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Citation:

Macdonald, F. A. (2020). Deep-time
paleoclimate proxies. *AGU Advances*, 1,
e2020AV000244. [https://doi.org/](https://doi.org/10.1029/2020AV000244)
10.1029/2020AV000244

Received 26 JUN 2020

Accepted 7 JUL 2020

Deep-Time Paleoclimate Proxies

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Abstract Pre-Cenozoic climate (>66 million years ago) has been reconstructed with climate sensitive sedimentary deposits. However, sedimentary records are inherently local and can be affected by topography and oceanic and atmospheric currents. Additionally, in tectonically active environments, the interpretation of glacial rocks can be ambiguous. Temperature and CO₂ proxies complement the record of climate sensitive sedimentary rocks. With samples that have been carefully screened for post-depositional alteration, carbonate clumped isotope thermometry has produced ocean temperature estimates that are consistent with the sedimentary record and CO₂ proxy data. Although there are many challenges for quantitative temperature reconstructions through Earth history, maximum temperature estimates are now being extracted across the onset of Cryogenian (720–635 million years ago) snowball Earth glaciations that follow the expected cooling trend.

As we participate in the current experiment of anthropogenic climate change, we look to the past to give us broader context and to bolster our model predictions for the future. We can measure CO₂ in bubbles trapped in ice cores to reconstruct climate change over the past million years, but predicted future climate change is much larger than anything that happened over this interval. To reconstruct episodes of extreme climate change and evaluate hypothesized geological and biogeochemical drivers, we need to go back much further in the geological record, where the main paleoenvironment archives are rocks. However, extracting temperature and CO₂ estimates from ancient rocks has proven challenging. Mackey et al. (2020) take on this challenge and present new clumped isotope thermometry from carbonate rocks that span the onset of the most extreme episode of climate change in the geological record, the ca. 717–660 Myr Sturtian Snowball Earth glaciation.

Prior to the Cenozoic, secular changes in climate state have largely been reconstructed by the latitudinal extent of large continental ice sheets (Figure 1) as recorded by glacial deposits, descriptively referred to as “diamictites” and genetically as “tillites.” The absence of continental glacial deposits for much of the Mesozoic and more than 75% of the Phanerozoic (Macdonald et al., 2019) supports the conclusion that we live in a relatively cool time, geologically speaking. Cooling trends and the waxing and waning of Paleozoic ice sheets have been reconstructed from the distribution of tillites across Gondwana (Crowell & Frakes, 1970). An earlier, more extreme climate state, referred to as Snowball Earth (Hoffman et al., 2017), has also been inferred from the latitudinal extent of diamictites, which were deposited in laterally extensive deposits in tropical marine basins at least twice during the Neoproterozoic (Figure 1).

Despite the great contribution of climate sensitive facies to reconstructing paleoclimate, the interpretation of climate state based solely on the paleolatitude of glacial rocks has limitations and ambiguities. For example, recent work has proposed that diamictite of the Konnarock Formation is glacial and records local pre-Sturtian glaciation (MacLennan et al., 2020). These units, dated with U–Pb on zircon on interbedded volcanic rocks, suggest that ice was present at tropical latitudes at ~751 Ma, but there is no clear evidence for large continental ice-sheets of this age elsewhere. To get around this apparent conundrum, MacLennan et al. (2020) suggest these diamictites were deposited in a high-altitude glacial lake during a climate similar to the last glacial maximum. Indeed, the extent of continental ice is also dependent on the distribution of continents, altitude, and lateral heat transport (Crowell & Frakes, 1970) and may not accurately track global average temperature, let alone atmospheric CO₂ concentration. Wouldn't it be nice if there was an independent proxy that we could use to reconstruct local temperatures and global CO₂ levels in the Neoproterozoic?

