

Linking paleocontinents through triple oxygen isotope anomalies

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Supplementary Information

1. Methods

Oxygen Isotopes

All samples were cut to remove weathered edges, and then crushed by hand in a cleaned agate mortar and pestle. Samples (~20 mg) were then dissolved into a 1 M sodium hydroxide (NaOH) – 0.05 M diethylenetriaminepentaacetic acid (DTPA) solution and shaken for 12 hours. Samples were then filtered and acidified with double distilled 6 N HCl, followed by the addition of drops of concentrated BaCl₂ solution allowing samples to reprecipitate. Samples were allowed to sit for 12 hours followed by centrifuging and washing with deionized water three times. Samples were then dried for 24 hours. This total procedure was then repeated once more before analysis (Bao et al., 2006).

For analysis samples (~10 mg) were loaded onto a stainless steel plate and loaded into a chamber and flooded with BrF_{5(g)}. Samples were then heated with a CO₂ laser releasing O_{2(g)} from SO_{4(s)} with ~30-40% yields. Samples were then run through a series of cryo-focusing steps to remove impurities and collected onto mol-seive. Samples of pure O_{2(g)} were then analyzed on a Thermo MAT-253 in dual inlet mode. Repeated measurements of inter-laboratory standards yielded a maximum uncertainty (1σ) on the entire analytical procedure to be < 0.05‰.

In the wet chemistry steps pyrite oxidation within BaSO₄ was not calculated to be a significant contaminant to justify removal through a chromium reduction solution as abundances of pyrite within samples was determined by microscopy (Crockford et al., 2016) to be a maximum of 0.5% in micritic phases and far less within BaSO₄. Although sample yields from lazing are not 100% repeated tests by Bao et al., (2008) determined no significant fractionations during this process, therefore we argue measured $\Delta^{17}\text{O}$ results are reflective of original SO₄ values.

Sulfur Isotopes

Sulfur isotope analyses for this study were made at McGill University's stable isotope laboratory. Samples were crushed and ~10 mg were placed into a Thode reduction solution (Thode et al. 1961) and heated. This process converted SO₄ to H₂S_(g) which was then carried in a N_{2(g)} stream and bubbled through zinc acetate to convert H₂S_(g) to ZnS_(s). ZnS_(s) was then converted to Ag₂S_(s) by reacting with AgNO_{3(aq)}. Ag₂S was then dried and weighed (~3 mg). For measurements, Ag₂S_(s) was converted to SF_{6(g)} by reaction with F_{2(g)} and heating. SF_{6(g)} was then purified via several cryofocusing steps followed by gas chromatography and measurement on a Thermo MAT-253 in dual inlet mode. Estimated total error on analyses and measurements is < 0.1‰ for $\delta^{34}\text{S}$ measurements.

2. Data

Table DR1: Triple oxygen ($\Delta^{17}\text{O}_{\text{SO}_4}$) and sulfur ($\delta^{34}\text{S}$) isotope data from Brazil and Finnmark (northern Norway) samples. Total analytical error on individual $\Delta^{17}\text{O}$ and $\delta^{34}\text{S}$ analyses is less than 0.05‰ and 0.1‰ respectively.

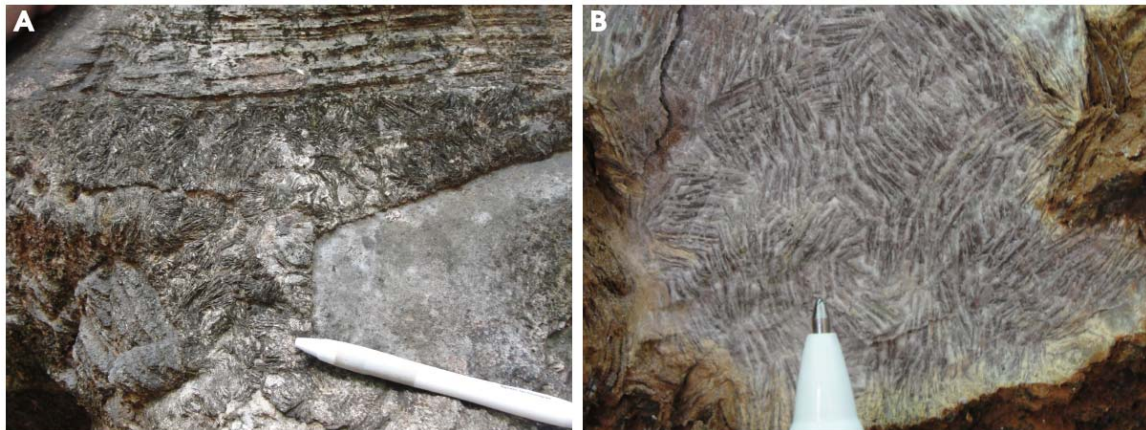
<i>Sample Name</i>	<i>Description</i>	$\Delta^{17}\text{O}(\text{‰})$	$\delta^{34}\text{S}(\text{‰})$
PCSL-1	Sete Lagoas Fm. Brazil	-0.87	
PCSL-2	Sete Lagoas Fm. Brazil	-0.80	30.6
PCSL-3	Sete Lagoas Fm. Brazil	-0.90	30.6
PCSL-4	Sete Lagoas Fm. Brazil	-0.80	32.2
PCSL-5	Sete Lagoas Fm. Brazil	-0.82	32.1
PCSL-6	Sete Lagoas Fm. Brazil	-1.05	25.7
PCSL-7	Sete Lagoas Fm. Brazil	-0.99	25.7
PCSL-8	Sete Lagoas Fm. Brazil	-0.89	26.6
PCSL-9	Sete Lagoas Fm. Brazil	-0.92	26.6
MF1505-0.5	Nyborg Fm. northern Norway	-0.41	
MF1504-0.28	Nyborg Fm. northern Norway	-1.02	17.9

