonate mineralogies including calcites, dolomites, siderites and magnesites was automatically reacted with  $H_3PO_4$  at 120 °C using the new Nu React carbonate device from Nu Instruments to determine their clumped isotope composition with a Perspective isotope ratio mass spectrometer. All the data were processed and transferred into the I-CDES90°C frame with a simultaneously analyzed carbonate standards to guarantee identical sample standard treatment. The reaction of extremely acid resistant mineralogies such as magnesite and siderite can now be done within one hour allowing a much higher and more reproducible sample throughput to study the formation of these mineralogies in more detail. The clumped isotope temperature evaluation was subsequently done with well constrained calcite specific temperature calibrations covering a wide temperature range. As for magnesites of known formation temperatures, the obtained clumped isotope temperatures verify that magnesite can be evaluated with calcite specific temperature calibrations, whereas siderites and dolomites give evidence for diverging acid fractionation values than calcite at this elevated reaction temperature. New analysis of isotopically scrambled dolomites and siderites should show a simple way to correct for these observed offsets to easily retrieve robust clumped isotope temperature estimates from hot temperature Nu React analysis.



## Establishing Methane Clumped Isotope Measurements on a High-Resolution IRMS: Methodological Challenges and Practical Insights

Ayrton L. F. Nascimento<sup>a</sup>, Gabriel F. dos Santos<sup>b</sup>, Hugo G. Machado<sup>a</sup>, Frederico Rodrigues<sup>a</sup>, Julio C. O. Ribeiro<sup>a</sup>, Alexandre A. Ferreira<sup>c</sup>, Boniek Gontijo<sup>a</sup>

<sup>a</sup> Centro de Excelência em Estudos Moleculares Energia e Petróleo (CEMEP), Federal University of Goiás, Goiânia, Brazil

<sup>b</sup> Institute of Chemistry, Federal University of Goiás, Goiânia, Brazil

<sup>c</sup> Division of Geochemistry, PETROBRAS Research and Development Center (CENPES), PETROBRAS, Rio de Janeiro, Brazil

Methane clumped isotopes, specifically  $^{13}\text{CH}_3\text{D}$  and  $^{12}\text{CH}_2\text{D}_2$ , represent the enrichment of rare, multiply substituted isotopologues relative to a stochastic (random) distribution [1–3]. These measurements serve as powerful geothermometers to determine formation temperatures and distinguish between biogenic, thermogenic, and abiotic sources.

Despite their utility, analysis is hindered by significant technical challenges. Conventional isotope-ratio mass spectrometers (IRMS) lack the resolution required to distinguish clumped species such as  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_3\text{D}$  or interfering isobars like  $^{17}\text{O}^+$  and  $^{16}\text{OH}^+$ , produced by  $\text{H}_2\text{O}$  fragmentation [1]. Consequently, high-resolution instruments achieving mass resolving powers of 20,000 to 42,000, such as the Thermo Scientific 253 Ultra, are necessary for the direct analysis of intact methane. Furthermore, due to the extreme rarity of these species, large sample sizes (~3 mL) and long integration times of up to 20 hours are required to achieve sufficient precision [2,3]. Meticulous extraction and purification are also essential to isolate pure methane and minimize isotopic fractionation while preserving original signals.

In this study, we report the stepwise establishment of methane clumped isotope measurements using a HR-IRMS Ultra 253. The workflow involved instrumental optimization, the development of acquisition protocols, and the implementation of sample purification strategies. Particular emphasis was placed on resolving critical analytical interferences, including isobaric overlap with water and ion source-induced species, through systematic tuning and alignment which are well documented challenges in high-resolution IRMS measurements [4]. Additionally, we address specific hardware troubleshooting that may provide valuable insights for the broader user community. Significant improvements in peak resolution and signal stability were achieved following these instrumental adjustments. The development of dedicated acquisition routines (LabBooks) enabled consistent data collection for both singly and doubly substituted isotopologues. Zero-enrichment experiments were performed to assess baseline behavior and measurement stability, providing initial constraints on analytical precision and reproducibility for  $\delta^{13}\text{C}$ ,  $\delta\text{D}$  and clumped isotope signals. Our results highlight that reliable measurements depend on the integrated control of ion source conditions, mass resolution, and sample purity. These findings establish a methodological foundation for future applications, including equilibrium experiments and temperature reconstructions of natural methane samples.

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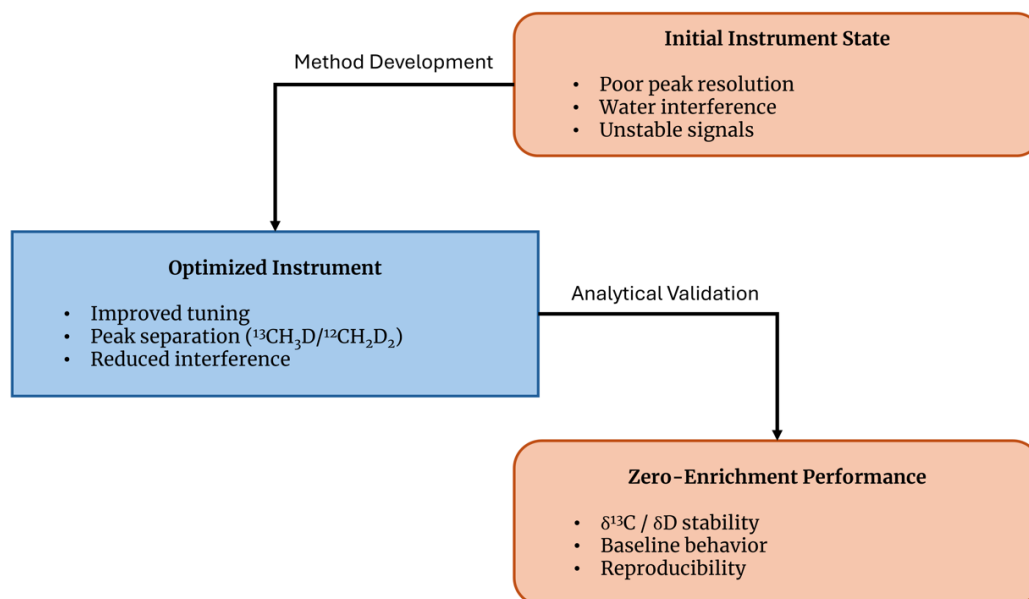


Figure 1: Evolution of instrumental performance during the implementation of methane clumped isotope measurements on a high-resolution IRMS. Initial tuning conditions showed limited peak resolution and significant interference from water and neighboring species, while optimized conditions enabled clear separation of target isotopologues ( $^{13}\text{CH}_3\text{D}$  and  $^{12}\text{CH}_2\text{D}_2$ ). Zero-enrichment experiments demonstrate the resulting signal stability and baseline analytical performance, providing a foundation for subsequent clumped isotope analyses.



## Isotopic Characterization of the Bargou–Sodga–Bous Sadia Karst Aquifer (northwestern, Tunisia)

Nesrine Nasri<sup>a,b</sup>, Fairouz Slama<sup>a</sup>, Intissar Ben Sahli<sup>a</sup>, Nicolas Patris<sup>c</sup>, Jean-denis Taupin<sup>c</sup>

<sup>a</sup> National Engineering School of Tunis (ENIT), LR99ES19 Laboratory of Modelling in Hydraulics and Environment (LMHE), University of Tunis El Manar, BP 37, 1002 Tunis, Tunisia

<sup>b</sup> University of Carthage, Higher Institute of Environmental Technologies, Urban Planning and Construction, Charguia II, 2035 Tunis, Tunisia

<sup>c</sup> Hydrosiences, University of Montpellier, IRD, CNRS, IMT Mines Alès, 34093 Montpellier, France

Groundwater is a critical freshwater resource, and its quality is essential for sustaining socio-economic development, particularly in karst systems where aquifers are highly complex. This study investigates the isotopic signature of the Bargou–Sodga–Bous Sadia Karst aquifer in Jebel Bargou, northwestern Tunisia. A total of 12 wells and 6 springs samples were collected in April and September 2025 to characterize the isotopic composition of water. Isotopic analyses, carried out on wells and springs in the Siliana–Bargou region, show a relative homogeneity of the oxygen-18 ( $\delta^{18}\text{O}$ ) and deuterium ( $\delta^2\text{H}$ ) ratios. The  $\delta^{18}\text{O}$  varies between  $-6.87\text{‰}$  and  $-6.17\text{‰}$ , while the  $\delta^2\text{H}$  varies between  $-39.4\text{‰}$  and  $-32.7\text{‰}$ , with mean values of  $-6.50\text{‰}$  and  $-36.9\text{‰}$ , respectively. These results reveal that the groundwater of the Siliana–Bargou region displays a homogeneous isotopic signature, typical of a meteoric origin. The high d-excess values (always above  $12\text{‰}$ ) are remarkable and may suggest either an important contribution of Mediterranean air masses. The isotopic compositions showed little variation across different sampling campaigns (2023 and 2025) and seasons (April and July), indicating that the aquifer system is stable and recharged uniformly through a permeable substratum. The use of isotopic tracers in this work provided valuable insights into the behavior of the Bargou karst aquifer system and the mineralization processes affecting the chemical composition of its waters. The isotopic data revealed that most samples are recharged by direct infiltration of rainfall originating from the Mediterranean region, with limited evaporation.