Phanerozoic CO₂ levels have been estimated using a variety of proxies including the carbon isotope composition of alkenones, liverwort and soil carbonates, boron isotopes on foraminifera, and the physical characteristics of leaf stomata (Figure 1); however, even with stringent quality control, estimates conflict with one

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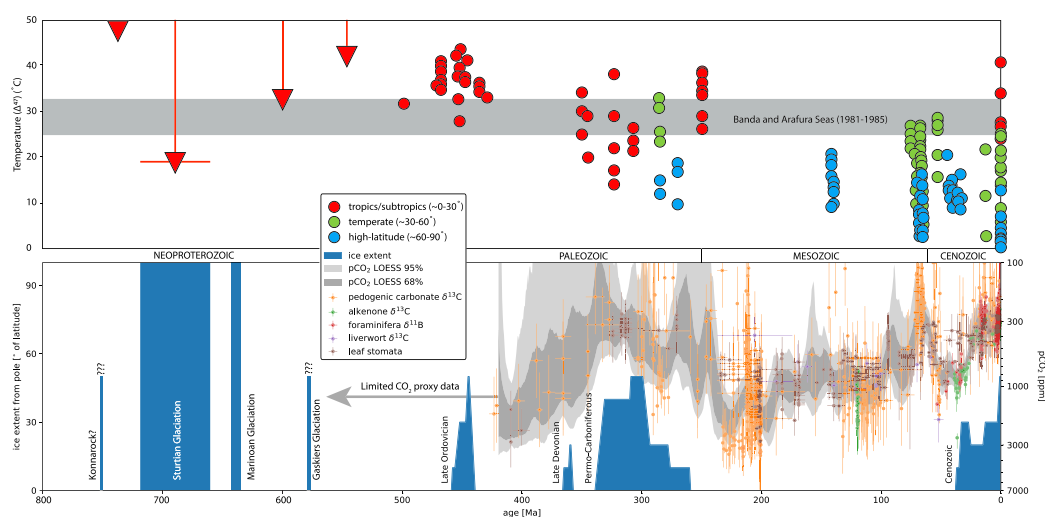


Figure 1. Below, latitudinal extent of large continental ice sheets away from the poles and compilation of $p\text{CO}_2$ proxies (Foster et al., 2017; Macdonald et al., 2019; Park et al., 2020), and above, Δ^{47} paleo-temperatures from screened mollusks and brachiopods in circles (Henkes et al., 2018) and minimum Δ^{47} paleo-temperatures from micrite in triangles with lines showing range of data extending off-scale and age uncertainty (Bergmann et al., 2018; MacKay et al., 2020), plotted with modern tropical temperature range in the Banda and Arafura Seas (Henkes et al., 2018).

another (with order of magnitude discrepancies) and probabilistic approaches cannot constrain $p\text{CO}_2$ at the 95% confidence level to within a few hundred parts per million for any given time interval, particularly prior to the Cenozoic (Foster et al., 2017; Park et al., 2020). The majority of the pre-Cenozoic CO_2 proxy data are from pedogenic carbonate, and scatter is likely related to diagenesis and assumptions regarding soil-respired CO_2 (Montanez, 2013). $\Delta^{17}\text{O}$ of sulfates have potential to extend $p\text{CO}_2$ estimates to the Proterozoic, but interpretations are convoluted with uncertainties in atmospheric oxygen levels and global primary production (Crockford et al., 2019). Nevertheless, despite these limitations, the $p\text{CO}_2$ proxy record for the Phanerozoic is broadly consistent with the ice extent record (Figure 1).

Phanerozoic seawater temperatures have been estimated with the temperature dependent fractionation of oxygen isotopes ($\delta^{18}\text{O}$) in carbonate rocks and fossils (Veizer & Prokoph, 2015). These estimates are hampered by uncertainties in the $\delta^{18}\text{O}$ composition of seawater, ice volume, vital effects, local temperature gradients, and diagenesis (Veizer & Prokoph, 2015). For the Cenozoic, $\delta^{18}\text{O}$ on benthic foraminifera can be used to avoid the effects of early diagenetic alteration driven by the advection of both seawater and freshwater on carbonate platforms and minimize vital effects and local temperature gradients. Temperature estimates from Cenozoic ocean drill cores can also be complimented by independent estimates from Mg/Ca ratios and TEX86, but for older rocks these measurements are compromised. Through the Mesozoic and most of the Paleozoic, diagenetically screened brachiopods and mollusk shells can be used to minimize the effects of alteration (e.g., Henkes et al., 2018; Veizer & Prokoph, 2015), but in the Neoproterozoic, without fossil shells, the recovery of paleo-temperatures is complicated by all of these issues.