MF1505-0.65	Nyborg Fm. northern Norway	-0.48
MF1501-0.15	Nyborg Fm. northern Norway	-0.44

3. Geological Settings

The Sete Lagoas Cap Carbonate

Fig. DR1: Images of barite occurrences from the Sete Lagoas Formation, Brazil.



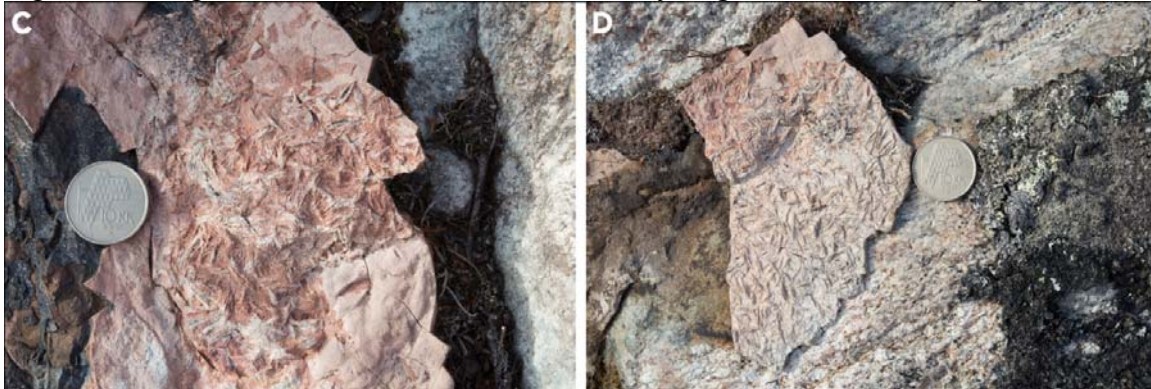
The post-Marinoan cap carbonate in east central Brazil is represented by the first ~35 m of the Sete Lagoas Formation, Bambuí Group, which sharply overlies Neoproterozoic glaciogenic rocks of the Jequitai Formation (with no evidence of reworking or hiatus), Mesoproterozoic sedimentary basins, or crystalline basement rocks of the São Francisco craton (Vieira et al., 2007; Caxito et al., 2012; Alvarenga et al., 2014). The Sete Lagoas cap dolomite forms the base of a cap carbonate interval and displays unusual sedimentary features that resemble many other post-Marinoan cap carbonate units worldwide, such as the distinguishable pale yellow to pink color of laminated and peloidal dolostones, its variable, although small average thickness (2 to 5 m), the presence of giant wave ripples, barite beds and finally the distinct negative carbon isotopic excursion with $\delta^{13}\text{C}$ values decreasing upward (-2 to -6.5‰) (Caxito et al., 2012; Alvarenga et al., 2014). These dolomites are overlain by a thicker (10 to 50 m) interval of laminated limestones containing seafloor cements (aragonite pseudomorphs and locally barites), negative $\delta^{13}\text{C}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ data constantly around 0.7074-0.7077. The Sete Lagoas cap carbonate occurs basin wide, despite the pink dolomite interval being locally absent in some cases, preserving only the 10s of meters of limestones with recurrent seafloor cements. The recently discovered late Ediacaran *Cloudina* index fossil

in the middle Sete Lagoas Formation (Warren et al., 2014) suggests an unconformity separating the lower post-Marinoan cap carbonate interval from the remaining late Ediacaran Bambuí basin (Uhlein et al., 2016).