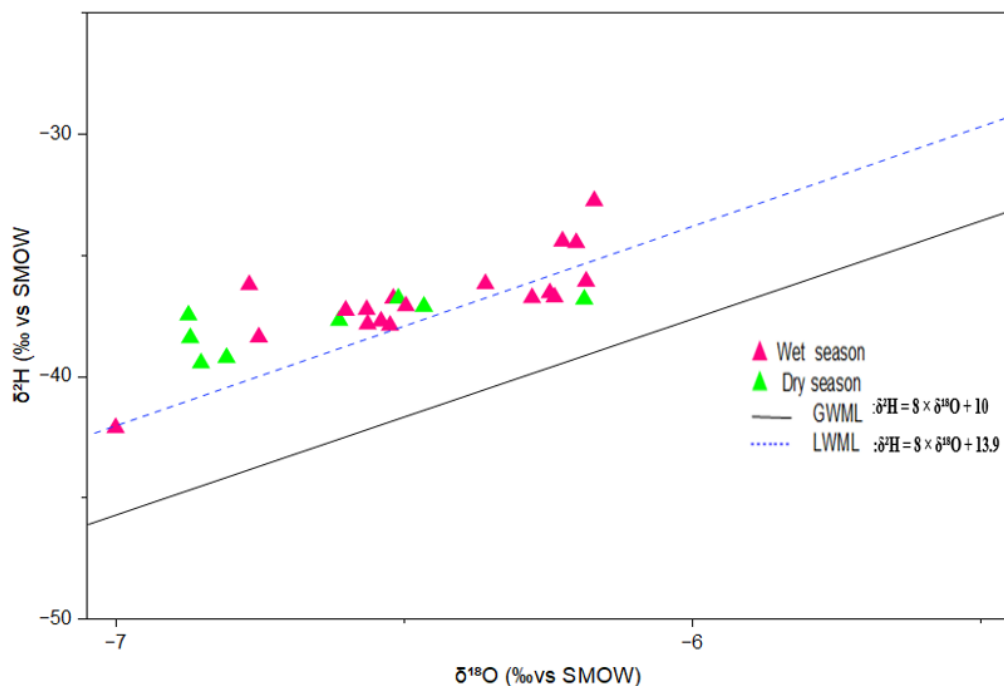


Figure 1:  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  Diagram from the Bargou–Sodga–Bous Sadia Karst Aquifer



## Recent Progress in Isotope Ratio Laser Spectroscopy of Clumped CO<sub>2</sub> and Triple Oxygen CO<sub>2</sub>

David D. Nelson<sup>a</sup>, Christoph Dyroff<sup>a</sup>, Scott C. Herndon<sup>a</sup>, Rick Wehr<sup>a</sup>, Payal Banerjee<sup>b</sup>, Zach Sharp<sup>b</sup>

<sup>a</sup> Aerodyne Research, Billerica, MA, United States

<sup>b</sup> Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, United States

In recent years, Isotope Ratio Laser Spectroscopy (IRLS) has been shown to be a powerful alternative to Isotope Ratio Mass Spectrometry (IRMS) for the measurement of the clumped isotopes of carbon dioxide as well as for its triple oxygen composition [1-4]. IRLS has some fundamental advantages with respect to IRMS. These include direct, specific detection of individual isotopologues (no iso-bar problem) and a measurement process that does not necessarily destroy the sample. In this paper we describe recent work attempting to exploit these advantages.

First, we describe our investigation of new spectroscopic windows for the measurement of the two most abundant clumped isotopologues of carbon dioxide. With this approach we specifically quantify <sup>16</sup>O<sup>13</sup>C<sup>18</sup>O and <sup>18</sup>O<sup>12</sup>C<sup>18</sup>O which are equal to the desired IRMS signals at masses 47 and 48 if the isobaric interferences could be removed.

Second, we present recent results exploiting the non-destructive nature of the measurement process. We demonstrate cryogenic recycling of our samples which are mixtures of CO<sub>2</sub> in buffer gas. This recycling allows us to perform dual inlet signal averaging without consuming additional sample. Additional testing is required to fully demonstrate measurement accuracy, but initial results are encouraging. Fully successful recycling would provide the capability to make high accuracy measurements even with dramatically smaller sample sizes. For example, it may be possible to measure the triple oxygen composition of CO<sub>2</sub> with samples as small as 25 μg of calcite while maintaining accuracy of at least 0.01‰.

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## Micro-Sample and High-Temperature Capable, Custom-Built System for Diverse Carbonate Clumped Isotope Analysis

Kozue Nishida<sup>a</sup>, Jakub Surma<sup>b</sup>, Wang Jingzhuo<sup>a</sup>, Keiga Endo<sup>a</sup>, Kozue Ando<sup>a</sup>, Yuichiro Ueno<sup>b</sup>, Stefano Bernasconi<sup>c</sup>

<sup>a</sup> Department of Transdisciplinary Science and Engineering, Institute of Science Tokyo, Tokyo, Japan

<sup>b</sup> Department of Earth and Planetary Sciences, Institute of Science Tokyo, Tokyo, Japan

<sup>c</sup> Geological Institute, ETH Zürich, Zürich, Switzerland

Carbonate clumped isotope ( $\Delta_{47}$ ) thermometry has become a powerful tool for reconstructing formation temperatures of carbonate minerals [1]. To expand the applicability of this technique to a wider range of carbonate materials, we have developed a new, low-cost, and highly versatile analytical system at the Institute of Science Tokyo. Our custom-built carbonate acid digestion and gas purification line is designed to accommodate both high-temperature reactions and micro-sample analyses. A key feature of our system is the acid-bath reactor with freely adjustable temperature settings. This capability makes the system suitable for analyzing dolomite and other carbonate phases that require elevated reaction temperatures. In addition, we incorporated a custom micro-volume device for CO<sub>2</sub> transfer into the dual-inlet IRMS, enabling clumped isotope measurements using as little as ~100 $\mu$ g of carbonate per analysis and thereby expanding  $\Delta_{47}$  analysis to micro-scale biogenic carbonates and rare or precious samples.

Carbonate samples are digested in 106% phosphoric acid, and CO<sub>2</sub> is purified through a Porapak (Q, 80-100 mesh) U-trap to remove hydrocarbon contaminants. Measurements are performed on a Thermo Scientific 253 Plus IRMS installed in 2025. For data standardization, we applied the framework of Bernasconi et al. (2021) using ETH-1, ETH-2, and ETH-3 as reference materials for the correction of  $\Delta_{47}$  values. To evaluate the analytical precision of our system, we analyzed ETH-4 as an independent check standard. Isotopic values ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$ ,  $\Delta_{48}$ ) are processed using Easotope.

In this poster, we introduce the design, performance, and operational flexibility of our analytical system. By providing an accessible and adaptable platform that supports both high-temperature and micro-sample analyses, we aim to advance temperature reconstructions from micro-scale biogenic carbonates and a wide range of carbonate lithologies, with applications spanning ecology, paleoclimatology, geology, and astronomy.

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## Dual Clumped Isotopes of Alkaline, Saline Lake Carbonates from the Cariboo Plateau and Atlin Playa, British Columbia, Canada

Ellen K. Olsen<sup>a</sup>, Hanna C. Leapaldt<sup>a</sup>, Miquela Ingalls<sup>a</sup>

<sup>a</sup> Department of Geosciences, The Pennsylvania State University, University Park, PA, USA

Carbonate minerals formed in terrestrial settings may provide insight into how continents respond to changing climate. Terrestrial carbonates capture a complementary record of Earth's dynamic climate that marine carbonates are relatively buffered against. However, interpreting isotopic data from lacustrine and wetland/palustrine environments can be complicated by metastable and mixed mineral assemblages, rapid mineralization, and wetting and drying cycles that lead to transient dissolved inorganic carbon (DIC) pools. To better understand terrestrial carbonates in the rock record, we first focus on carbonate precipitation in modern saline, alkaline lakes of the Cariboo Plateau and Atlin Playa in British Columbia, Canada. Sediments from these lakes are characterized by a range of calcium, magnesium, and sodium carbonate minerals [1,2]. The well-quantified temperature dependence of  $\Delta_{47}$  and  $\Delta_{48}$  in carbonate minerals precipitated in isotopic equilibrium [3] provides a foundation from which to explore disequilibrium dual clumped isotopes and the potential paleoenvironmental information they record.

