

 $$\ensuremath{\mathbb{C}}\xspace$  2023 The Authors Published by the European Association of Geochemistry

# Earth's first glaciation at 2.9 Ga revealed by triple oxygen isotopes

A. Hofmann<sup>1\*</sup>, I.N. Bindeman<sup>2</sup>

### Abstract





We here report the lowest (~3 ‰ VSMOW)  $\delta^{18}O$  values for any weathering-related sedimentary rock in Earth's history, from shales and diamictites of the Mesoarchaean Pongola Supergroup of South Africa. This volcano-sedimentary succession was deposited in a shallow epeiric sea on continental crust of the Kaapvaal Craton and includes the record of the Earth's oldest surface glaciation. Oxygen isotope data of shales of the Mozaan Group indicate gradual climatic cooling of the surface environments that culminated in glacial conditions at ~2.90 Ga. Mathematical inversion of measured  $\Delta^{'17}O$  and  $\delta^{18}O$  values results in  $\delta^{18}O$  values around -20‰ for weathering waters, suggesting cold climate conditions. These observations suggest continental weathering of the Kaapval Craton involving low  $\delta^{18}O$  meteoric waters, possibly in a near-polar position.

Received 20 March 2023 | Accepted 6 May 2023 | Published 13 June 2023

### Introduction

The Pongola Supergroup is the tectonically least disturbed Mesoarchean volcano-sedimentary sequence on Earth (Luskin et al., 2019). Its deposition started at 3.0 Ga in an epicontinental sea that flooded the Kaapvaal Craton, which had become a stable continent ~100 Myr earlier, but experienced extension and subsidence (Paprika et al., 2021). The Pongola Supergroup contains the oldest purported glacial deposits (von Brunn and Gold, 1993; Young et al., 1998). Mesoarchaean diamictites of possible glacial origin were first described from the time-equivalent West Rand Group of the Witwatersrand Supergroup (Wiebols, 1955), although formation modes other than glacial processes have been proposed, such as by cohesive debris flows (Martin et al., 1989). Despite their importance for the evolution of Earth's climate through time, a glacial setting for the Pongola diamictites remains a matter of debate. As the oxygen isotopic composition of surface materials is strongly dependent on latitude and climate, we have applied triple oxygen isotope analysis to scrutinise their origin. We report  $\delta^{18}$ O values of shales and diamictites lower than any siliciclastic deposits analysed so far, supporting glacial conditions during deposition of the Pongola Supergroup.

## **Geological Setting**

The Archaean Pongola Supergroup is a volcano-sedimentary succession that was deposited between 2.99 and 2.87 Ga on continental crust of the south-eastern part of the Kaapvaal Craton (Fig. 1a; Gumsley *et al.*, 2015; Luskin *et al.*, 2019). It is lithologically and stratigraphically similar to the Witwatersrand

Supergroup and underlying Dominion Group, and together they form the oldest preserved cratonic cover succession (Beukes and Cairncross, 1991; Paprika *et al.*, 2021). Two groups comprise the Pongola Supergroup: the lower Nsuze Group, dominated by volcanic rocks ranging from flood basalt to rhyolite, and the upper Mozaan Group, dominated by shallow marine siliciclastic sedimentary rocks (Luskin *et al.*, 2019). Chemical sedimentary rocks, including banded iron formation (BIF) and stromatolitic carbonates, Mn-rich shales, and palaeosols provide an exceptional record of surface processes in the Mesoarchean and indicate shallow-marine oxygen oases under an anoxic atmosphere (Siahi *et al.*, 2016; Eickmann *et al.*, 2018; Ossa *et al.*, 2018; Heard *et al.*, 2021).

The Mozaan Group overlies the Nsuze Group disconformably, the latter as young as  $2954 \pm 8$  Ma, the youngest age of the correlative Dominion Group (Paprika et al., 2021). The Mozaan Group is ~5 km thick and consists largely of shallow marine sandstone and shale deposited in an intracratonic sea subjected to sea-level oscillations (Beukes and Cairncross, 1991). Despite regional metamorphism to lower greenschist facies grade, rocks are extremely well preserved, not requiring the usage of terminology for metamorphic rocks. Following Luskin et al. (2019) and references therein, it is subdivided into ten formations (Fig. 1b). At the base is the Singeni Formation, consisting of two fluvial to shallow-marine sandstone units separated by a unit of shale and BIF. The Ntombe Formation is a transgressive sequence of ferruginous shale, siltstone, and sandstone and is overlain by compositionally similar marine highstand deposits of the Thalu Formation. Both formations contain shales enriched in Mn-carbonate, derived diagenetically from Mn(IV)-oxyhydroxides that precipitated in oxygenated