The temperature of carbonate precipitation can also be measured directly with carbonate clumped isotope thermometry (Δ_{47}), which is based on the temperature-dependent clumping of ^{13}C and ^{18}O into multiply-substituted carbonate isotopologues (e.g., Henkes et al., 2018). The Δ_{47} temperatures can be combined with mineral $\delta^{18}\text{O}$ values to calculate the source fluid composition and refine the $\delta^{18}\text{O}$ of seawater in deep-time (Henkes et al., 2018). With diagenetic screening, and accounting for latitude dependence of shallow water carbonate platforms, Δ_{47} temperatures record a secular signal through the Phanerozoic that is consistent with both the CO_2 proxy records and the latitudinal extent of large continental ice sheets (Figure 1). However, also like pedogenic carbonate CO_2 measurements, these data have a lot of scatter, due largely to early diagenesis and local temperature gradients on platforms, but also due to the overprinting of solid state reordering, which can be accounted for with forward modeling (Henkes et al., 2018). Consequently, it has been unclear how to extend Δ_{47} paleothermometry to the Neoproterozoic, where there are no fossil shells, and you are largely limited to diagenetically altered platform carbonate rocks.

Mackey et al. (2020) present Δ_{47} results from Neoproterozoic carbonate deposited before and during the Sturtian glaciation at tropical latitudes in Svalbard. These rocks are one of the best available targets for extending the Δ_{47} paleothermometer into the Proterozoic because Svalbard preserves low-grade pre-glacial carbonate and glacial deposits with carbonate mud (micrite) and cements, and we expect a large temperature difference between pre-glacial and syn-Snowball environments (Hoffman et al., 2017). Mackey et al. (2020) see such a signal, reporting mean glacial Δ_{47} temperatures that are $26 \pm 10^\circ\text{C}$ cooler than pre-glacial strata with four samples $<25^\circ\text{C}$. Although these temperatures are relatively warm (Figure 1) and may reflect early diagenetic temperatures, alteration and solid state reordering during subsequent burial result in higher paleotemperatures, so these data should be interpreted as maximum constraints. The interpretation is also reliant on the assumption that the difference in primary Δ_{47} values resulting from initial formation temperature is maintained during subsequent processes such as solid-state reordering during burial. Importantly, through careful petrography and sample selection, Mackey et al. (2020) deliver a recipe for extracting the lowest Δ_{47} temperatures from diagenetically altered, ancient micritic carbonate, and cements. Additionally, the extracted glacial $\delta^{18}\text{O}$ fluid values are within error of hematite $\delta^{18}\text{O}$ values from Sturtian glacial deposits, consistent with both cooling and formation of a large volume of ice during Snowball Earth (Galili et al., 2019).

Together, the latitudinal distribution of climate sensitive sedimentary rocks, $p\text{CO}_2$ proxies, and temperature proxies are forming a consistent picture of long-term climate change associated with the geological carbon cycle (Figure 1). And yet, we still do not know if these episodes of geological climate change are the result of changes in volcanic outgassing, changes in paleogeography and global weatherability, evolutionary changes in biogeochemical cycles, or some combination of these factors. Although Δ_{47} on carbonate cements and micrite may never be able to achieve the accuracy of surface temperatures retrieved from fossil shells due to the propensity of resetting, the contribution by Mackey et al. (2020) offers a roadmap for reconstructing maximum temperatures from ancient carbonate platforms, which constitute our greatest biogeochemical deep-time data repository. As both the timing and magnitude of long-term climate change are further refined, we will have new opportunities to test hypotheses for geological and biogeochemical drivers of long-term climate change.

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