Wetting and drying cycles that are common in saline to alkaline lakes and wetlands [1,2] may lead to a disequilibrated DIC pool, dominated by kinetic isotope effects from the rate-limiting  $\text{CO}_2$  hydration/hydroxylation and  $\text{HCO}_3^-$  dehydration/dehydroxylation reactions. When these kinetic isotope effects (KIEs) are recorded in carbonate minerals, they manifest as opposing deviations from the  $\Delta_{47}$ - $\Delta_{48}$  equilibrium line. Wetting cycles are expected to cause  $\text{CO}_2$  absorption processes and  $+\Delta_{47}/-\Delta_{48}$  KIEs, while drying cycles cause  $\text{CO}_2$  degassing processes and  $-\Delta_{47}/+\Delta_{48}$  KIEs [3]. Preliminary results of carbonates precipitating in five unique, shallow lakes record disequilibrium dual clumped isotope compositions in line with  $\text{CO}_2$  degassing processes, suggesting the sediments may dominantly reflect the drying cycles.

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# Why caring about precise notations and accurate triple oxygen isotope data?

Andreas Pack<sup>a</sup>

<sup>a</sup> Geoscience Center, University of Göttingen, Göttingen, Germany

Since the groundbreaking measurements of all three oxygen isotopes in meteorites published by the Chicago group in 1973,  $\Delta^{17}\text{O}$  has been pivotal in investigating mass-independent processes in the early Solar System and Earth's atmosphere [1]. Pioneering research around the year 2000 resolved subtle, purely mass-dependent variations in  $\Delta^{17}\text{O}$  [e.g., 2,3]. These advances have provided novel insights into hydrological processes and paleoclimatic reconstructions. Subsequently, similar small  $\Delta^{17}\text{O}$  variations were identified in rocks and minerals, opening new avenues to study water–rock interactions and enriching the toolkit available to paleo-climatologists [4]. The interplay between atmospheric gases with isotopic anomalies and mass-dependent fractionation in waters and rocks is now central to cosmo-, geo-, and atmospheric chemistry as well as the biosciences [5].

For the diverse communities involved, a precise—and ideally unified—definition of “ $^{17}\text{O}$ -excess” is paramount. I propose adopting the definition:

$$\Delta^{17}\text{O} = \ln(\delta^{17}\text{O} + 1) - 0.528 \times \ln(\delta^{18}\text{O} + 1) \quad (\text{Eqn. 1})$$

where  $\ln(\delta^{18}\text{O} + 1)$  is the linearized form of the classical  $\delta$ -notation [6]. The value 0.528 was originally derived as the slope of the line connecting SLAP and VSMOW in  $\ln(\delta^{17}\text{O} + 1)$  vs.  $\ln(\delta^{18}\text{O} + 1)$  space, which passes through the origin [7]. Early regression analyses of meteoric waters supported this slope numerically, though the line exhibits a small non-zero intercept, and neither SLAP nor VSMOW lie exactly on it [8]. Furthermore, meteoric waters are now understood to define a curve, not a straight line, in this space [9]. Thus, the popularity of the 0.528 slope is conventional, lacking direct physical meaning, but serves as a useful reference agreed upon for comparability.

Using system-specific slopes—such as 0.516 in atmospheric sciences or 0.5305 for sulfates—may hinder the comparison of tabulated and plotted data across studies. The purpose of the  $\Delta^{17}\text{O}$  notation is primarily to visualize subtle deviations from the nearly perfect correlation between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ , not to tie the reference slope to a single physical process. Employing a zero intercept ensures that VSMOW is defined as  $\Delta^{17}\text{O} = 0.000\text{‰}$ , currently the only material with adequately characterized composition at the required precision of  $\sim 0.005\text{‰}$ .

Two-point calibration strategies using both VSMOW and SLAP can improve inter-laboratory comparability, but will advance the field only if SLAP's composition is known to sufficient accuracy. Any inaccuracy in SLAP propagates into experimental determinations of the triple oxygen isotope fractionation exponent ( $\theta$ ), complicating comparison with theoretical predictions. Theory itself is always referenced to the VSMOW scale and does not know anything like a VSMOW–SLAP scale, further underscoring the need for accuracy in reference material composition.

Efforts must therefore focus on precise measurement of SLAP relative to VSMOW. While analytical advances now permit the resolution of  $\Delta^{17}\text{O}$  differences at the sub-ppm level—such as the Earth–Moon difference of  $0.002 \pm 0.008\text{‰}$  [10]—the uncertainty in SLAP ( $> 0.02\text{‰}$ ) lags behind. Agreement on nominal values for reference materials, solely for intercomparability, risks the need to later revise published datasets. True progress requires community-wide campaigns to determine the composition of SLAP at the  $0.00x\text{‰}$  level (or better), rather than accepting approximations that may prove misleading and result in inaccurate measurements that then cannot be explained by theory.

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## Assessing the Influence of Seawater pH on Clumped Isotope Thermometry ( $\Delta_{47}$ ) in Cultured Large Benthic Foraminifera

Marion Peral<sup>a,b</sup>, Julie Meilland<sup>c,d</sup>, Inigo A. Muller<sup>b</sup>, Steven Goderis<sup>b</sup>, Philippe Claeys<sup>b</sup>

<sup>a</sup> now at: Univ. Bordeaux, CNRS, Bordeaux INP, EPOC, UMR 5805, F-33600 Pessac, France

<sup>b</sup> Archaeology, Environmental Changes & Geo-Chemistry, Vrije Universiteit Brussel, Brussels, Belgium

<sup>c</sup> now at: CEREGE – Environmental Geosciences Research and Teaching Centre, French National Centre for Scientific Research, Aix-en-Provence, 13545, France

<sup>d</sup> MARUM, Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Clumped isotope thermometry ( $\Delta_{47}$ ) in foraminiferal calcite is a powerful tool for reconstructing past ocean temperatures, yet its sensitivity to secondary effects and potential disequilibrium effects remains debated, specifically in benthic foraminifera [1]. To address this, we cultured the large benthic foraminifer *Ammonia lobifera* under controlled pH conditions (7.54–8.55) and measured  $\Delta_{47}$ . The  $\Delta_{47}$  values remained slightly variable across the pH range, with a  $\sim 0.02\text{‰}$  changes.

This weak  $\Delta_{47}$ –pH relationship may support a small effect to carbonate chemistry variations in modern marine environments. Subtle  $\Delta_{47}$  variability suggests the presence of minor kinetic effects during biomineralization. These results align with emerging dual clumped isotope ( $\Delta_{47}$ – $\Delta_{48}$ ) evidence indicating that foraminiferal calcite can record detectable disequilibrium signals in large benthic foraminifera [2].

Our study highlights the value of dual clumped isotope approaches to diagnose and correct for potential kinetic biases. These findings have important implications for refining paleotemperature reconstructions, particularly in contexts where seawater pH may have deviated from modern conditions.

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## Quantification of $^{17}\text{O}$ Fractionation during Phosphoric Acid Digestion of Carbonate between 25° and 110°C

Marie Pesnin<sup>a,b\*</sup>, Fabian Zahnw<sup>a,b</sup>, Andreas Pack<sup>a</sup>, Daniel Herwartz<sup>b</sup> and David Bajnai<sup>a</sup>

<sup>a</sup> Institute for Geology, Mineralogy and Geophysics, Ruhr University Bochum, Germany

<sup>b</sup> Geoscience Center, University of Göttingen, Germany

Over the past decades, a wide range of analytical techniques has been developed to enable precise measurements of  $\Delta^{17}\text{O}$  in carbonates e.g., [1,2]. However the accuracy of this proxy remains limited by poorly constrained isotope fractionation during sample preparation steps. In particular, most approaches to determine the  $\Delta^{17}\text{O}$  of carbonate rely on phosphoric acid digestion, a process known to introduce systematic oxygen fractionation that depends on carbonates mineralogy and acid temperature. While the effect of this fractionation on carbonates  $\delta^{18}\text{O}$  values has been extensively studied, the corresponding impact on oxygen-17 remain unconstrained for many carbonate phases [1]. This unknown factor, likely contribute to interlaboratory variability [2] in measured carbonate  $\Delta^{17}\text{O}$  values, limiting cross-study comparability and raising concerns about the accuracy of reported  $\Delta^{17}\text{O}$  values, particularly when mixed-carbonate phases are involved.