<sup>1.</sup> Department of Geology, University of Johannesburg, South Africa

<sup>2.</sup> Department of Earth Sciences, 1272 University of Oregon, Eugene OR 97403, USA

<sup>\*</sup> Corresponding author (email: ahofmann@uj.ac.za)



**Figure 1** (a) Simplified geological map showing the distribution of the Nsuze and Mozaan groups of the Pongola Supergroup and its location within the Kaapvaal Craton. (b) Stratigraphy of the Mozaan Group of the Pongola Supergroup (Luskin *et al.*, 2019). Distribution of  $\delta^{18}$ O in shales and diamictites with depth in PNG cores and surface samples from Klipwal Mine area. KM, Klipwal Member.

surface waters (Ossa *et al.*, 2018). The Hlashana Formation is dominated by cross-bedded sandstone of a current-dominated shelf sea environment and is overlain by the Delfkom Formation, composed of sandstone, shale, and diamictite, the focus of this study. The youngest concordant detrital zircon date of  $2903 \pm 14$  Ma from a sandstone of this formation provides a maximum depositional age (Zeh and Wilson, 2022). For the description of the units higher up in the Mozaan Group stratigraphy, the reader is referred to Luskin *et al.* (2019). A dolerite sill dated at  $2869 \pm 5$  Ma provides a minimum age for Mozaan Group deposition (Gumsley *et al.*, 2015). The Delfkom Formation and its diamictites were thus deposited between 2.90 and 2.87 Ga.

### Sampling and Petrography

Stratigraphically resolved sampling of diamictite and shale from the Delfkom Formation was conducted in the Klipwal Mine area (Fig. 1a; von Brunn and Gold, 1993). At this locality, four diamictite units have been described that are interbedded with ferruginous shale, quartz arenite and conglomerate (Fig. S-1). The most prominent of the diamictite units is the Klipwal Member that has been sampled for this study together with several samples of underlying shale. The shales consist largely of silt-sized detrital quartz, detrital and diagenetic feldspar, euhedral chlorite, disseminated magnetite and some euhedral pyrite and Ti-oxide (Fig. S-2). The composition of diamictite has been described by von Brunn and Gold (1993) and Young *et al.* (1998), and its matrix is compositionally similar to the shale (Fig. S-3).

Shale samples were also obtained from two deep borehole cores (PNG2, PNG3) drilled in 1988 by the AngloGold Exploration Division (Fig. 1a). The boreholes intersected lower stratigraphic units of the Mozaan Group, including the Sinqeni, Ntombe and lower Thalu formations (Figs. 1b, S-4). A limited geochemical dataset of samples from PNG2 have been reported by Ossa *et al.* (2018). The shales are ferruginous, consisting largely of silt-sized detrital quartz in a predominantly chlorite matrix with total organic carbon contents of <1 wt.%.

### **Isotopic Composition**

All samples were subjected to oxygen (including  $\Delta'^{17}$ O) and hydrogen isotope analysis at the University of Oregon (Table S-1) and all data are reported relative to VSMOW. Samples from the Klipwal Mine area were also analysed for major element contents at the University of Johannesburg (Table S-2). Analytical procedures are outlined in the Supplementary Information.

Shale samples from drill core PNG2 (n = 8) cover the Ntombe and lower Thalu formations. The  $\delta^{18}$ O values are relatively constant throughout the core, averaging  $8.1 \pm 0.9$  ‰. The  $\delta$ D values average  $-74.8 \pm 4.6$  ‰, excluding the two stratigraphically uppermost samples that range between -119.9 and -100 ‰.

Drill core PNG3 intersected the Thalu Formation. The  $\delta^{18}$ O values of shale samples (n = 9) from this core are lighter compared to those of PNG2, averaging  $6.6 \pm 0.6$  ‰. The  $\delta$ D values are relatively constant throughout the core, averaging  $-56.3 \pm 7.2$  ‰.

Shale (n = 5) and diamictite (n = 5) samples obtained from fresh outcrop around Klipwal Mine show even lighter  $\delta^{18}$ O values, with shale averaging  $2.9 \pm 0.3 \%$  and diamictite averaging  $4.7 \pm 1.4 \%$ . The  $\delta$ D values show some scatter, with shale of the Delfkom Formation averaging  $-73.2 \pm 16.4 \%$  and diamictite averaging  $-83.1 \pm 14.5 \%$ . There are moderate positive correlations between  $\delta^{18}$ O values vs. SiO<sub>2</sub> ( $R^2 = 0.42$ ) and K<sub>2</sub>O ( $R^2 = 0.41$ ).  $\delta$ D values neither correlate with major element contents nor with  $\delta^{18}$ O values (Fig. S-5).