In the central part of the basin (northern Minas Gerais), the Sete Lagoas Formation outcrops above gneissic rocks of a former basement paleo-high. Its first 10 m represents the cap carbonate interval, with a 1 m-thick pale pink dolomite overlain by laminated limestones. The sampled barite levels are the first documented occurring in the Bambuí Group and are located in the last centimeters of cap dolomite. It comprises mainly thin (1 to 8 cm) and stratiform levels of white to light blue barite minerals with a pearly lustre, bladed crystal habit and high specific gravity ($\sim 4.5 \text{ g/cm}^3$) (Fig. DR1). Laterally, the barite levels occur as veins and as major void-filling cement in tepee structures.

The Nyborg Cap Carbonate

Fig. DR2: Images of barite occurrences from the Nyborg Formation, Norway.



The Marinoan glaciation in northern Norway is recorded in the Gaissa Basin in the Tanafjord-Varangerfjord region. This succession preserves a portion of the interglacial period (Grasdal Formation), which is separated from the overlying Marinoan diamictite (Smalfjord Formation) and Marinoan cap carbonate (Nyborg Formation) by a subglacial erosion surface (Rice et al., 2012). Owing to a lack of radiometric ages in the Gaissa Basin, this package of sedimentary rocks is interpreted to correspond the Marinoan glaciation through use of carbon isotope chemostratigraphy, and stratigraphic and sedimentological correlation (Halverson et al., 2005; Rice et al., 2012). The Nyborg Formation may be deposited either on top of the Smalfjord Formation or crystalline rocks

of the Fennoscandian Shield. Barite samples collected from the Nyborg Formation were found conformably overlying the crystalline basement in lenses and horizons ranging in thickness between 1 and 30 cm. Morphology of barite units range from massive to bedded, with some outcrops exhibiting rosettes and bladed morphology.

4. Interpreting $\Delta^{17}\text{O}$ anomalies

The $\Delta^{17}\text{O}$ composition of tropospheric O_2 is a function $p\text{CO}_2$, $p\text{O}_2$ and the flux of O_2 from the biosphere that approximates gross primary production (*GPP*). Early interpretations of $\Delta^{17}\text{O}$ anomalies within post-Marinoan strata assumed high *GPP* in the wake of the Marinoan glaciation and therefore calibrated results with existing ice-core records, leading to $p\text{CO}_2$ estimates >0.1 bar (Blunier et al., 2002; Bao et al., 2008). A challenge to this interpretation rightly highlighted that an alternative scenario to produce observed $\Delta^{17}\text{O}$ anomalies would be moderate $p\text{CO}_2$ but greatly diminished *GPP* (Sansjofre et al., 2012). Refined calculations, that do not have to assume a constant residence time of O_2 in the atmosphere (Cao and Bao, 2013), quantified such a scenario. Cao and Bao (2013) estimated requisite *GPP* levels to impart inferred $\Delta^{17}\text{O}_{\text{SO}_4}$ from syn-deglacial lakes in Svalbard under a range of $p\text{O}_2$ conditions and put forward that *GPP* would have to be at least 80-97% reduced from modern levels. This scenario, however, runs contrary to evidence of vigorous primary production (Kunzmann et al., 2012; John et al., 2017) potentially stimulated by vigorous post-glacial weathering (Kasemann et al., 2014). It is important to note however that such a low *GPP* - $\Delta^{17}\text{O}$ anomaly scenario may be possible at other times in Earth history with the correct atmosphere-biosphere conditions (Crockford et al., 2014).

Beyond imparting $\Delta^{17}\text{O}$ anomalies to tropospheric O_2 is the translation of this signal into the sedimentary record through SO_4 . While experimental observations calibrate the contribution of O_2 to SO_4 during sulfide oxidation ($\sim 8\text{-}30\%$; Balci et al., 2007; Kohl and Bao, 2011), the integrated expression of $\Delta^{17}\text{O}$ signatures within SO_4 reservoirs will also reflect a balance of input (sulfide oxidation, reoxidation, evaporite weathering) and output fluxes (microbial sulfur cycling, sulfate deposition). In the case of anomalous conditions generated in a Snowball Earth scenario, all processes beyond

anomalous O₂ sulfide oxidation will dilute and remove anomalous $\Delta^{17}\text{O}$ values from sulfate.

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