To fill this gap, we characterized the  $^{17}\text{O}$  acid fraction factor (AFF,  $\theta_{(\text{CO}_2\text{-acid}/\text{CaCO}_3)}$ ) for a suite of carbonates: calcites including reference material IAEA603 and NBS18, aragonite, dolomite and witherite. We investigate the sensitivity of  $\theta$  to the acid temperature by reacting carbonates with supersaturated  $\text{H}_3\text{PO}_4$  (104%) over a temperature range of 25° to 110°C. We further investigated the effect of reaction vessel on  $\theta$  values by performing digestion using two common setups: i) sealed individual vial, ii) common acid bath. In parallel, we determined the bulk oxygen isotopic composition of carbonates, applying recently developed TORCH technique ([3], see Zahnw et al, this workshop). The TORCH approach combined high-temperature conversion elemental analysis (TC/EA) with high-voltage glow discharge to achieve quantitative oxygen extraction from  $\text{CaCO}_3$  as  $\text{CO}$  and its subsequent conversion to  $\text{CO}_2$ . Based on obtained  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values of  $\text{CO}_2$  (using TILDAS laser spectroscopy [4]) from carbonate reduction and acid digestion, we calculated  $\theta_{(\text{CO}_2\text{-acid}/\text{CaCO}_3)}$  for each acid reaction temperature.

Our results indicate that empirical  $\theta_{(\text{CO}_2\text{-acid}/\text{CaCO}_3)}$  closely match theoretical values [5]. They further confirm that  $^{17}\text{O}$  AFF is only slightly sensitive to acid temperature, decreasing with increasing temperature. Importantly, our results, suggest that methodological biases associated with acid treatment of carbonates may strongly affect reported  $\Delta^{17}\text{O}$  values of carbonate and explain part of the persistent interlaboratory discrepancies [2].

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# Combining Triple-oxygen and Clumped isotopes analyses of carbonate sedimentary successions to shade light on diagenetic processes

Vittoria Pinto<sup>a</sup>, Luca Aldega<sup>a</sup>, Eugenio Carminati<sup>a</sup>, Luigi Dallai<sup>a</sup>

<sup>a</sup> Department of Earth Sciences, “Sapienza” University of Rome, Rome, Italy

Sedimentary successions that were buried and later uplifted represent a suitable natural setting for testing carbonate clumped isotopes' thermometry with respect to bond reordering [1]. Due to the prolonged exposition of the carbonate at high temperatures, its original clumped isotopes signature can be reset, and the measured  $\Delta_{47}$  value would be translated into an “apparent” temperature, intermediate between the original and the maximum achieved [2]. For this case study, a sedimentary succession in the Appennines (Central Italy), covering the period from the Upper Jurassic to the Upper Cretaceous. The succession is made of limestones and dolostones interlayered with marls levels. We performed  $\Delta_{47}$  measurements along with triple-oxygen analyses and clay mineralogy (XRD analyses of the  $<2\mu$  fraction of Illite-Smectite mixed layers, to derive R-indexes). Clay mineralogy has been used as an independent temperature proxy, to compare the Maximum Burial Temperature (MBT) with the clumped isotopes signal. Triple-oxygen analyses, on the other hand, were useful to evaluate differences in the temperature registered by diagenetically altered samples [3]. Based on the R-indexes from marls levels, the deeper strata seem to have reached temperatures higher than 100°C. The samples analyzed for triple-oxygen display disequilibrium  $\Delta^{17}\text{O} - \delta^{18}\text{O}$  values, pointing to diagenetic alteration due to burial. Clumped isotopes values yield an increasing temperature trend through the strata, within the range of 2–13°C (calibration of [4]), in general agreement with the geothermal gradient. Our results overall suggest that the MBT was not high enough – or the exposition time was not long enough – to reset the original clumped isotopes compositions. It seems more likely that the carbonates either preserved their original signature or were recrystallized at low, ambient temperatures, reflecting the isotopic signature of infiltrating meteoric water. This case study may be useful to evaluate the applicability of the clumped isotopes thermometer to other similar geological contexts.

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# Assessing vital effects and paleoclimate reconstructions in turrnellid gastropods with clumped isotopes ( $\Delta_{47}$ )

Alex A. Quizon<sup>a</sup>, Sierra V. Petersen<sup>a</sup>, Serena R. Scholz<sup>b</sup>

<sup>a</sup> Department of Earth & Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA

<sup>b</sup> Department of Earth & Planetary Sciences, Yale University, New Haven, CT 06511, USA

Turrnellids are widespread in the fossil record of the past ~130 million years and are frequently used for paleoenvironmental reconstruction through stable isotope analysis (e.g.,  $\delta^{18}\text{O}$  sclerochronology) [1,2]. The ability of clumped isotope thermometry ( $\Delta_{47}$ ) to avoid some of the limitations of traditional  $\delta^{18}\text{O}$  paleothermometry makes its application a natural next step in using turrnellids for paleoclimate research. However, preliminary  $\Delta_{47}$  measurements from modern turrnellids suggested that they may precipitate their shells out of isotopic equilibrium (i.e., exhibit vital effects – or “biologically driven isotopic fractionations” [3]), resulting in a cold bias in reconstructed temperatures [4]. In this study, we expand on this work through  $\Delta_{47}$  measurements of two more modern and seven Mid-Miocene turrnellids collected from the Guajira Peninsula of Colombia.

We find that the new modern turrnellid data support the previous finding of a ~6°C cold bias in  $\Delta_{47}$ -temperatures. Mid-Miocene  $\Delta_{47}$ -temperatures are 19–27°C, which is much colder than modern. When adjusted to account for the ~6°C bias seen in modern shells, mid-Miocene temperatures fall between ~25–33°C and become consistent with other regional proxy estimates that suggest mild Mid-Miocene warming relative to modern conditions. Temperatures appear to have briefly decreased between ~16.5 and ~15 Ma, possibly indicative of a local upwelling pulse amidst peak warmth during the Mid-Miocene Climatic Optimum (MMCO).

Subannual sampling indicates that temperature seasonality was reduced (as expected at the tropics) while the amplitude of  $\Delta_{47}$ -derived  $\delta^{18}\text{O}_w$  seasonality was ~1–2‰, which is consistent with previously proposed enhanced seasonality of precipitation relative to modern during the MMCO [5]. In conclusion, it is still possible to use turrnellids for preliminary paleoenvironmental reconstructions, although more work should be done to further explore vital effects and refine precipitation mechanisms in turrnellids (i.e., obtain more  $\Delta_{47}/\Delta_{48}$  measurements, increase number of species/localities).

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## Exploring Long-term Oligocene to mid Miocene Temperature Change in the Tasmanian Sea: How do Clumped Isotopes in Coccoliths Compare?

Addison Rice<sup>a</sup>, Stefano M. Bernasconi<sup>a</sup>, Madalina Jaggi<sup>a</sup>, and Heather M. Stoll<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zürich, Zürich, Switzerland

Coccoliths are calcitic nanoliths made by certain marine photosynthesizing haptophyte algae, and are highly abundant in carbonate-rich marine sediments. Their formation in the surface ocean and the large quantities available make them an ideal target for clumped isotope ( $\Delta_{47}$ ) analysis for marine paleothermometry. We measured clumped isotopes in coccolith-rich size fractions (i.e., 5–8  $\mu\text{m}$ ) in Oligocene–Miocene sediments at ODP Site 1168 in the Tasmanian Sea. The resulting temperatures were compared to previously published results from biomarker-based proxies from the same site [1,2].

Proxy temperatures significantly differ, with  $\Delta_{47}$  values generally 8–10 °C cooler than biomarker-based sea surface or 0–200 m temperature estimates. This discrepancy cannot be explained by applying a seasonal or depth bias based on the modern range of photic zone temperatures.

We further examined long-term temperature changes by binning data in three multi-million-year bins: Late Oligocene (LO; 27–25 Ma), Oligocene–Miocene Transition (OMT; 24–22 Ma), and early–mid Miocene (pre-MCO; 20–16 Ma). Estimates of temperature change between each bin differs per proxy (Fig. 1). For example, from the OMT to pre-MCO, the alkenone-based  $U_{37}^{K'}$  proxy indicates  $\sim 2$  °C of cooling, whereas  $\Delta_{47}$  values indicate  $\sim 3$  °C of warming. Changes in ecological mixing effects or physiological effects of, for example, nutrient availability, and the impact of the calibration basis (i.e., growth temperature in culture vs. empirical calibration using surface sediments) will be explored as a possible explanation of these discrepancies.

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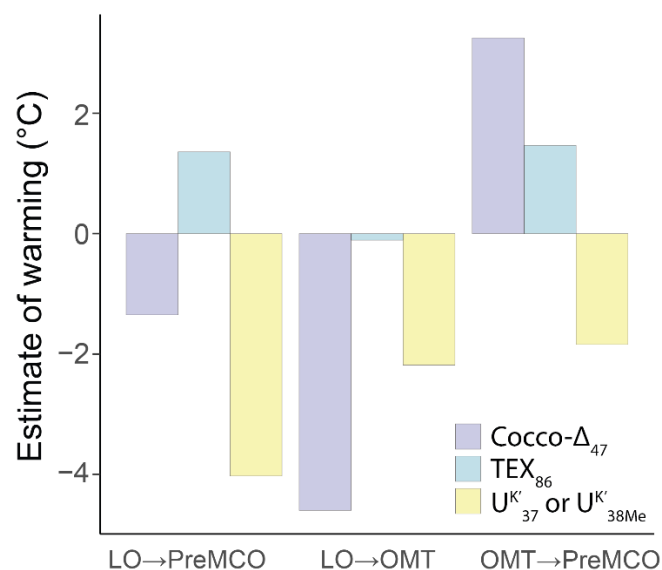


Figure 1: Estimate of the degree of warming between LO, OMT, and pre-MCO time periods at Site 1168 from three paleothermometers: cocco-  $\Delta_{47}$  (calibrated to growth temperature), TEX<sub>86</sub> (calibrated to depth-integrated 0–200 m temperatures), and U<sub>37</sub><sup>K'</sup> (calibrated to sea surface temperature).



## Climate Chamber Calibration of Earthworm Biospheroids for Quantitative Paleothermometry

Andrea Czébély<sup>a,b,c</sup>, Gábor Újvári<sup>d,e</sup>, Diána Kiss<sup>a</sup>, Marianna Túri<sup>a</sup>, László Rinyu<sup>a</sup>

<sup>a</sup> Isotope Climatology and Environmental Research Centre (ICER), HUN-REN Institute for Nuclear Research (ATOMKI), Debrecen, Hungary

<sup>b</sup> Doctoral School of Earth Sciences, University of Debrecen, Debrecen, Hungary

<sup>c</sup> Department Isotoptech Zrt., Debrecen, Hungary

<sup>d</sup> Institute for Geological and Geochemical Research, HUN-REN Research Centre for Astronomy and Earth Sciences, Budapest, Hungary

<sup>e</sup> CSFK, MTA Centre of Excellence, Budapest, Hungary

Quantitative reconstructions of continental climate change frequently rely on isotopic analyses of secondary carbonates preserved in loess–paleosol sequences. Among the various biogenic carbonates examined, earthworm-secreted biospheroids (EBS) have recently gained attention as potential a paleo–environmental proxy. The stable oxygen and carbon isotope compositions of EBS [1,2], as well as their applicability in establishing radiocarbon-based age–depth models [3,4], have been increasingly explored. However, the suitability of EBS for clumped isotope thermometry remains uncertain.

To address this question, we initiated long-term, controlled climate chamber experiments in 2023 under tightly regulated environmental conditions. Earthworms (*Aporectodea caliginosa*, *Aporectodea rosea*, *Octodrilus transpadanus*, *Allolobophora leoni* and *Lumbricus rubellus*) were reared at seven fixed temperatures (8, 11, 13, 15, 18, 20, and 22°C), while additional environmental parameters, including soil moisture, atmospheric CO<sub>2</sub> concentration, and the stable isotope compositions of both diet and spray solution were strictly regulated. This study is aimed to understand whether EBS formation is influenced by vital effects and to quantify the extent to which their isotopic signatures deviate from temperature-dependent equilibrium precipitation.

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## Clumped isotope constraints on the origin of methane hydrate from the Amazon Cone

Luiz Frederico Rodrigues<sup>a,b,c</sup>, Alexis Gilbert<sup>c</sup>, Malavika Sivan<sup>c</sup>, Adolpho Augustin<sup>b</sup>, Mayuko Nakagawa<sup>d</sup>, Satoko Owari<sup>e</sup>, Thomas Röckmann<sup>c</sup>, João M. Ketzer<sup>f</sup>, José A. Cupertino<sup>b</sup>, Daniel Praeg<sup>g</sup>, Cleverton G. Silva<sup>h</sup>, Sébastien Migeon<sup>g</sup>, Dennis Miller<sup>i</sup>, Boniek Vaz<sup>a</sup>, Farid C. Junior<sup>b</sup>

<sup>a</sup> Federal University of Goiás, Goiás, Brazil

<sup>b</sup> University of the Sinos River Valley, Porto Alegre, Brazil

<sup>c</sup> Institute of Marine and Atmospheric Research Utrecht, Utrecht University, Utrecht, Netherlands

<sup>d</sup> Earth and Planetary Science Department, Institute of Science Tokyo, Tokyo, Japan

<sup>e</sup> Tokyo University of Marine Science and Technology, Tokyo, Japan

<sup>f</sup> Faculty of Health and Life Sciences, Linnaeus University, Kalmar, Sweden

<sup>g</sup> Géoazur, Nice, France

<sup>h</sup> Universidade Federal Fluminense, Niterói, Brazil

<sup>i</sup> Leopoldo Américo Miguez de Mello Research, Development and Innovation Center, Rio de Janeiro, Brazil

The studies of deep-sea gas venting associated with occurrences of gas hydrates in the Amazon Cone has increased the interest of the world scientific community in understanding the role of the Amazon region in the Earth's climate system [1] Gas plumes have been observed in several areas, suggesting the climate-driven dissociation of gas hydrates [2,3]. Here, we present data from gas hydrates that were sampled during the AMARYLLIS, AMAGAS campaign offshore Brazil in May–June 2023. Results of the methane stable isotopes ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of hydrate-bound for the Amazon fan indicated the dominant microbial origin ( $\delta^{13}\text{C}$  and  $\delta\text{D}$  of  $-90\%$  to  $-70\%$  V-PDB and  $-250$  to  $-150\%$  V-SMOW). Regarding clumped isotopes,  $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$  values from  $+5.5\text{‰}$  and  $+16.6\text{‰}$ , respectively. The hydrate samples are located around the thermodynamic equilibrium line in the  $\Delta^{13}\text{CH}_3\text{D}$  vs.  $\Delta^{12}\text{CH}_2\text{D}_2$  space, and their isotopic compositions correspond to apparent temperatures of  $30_{-13}^{+15}$  and  $43_{-10}^{+13}$  °C for  $\Delta^{13}\text{CH}_3\text{D}$  and for  $\Delta^{12}\text{CH}_2\text{D}_2$ , respectively. Given the geothermal gradient in the area, this temperature corresponds to a depth of about 1400 meters suggesting methane is migrating upwards with deeper fluids. These observations concur with seismic evidence of signal wipe-outs consistent with the rise of gas-bearing fluids along the faults.

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# Simulating Solid State Isotope Reordering of C–O Bonds in the Framework of Trigonal Carbonate Mineral: A Probabilistic Approach

Uri Ryb<sup>a</sup>, Helen Eisenberg<sup>b</sup>, Roi Baer<sup>b</sup>

<sup>a</sup> Institute of Earth Sciences, The Hebrew University of Jerusalem, Jerusalem, Israel

<sup>b</sup> Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Solid-state isotopic reordering of C–O bonds has been shown to alter the clumped isotope values of carbonate minerals subjected to elevated temperatures in both controlled heating experiments and geological settings. Understanding the kinetics of this process is imperative for reconstructing both the initial formation temperatures and the thermal histories experienced by carbonate mineral samples. Previous studies have considered increasingly complex mechanisms and reaction networks to explain the non-first-order reaction progress trends revealed by laboratory and natural experiments [e.g., 1–3]. Recent observations and models associate such deviations from first-order kinetics with differences in the activation energy required for isotope exchange along specific vectors connecting oxygen sites within the crystal lattice [3, 4]. The underlying atomistic mechanisms and activation energies of some of these vectors have recently been investigated using computationally expensive constrained ab initio molecular dynamics and density functional theory (cAIMD+DFT) models [5].

Here, we develop a computationally efficient probabilistic model that tracks the reaction progress of clumped isotope values through isotope exchange reactions among oxygen sites within the framework of trigonal carbonate minerals. When informed by vector-specific activation energies derived from cAIMD+DFT simulations for a defect-free lattice, our model fails to predict the reaction progress trends observed in controlled heating experiments. Fitting these data requires that lower activation energies persist between a limited number of oxygen sites within the crystal lattice. Such a scenario may be enabled by lattice defects. Our model bridges the gap between atomistic- and mineral-scale kinetics of solid-state reordering and can serve as a platform for predicting the effects of mineral cation composition, lattice impurities, cation ordering, and deformation on observed clumped isotope compositions.

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## Atlantic upper-ocean temperature reconstructions from coccolith and foraminiferal clumped isotopes ( $\Delta_{47}$ ) across the Late Miocene

Madeleine Santos<sup>a</sup>, Madalina Jäggi<sup>a</sup>, Stefano Bernasconi<sup>a</sup>, Heather Stoll<sup>a</sup>

<sup>a</sup> Department of Earth and Planetary Sciences, ETH Zurich, Zurich, Switzerland

Reconstructing ocean temperature evolution and carbon cycling across the Late Miocene is critical for understanding the mechanisms driving long-term global cooling. Here, we present new coccolith clumped isotope ( $\Delta_{47}$ ) temperature reconstructions from ODP Site 1088 (South Atlantic), spanning the Late Miocene cooling interval (~8.5 to 5.5 Ma). These data provide absolute temperature estimates from coccolith calcite and allow direct comparison with alkenone-derived sea surface temperatures ( $U^{k'}_{37}$ ), which are calibrated to surface ocean conditions and produced by the same haptophyte organisms.

$\Delta_{47}$ -derived temperatures range from ~5 to 17°C and exhibit a clear cooling trend, in broad agreement with  $U^{k'}_{37}$  SSTs. However,  $U^{k'}_{37}$  temperatures are consistently ~4–10°C warmer, likely reflecting their calibration to near-surface conditions, whereas coccolith  $\Delta_{47}$  temperatures may record calcification deeper in the photic zone and/or the influence of secondary calcite infilling. Both proxies indicate substantial cooling of ~10°C between ~8.5 and 5.5 Ma.

In parallel, coccolith-based PIC/POC ratios decrease across the same interval, suggesting reduced calcification relative to organic carbon production and potential changes in coccolithophore physiology under evolving temperature and CO<sub>2</sub> conditions. Building on these new temperature constraints, we will recalculate previously published  $\epsilon_p$  estimates across the Late Miocene cooling interval using coccolith  $\Delta_{47}$ -derived temperatures, providing improved constraints on carbon isotope fractionation and atmospheric CO<sub>2</sub>.

Finally, comparison of coccolith and foraminiferal  $\Delta_{47}$  temperatures provides a direct constraint on upper-ocean thermal structure. The temperature offset between these datasets reflects vertical gradients within the upper water column, with larger offsets indicating a steeper thermocline and stronger stratification, and smaller offsets implying a shallower, more weakly stratified system. Tracking the evolution of this gradient across the Late Miocene cooling interval allows us to test whether upper-ocean stratification weakened along with declining temperatures and CO<sub>2</sub>.



## Mass-dependent diffusion in corals is resolvable with triple-oxygen isotopes, but further constraint is needed

Philip Staudigel<sup>a</sup>, David Bajnai<sup>b</sup>, Daniel Herwartz<sup>c</sup>, Jens Fiebig<sup>a</sup>

<sup>a</sup> Institute of Geosciences, Goethe-University Frankfurt, Germany

<sup>b</sup> University of Göttingen, Germany

<sup>c</sup> Institute of Geosciences, Ruhr University Bochum, Germany

<sup>a</sup> Institute of Geosciences, Goethe-University Frankfurt, Germany

Models for coral calcification are, by necessity, limited by the number of geochemical and isotopic parameters that can be measured and simulated. Thus, when kinetic factors such as CO<sub>2</sub> diffusion, hydration, hydroxylation, pH variation, carbonic anhydrase concentration, mineral precipitation rate, and more are considered variables, then it is necessary to either experimentally constrain or have a chemical or isotopic proxy for each one. To this end, we have constructed a numerical model for coral calcification that includes  $\delta^{13}\text{C}$ ,  $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$ ,  $s\Delta_{48}$ , as well as boron chemistry. With this model, we find that several factors directly influence the  $\Delta^{17}\text{O}$  of precipitating carbonate, of particular interest are kinetic factors associated with CO<sub>2</sub> diffusion and bicarbonate incorporation into the carbonate crystal lattice (the B2 reaction from Watkins et al., 2025). Although this second reaction could be constrained experimentally, no such data have ever been published; however, we find that no single value for the relationship between <sup>17</sup>O and <sup>18</sup>O kinetics fully describes the variance in coral  $\Delta^{17}\text{O}$  values [1]. Conversely, we find that some mass-dependent isotope fractionation of CO<sub>2</sub> during diffusion across the calicoblastic cell membrane is sufficient to describe the measured  $\Delta^{17}\text{O}$  values of corals. This is important, because earlier modeling efforts for  $\Delta_{47}$  and  $\Delta_{48}$  values assumed no such fractionation [2], although earlier models for carbon and oxygen isotopes in corals did include such fractionation [3], we conclude that these parameters should be re-evaluated when experimental results for  $\Delta^{17}\text{O}$  kinetics during mineral formation are available.

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## Submarine Groundwater Discharge into the Plio-Pleistocene Florida Platform Suggested by Clumped Isotope Sclerochronology

Zeyang Sun<sup>a</sup>, Ethan L. Grossman<sup>a</sup>

<sup>a</sup> Department of Geology and Geophysics, Texas A&M University, 77843 TX, United States

The great diversity and density of marine molluscan fauna on the Florida Platform suggest a high marine biological productivity. However, it remains unclear whether this enhanced productivity was driven by upwelling or submarine groundwater discharge (SGD). Here, we applied clumped isotope thermometry ( $\Delta_{47}$ ) to *Conus* shells from two contrasting units of the Plio-Pleistocene Pinecrest Beds to reconstruct the seasonal temperatures ( $T\Delta_{47}$ ) and oxygen isotopes of seawater ( $\delta^{18}O_w$ ). The shells from Unit 7 (2.5 to 3.5 Ma), which contain a typical marine faunal assemblage, show temperatures ranging from 13 to 27°C. The shells from Unit 4 (2.0 to 2.5 Ma), with their combination of marine and freshwater shells, show weaker seasonality with  $T\Delta_{47}$  between 17°C and 24°C. Reconstructed  $\delta^{18}O_w$  values for Unit 7 vary from -1.3 to 1.1‰ (VSMOW) with a mean of 0.12‰ and correlate negatively with temperatures. In contrast,  $\delta^{18}O_w$  values for Unit 4 are unusually high (-0.2 to 3.0‰ with a mean of 1.6‰). Comparison of our data with the seasonal patterns of temperature and seawater  $\delta^{18}O$  for the modern Florida Bay indicates that Unit 7 was deposited in an offshore marine environment whereas Unit 4 was deposited in a brackish-estuarine environment. The high  $\delta^{18}O_w$  values correlating with summer temperatures point to the input of evaporative freshwater, rather than upwelling, into the Florida Platform through SGD during the summer rainy period. Further study of the clumped isotope sclerochronology of additional gastropod shells from Unit 7, Unit 4, and the Florida Bay will help to understand the influence of SGD on the high productivity of the Plio-Pleistocene Florida Platform.



## Investigation of Dual Clumped Isotope Fractionation Using Farmed Calcite precipitated on Curved Glass Plates

Peter K. Swart<sup>a</sup>, Sevag Mehterian<sup>a</sup>, Monica Arienzo<sup>a,b</sup>, Chaojin Lu<sup>a,c</sup>

<sup>a</sup> Department of Marine Geosciences, RSMAES, University of Miami, Miami Fl 33145

<sup>b</sup> Desert Research Institute, Division of Hydrologic Sciences. Reno NV

<sup>c</sup> School of Geosciences, China University of Petroleum, Qingdao, China, 266580

Although speleothems are widely used for paleoclimate research, they are known to frequently form in isotopic disequilibrium, not only with respect their  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values [1], but also  $\Delta_{47}$  and  $\Delta_{48}$  [2,3]. To investigate disequilibrium in all these proxies, we ‘farmed’ calcite in a cave in the Bahamas [4] using curve glass plates designed to mimic the precipitation behavior of the stalagmite as a saturated water drop impacted the plate, near the center, and then continued to form calcite as the water moved towards the edges of the plate (Figure 1). Using these plates the water pathway had a define movement from the impact site towards the edge and therefore the evolution of the  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta_{47}$  and  $\Delta_{48}$ , could be clearly traced. In total 10 plates were deployed for 5 to 6-month intervals over 3 years. During this time the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of water and dissolved inorganic carbon and rate of precipitation were measured [4]. While there were some varying trends between plates and in different portions of cave that may be related to rates of calcite precipitation, the most common pattern was that the central region showed  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values that were the closest to expected equilibrium values, with both values becoming increasing more positive towards the margins. In some of the plates changes in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values were at large as 3–4‰. Such variation was unrelated to temperature and the isotopic composition of the water, and questions the validity of examining lateral variation in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values as an indicator of equilibrium [1]. Although the  $\Delta_{47}$  and  $\Delta_{48}$  values were never close to equilibrium, values approached expected values in the central region. Different models of formation will be discussed.

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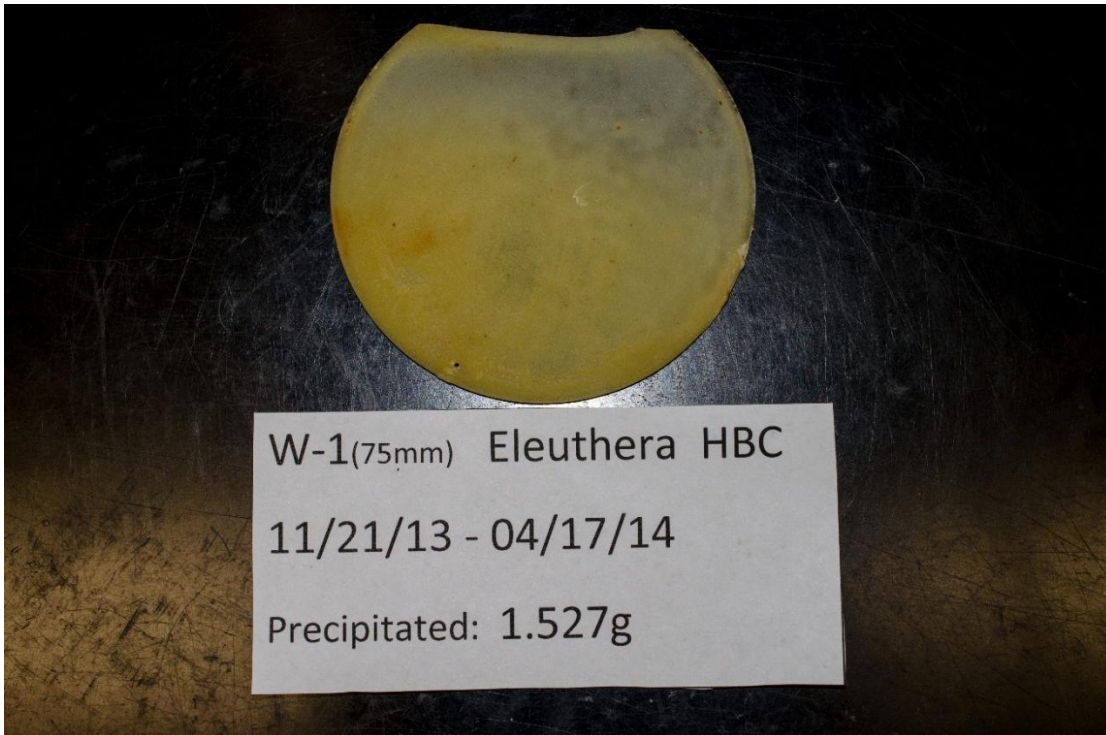


Figure 1: Example of precipitation that occurred on a curved plate in the West room of Hatchett Bay Cave, Bahamas [4]. The amount of precipitated calcite was calculated using the change in weight during the deployment. Up to 30~  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values could be measured from the center to the margin and about 10  $\Delta_{47}$  and  $\Delta_{48}$  values.



## Revisiting the Clumped Isotope to Temperature Calibration for Foraminifera

Victoria E. Taylor<sup>a</sup>, Alison M. Piasecki<sup>b</sup>, Stijn De Schepper<sup>a</sup>, Juliane Müller<sup>c</sup>, Sandrine Le Houedec<sup>d</sup>, Maja Schneider<sup>e</sup>, Ralf Schiebel<sup>e</sup>, A. Nele Meckler<sup>a</sup>

<sup>a</sup> Department of Earth Sciences and Bjerknes Centre for Climate Research, Bergen, Norway

<sup>b</sup> US Geological Survey, Denver, Colorado, USA

<sup>c</sup> Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

<sup>d</sup> Laboratoire de Géologie de Lyon, Lyon, France

<sup>e</sup> Max Planck Institute for Chemistry, Mainz, Germany

Emerging offsets between clumped isotope thermometry and more classical temperature proxies have placed a renewed focus on clumped isotope to temperature calibrations for foraminifera. A large part of the persistent uncertainty derives from the challenge of determining accurate calcification temperatures for core-top samples, which is particularly challenging for planktic foraminifera. Due to uncertainties related to the water depth and season of calcification, most calibrations rely on foraminifera  $\delta^{18}\text{O}$  to constrain apparent calcification temperatures, with additional uncertainty arising from defining the fractionation factor between oxygen-18 as well as species-specific vital effects.

Offsets between available clumped isotope calibrations are most acute at the cold end of the ocean temperature range where some calibrations appear to yield unrealistically cold ocean temperatures when applied to foraminifera. Recent work has furthermore proposed systematic offsets between planktic and benthic foraminifera, which are typically combined in foraminifera-based calibrations, calling for further investigations.

Here we seek to revisit the foraminiferal-specific clumped isotope to temperature calibration by (i) increasing foraminiferal constraints at the cold end of the ocean temperature range, (ii) supplementing existing calibration data with additional data which are independent of  $\delta^{18}\text{O}$ -informed apparent calcification temperatures, and (iii) testing for offsets between planktic and benthic foraminifera. For the latter, we analyse paired planktic and benthic foraminifera from core-tops along the Antarctic shelf in the Weddell Sea, where the water column is weakly stratified such that planktic and benthic foraminifera should calcify at the same temperature.



## Testing for Species-Specific Offsets in Benthic Foraminiferal Clumped Isotopes

Victoria E. Taylor<sup>a</sup>, Heidi Bernhoft von Obstfelder<sup>b</sup>, A. Nele Meckler<sup>a</sup>

<sup>a</sup> Department of Earth Sciences and Bjerknes Centre for Climate Research, University of Bergen, Bergen, Norway

<sup>b</sup> Department of Earth Sciences, University of Bergen, Bergen, Norway

Our understanding of past climates relies heavily on geochemical proxy records measured on the fossilized remains of deep-sea dwelling benthic foraminifera. Many of these geochemical proxies, including  $\delta^{18}\text{O}$  and Mg/Ca, exhibit species-specific offsets in benthic foraminifera. These offsets, collectively known as ‘vital effects’, arise from physiological, kinetic, and environmental factors, resulting in species-specific deviations between test chemistry and seawater equilibrium. For accurate palaeoclimate reconstructions, corrections and/or species-specific calibrations are typically required to account for benthic foraminiferal species-specific offsets.

For clumped isotope thermometry, no discernable species-specific offsets have so far been detected in benthic foraminiferal core-top calibration datasets [1]. The absence of such effects greatly increases the feasibility of obtaining high-precision and/or high-resolution clumped isotope records from sediment cores where benthic foraminiferal abundance is limited, as it allows for the combining of multiple different species for the measurements. However, clear evidence for the validity of this approach beyond the initial calibration efforts is lacking.

To further validate this assertion, here we present a series of multiple well-replicated monospecific benthic foraminiferal clumped isotope temperatures from the same samples. We obtained these parallel data from both core-top samples and geological samples from multiple time intervals throughout the Cenozoic, spanning a variety of environmental conditions, sediment lithologies, and burial depths. By working in the geological record and at different locations, we can test whether any inter-species offsets are site- or time-specific and cross-check extinct genera and species against extant species which are constrained by core-top calibrations.

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## Modern, Low-Temperature Dolomite from the Coorong Region, South Australia

Julia Wilcots<sup>a,b</sup>, Adam C. Maloof<sup>a</sup>, Kristin D. Bergmann<sup>c</sup>

<sup>a</sup> Department of Geosciences, Princeton University, Princeton, NJ, USA

<sup>b</sup> Department of Earth and Environmental Sciences, University of Minnesota, Minneapolis, MN, USA

<sup>c</sup> Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA, USA

The lakes of the Coorong region, South Australia precipitate large volumes of primary dolomite and magnesite sediments, unlike virtually every other marine-fed system in the world. For the past six decades, researchers have used the Coorong as a natural laboratory in which to study dolomite formation, asking what drives Mg-carbonate precipitation in this system, and whether we can use the Coorong as an analogue for the abundant dolomites in the rock record. Multiple hypotheses, primarily based on oxygen isotopic evidence, have been proposed to explain the precipitation of Mg-carbonates in this system: perhaps sulfate-reducing bacteria mediate dolomite precipitation during the hottest times of the year; or dolomite precipitates quickly from hot, evaporatively-enriched brines; or dolomite precipitates abiotically and slowly from more “normal” waters. Each of these mechanisms should leave a different isotopic fingerprint on the resulting precipitates; carbonate clumped isotopes ( $\Delta_{47}$ ) are uniquely poised to simultaneously constrain precipitation temperatures, oxygen isotopic composition of precipitating waters, and, with the addition of dual-clumped ( $\Delta_{48}$ ), whether any microbial metabolisms are involved. In our initial study of surficial and sub-surface dolomite muds from Pellet Lake, we report  $\Delta_{47}$  mineral formation temperatures of 14 to 25( $\pm 4$ )°C and calculate  $\delta^{18}\text{O}_w$  of 1.5 to 4.1‰, both representative of “normal” conditions in the Coorong region. Our results suggest that, here, dolomite precipitates at low temperatures and faithfully records environmental parameters. This finding may have bearing on how we interpret both the presence and geochemistry of ancient dolomites — perhaps dolomite does not require a unique set of hypersaline, highly evaporitic, anoxic, hot, or diagenetic conditions to form.



## Unified Automated Triple Oxygen and Hydrogen Isotope Analysis of Water, Organics, and Non-Silicates on the VSMOW-SLAP Scale

Fabian Zahn<sup>a,b</sup>, Lars L. Alfke<sup>b</sup>, Marie Pesnin<sup>a,b</sup>, Kathrin Listl<sup>c</sup>, Andreas Pack<sup>b</sup> and Daniel Herwartz<sup>a</sup>

<sup>a</sup> Institute of Geosciences, Ruhr University Bochum, Germany

<sup>b</sup> Geoscience Center, University of Göttingen, Germany

<sup>c</sup> Department of Geography, McGill University, Canada

Triple oxygen isotope measurements ( $\Delta^{17}\text{O}$ ) for silicates and oxides are routinely achieved by laser fluorination. Novel analytical approaches for other solid or liquid materials (e.g., sulfates, phosphates, carbonates, organics, and water) have only recently achieved ~10 per meg analytical reproducibility [1–5]. However, unified workflows that accommodate all of these diverse matrices are required to accurately report all data on VSMOW-SLAP scale. Respective studies remain scarce [3,5].

Here we present an advancement of the fully automated high-temperature conversion elemental analyzer (TC/EA) sample oxygen to CO reduction, CO to CO<sub>2</sub> high-voltage glow-discharge conversion, CO<sub>2</sub> laser spectroscopy (TILDAS) triple oxygen isotope workflow (called “TORCH”) recently developed at the University of Göttingen [5]. The TC/EA approach enables consistent treatment of diverse materials, including encapsulated waters, and supports robust scaling [3,5]. Using this workflow, analytical reproducibility of 14 per meg in  $\Delta^{17}\text{O}$  and 0.3‰ in  $\delta^{18}\text{O}$  has been demonstrated for sulfates, water, and organics [5] and is presently explored for carbonates (see Pesnin et al., this meeting) and phosphates.

Building on the same TC/EA run, we additionally collected the chromatographically separated H<sub>2</sub> peak from hydrogen-bearing samples on a liquid-nitrogen-cooled activated-charcoal trap. We measured  $\delta^2\text{H}$  by dual-inlet IRMS against bottled H<sub>2</sub> reference gas calibrated using VSMOW2 and SLAP2 water capsules. Tests on multiple waters and organic materials, including wood  $\alpha$ -cellulose, yielded  $\delta^2\text{H}$  reproducibility of 0.5‰ for water and 2‰ for  $\alpha$ -cellulose. Combined, automated  $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ - $\delta^2\text{H}$  measurements provide a powerful new toolbox for (paleo-)environmental applications involving subtle  $\Delta^{17}\text{O}$  variations.

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## Towards improved inter-laboratory compatibility of clumped-isotope measurements for low- $\delta D$ biogenic methane

Naizhong Zhang<sup>a</sup>, Stefano Bernasconi<sup>b</sup>, Bibhasvata Dasgupta<sup>c</sup>, John M. Eiler<sup>d</sup>, Lukas Emmenegger<sup>a</sup>, Alexis Gilbert<sup>c</sup>, Laetitia Guibourdenche<sup>e</sup>, Wenmin Jiang<sup>f</sup>, Yun Li<sup>f</sup>, Jan Meissner<sup>a,b</sup>, Shuhei Ono<sup>g</sup>, Zhiyong Pang<sup>h</sup>, Yuichiro Ueno<sup>i</sup>, Xinchu Wang<sup>h</sup>, Edward D. Young<sup>e</sup>, Joachim Mohn<sup>a</sup>

<sup>a</sup> Laboratory for Air Pollution / Environmental Technology, Empa, Dübendorf, Switzerland

<sup>b</sup> Department of Earth and Planetary Sciences, ETH Zürich, Zürich, Switzerland

<sup>c</sup> Institute for Marine and Atmospheric research Utrecht, Utrecht University, Utrecht, the Netherlands

<sup>d</sup> Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

<sup>e</sup> Department of Earth, Planetary, and Space Sciences, UCLA, Los Angeles, CA, USA

<sup>f</sup> Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

<sup>g</sup> Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA, USA

<sup>h</sup> School of Earth System Science, Tianjin University, Tianjin, China

<sup>i</sup> Department of Earth and Planetary Sciences, Institute of Science Tokyo, Tokyo, Japan

Methane clumped isotopes ( $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$ ) provide key constraints for distinguishing methane formation pathways and post-genetic processes. Their growing application has attracted an increasing number of laboratories, raising the need for improved compatibility across laboratories and analytical techniques, including high-resolution isotope ratio mass spectrometry (HR-IRMS; e.g., Ultra 253 and Panorama) and laser spectroscopy (QCLAS). To date, most community-wide comparisons have focused on thermogenic-like methane with moderate bulk isotopic compositions ( $\delta D > -200\text{‰}$ ), for which generally acceptable agreement has been reported [1–3]. In contrast, biogenic methane with very low  $\delta D$  values (e.g.,  $< -300\text{‰}$ ), typical of microbial production, poses greater analytical challenges because of the lower abundances of clumped isotopologues, particularly  $^{12}\text{CH}_2\text{D}_2$ . However, the compatibility of methane clumped-isotope measurements for such low- $\delta D$  biogenic samples has not yet been systematically benchmarked across laboratories and techniques.

To assess inter-laboratory consistency for low- $\delta D$  methane, we distributed a biogenic methane sample ( $\delta D = -330\text{‰}$ ,  $\delta^{13}\text{C} = -57\text{‰}$ ;  $\text{CH}_4 > 97\%$ ) from a biogas plant in Switzerland to nine laboratories worldwide. Preliminary results show a much broader spread than expected from nominal analytical uncertainties, with offsets exceeding  $\sim 3\text{‰}$  for  $\Delta^{13}\text{CH}_3\text{D}$  and  $\sim 20\text{‰}$  for  $\Delta^{12}\text{CH}_2\text{D}_2$ , compared with typical uncertainties of  $\sim 0.3\text{‰}$  and  $\sim 1.5\text{‰}$ , respectively. This spread is observed not only across different analytical platforms, but also among laboratories using similar instrumentation.

At the workshop, we will discuss possible causes of these discrepancies and present example strategies for addressing them in both HR-IRMS and QCLAS measurements. Building on this initial dataset, we suggest a more formalized community intercomparison focused on low- $\delta D$  biogenic methane. Such an effort would help diagnose technique- and protocol-dependent biases, improve calibration strategies, and establish a more robust analytical framework for interpreting microbial methane clumped-isotope signatures.

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## Dual Clumped Isotope Signature in Impactites: The Houghton Case Study

Xianye Zhao<sup>a</sup>, Inigo A. Müller<sup>a</sup>, Swagata Chaudhuri<sup>a</sup>, Gordon R. Osinski<sup>b</sup>, Philippe Claeys<sup>a, c</sup>

<sup>a</sup> Archaeology, Environmental Changes and Geo-Chemistry (AMGC), Vrije Universiteit Brussel, 1050 Brussels, Belgium

<sup>b</sup> Department of Earth Sciences, University of Western Ontario, 1151 Richmond Street, London, Ontario N6A 5B7, Canada

<sup>c</sup> Pacific Center for Isotopic & Geochemical Research, Department of Earth, Ocean & Atmospheric Sciences, University of British Columbia, Vancouver, BC V6T1Z4, Canada

Clumped isotope thermometry has recently been applied to constrain the thermal evolution of meteorite impact structures and associated fluid activity, yet two key uncertainties remain: (1) the kinetic fractionation effect on  $\Delta_{47}$ -based temperature and (2) intensity difference in post-impact fluid activity among contrasting impact settings (e.g., marine versus terrestrial settings, and impact structures of different diameters). This study presents the dual clumped isotope analyses on carbonate-bearing impactites from the Houghton impact structure (Devon Island, Canada). The carbonate-dominated target rock at Houghton structure makes its impactites well-suited for clumped-isotope thermometry. Moreover, it provides an important reference for assessing the intensity of fluid activity following the impact event in a terrestrial setting. In this study, calcite and dolomite were distinguished within impactites of various lithologies and then microdrilled separately. A subset of the samples analyzed with our NuCarb-Perspective IS setup was first pretreated with NaOCl to assess potential contamination effects. Results indicate that (near-)equilibrium clumped isotope signatures are recorded in all analyzed samples across different impactite lithologies and carbonate minerals. Multiple impactites record high temperatures (with a maximum of  $334.9^{+81.4}_{-58.0}$  °C preserved in calcite clast within impact melt rock), far exceeding those recorded by the unshocked matrix rocks, indicating that these high-temperature signatures originated from impact-induced heating. Meanwhile, the new isotope data of the studied samples show little evidence of hydrothermal activity at the Houghton impact structure.