### Discussion

Diamictites of the Mozaan Group were first described by von Brunn and Gold (1993). They reported the presence of a highly varied suite of extra-basinal clasts, some of which being striated and faceted, and argued for their emplacement by gravity flows derived from highland glaciers. Young *et al.* (1998) noted moderate CIA values (Chemical Index of Alteration, 66.8 on average) and high Fe-oxide contents in diamictites and interbedded shales. This was regarded in support of a glacial origin of the diamictites, by analogy with Neoproterozoic glaciogenic diamictites. They further reported the rare presence of dropstones, indicative of clast-charged floating glacier ice at the time of deposition.

The oxygen isotope composition of shales (and other mud-dominated rocks such as diamictites) largely reflects weathering conditions, specifically the isotopic composition of the meteoric water during formation of clays at weathering temperature, generally leading to higher than crustal  $\delta^{18}$ O values, and well above the mantle value of 5.7 ‰ (Bindeman et al., 2016 and references therein). Values of  $\delta^{18} O$  broadly increase through Earth history from ~10 ‰ in the Archaean to ~15 ‰ in the Phanerozoic (Fig. 2), linked to the combined effects of crustal differentiation and incorporation of isotopically heavy weathering products into the crust over time. Strong downward shifts of  $\delta^{18}$ O values by several per mille in the Palaeoproterozoic and Neoproterozoic (Fig. 2) have generally been attributed to glaciations, as meteoric waters in glacial settings have very low  $\delta^{18}$ O values, and glacial rock flour contains less weathered clastic materials (Nesbitt and Young, 1982) lower in  $\delta^{18}$ O.

Average  $\delta^{18}$ O values for Mesoarchaean (3.2–3.0 Ga) shales have been reported as 9.7±2.4 ‰ (Bindeman *et al.*, 2016). Our values for shale samples from PNG2 from the lower part of the Mozaan Group fall within this average. Stratigraphically upwards, shales from PNG3 show lower values, and this decrease culminates in  $\delta^{18}$ O values for shales and diamictites of the Delfkom Formation lower than mantle. These data indicate weathering of Thalu and Delfkom formations source materials by meteoric waters with progressively decreasing  $\delta^{18}$ O values, potentially culminating in weathering by ultralow  $\delta^{18}$ O waters. Thus, there is strong evidence for climatic cooling during deposition of the lower Mozaan Group, eventually giving rise to a glacial environment during Delfkom Formation deposition. We note that diamictites of the Mozaan Group and Afrikander Formation of the West Rand studied by



Figure 2 Oxygen isotope evolution of shales (Bindeman et al., 2016) and diamictites (Gaschnig et al., 2016) through time, and data from this study. Stippled lines point to Palaeo- and Neoproterozoic as well as Permo-Carboniferous glaciations.

Gaschnig *et al.* (2016) also contain low (<6 ‰)  $\delta^{18}$ O values overlapping with our data (Fig. 2).

Positive correlations of  $\delta^{18}O$  values with SiO<sub>2</sub> and K<sub>2</sub>O in Delfkom Formation shales and diamictites indicate higher  $\delta^{18}O$  values for detrital quartz and K-feldspar compared to the matrix. The  $\delta D$  values of our samples are similar to those of average modern shales and crustal fluids (Sheppard and Gilg, 1996). The lack of correlation between  $\delta^{18}O$  and  $\delta D$  values (Fig. S-5) suggests isotopic re-equilibration with diagenetic and/or metamorphic fluids during recrystallisation of the chlorite precursor material and chlorite itself. No weathering history of the sediment source is thus preserved in the  $\delta D$  values of the Mozaan Group.

The CIA values of our samples (Table S-2) are not unlike pre- and post-2.9 Ga shales (Bindeman et al., 2016). They range from 60, translating to ~20 % clay weathering product and ~80 % unweathered silicates, to 97, representing almost pure clay. The average CIA value is 69.9 for diamictite and 75.2 for shale. This makes sense as diamictites contain unweathered clasts of quartz and feldspar, as also indicated by slightly higher  $\delta^{18}$ O values compared to shales. *Via* mass balance, we can derive the "weathering product" in equilibrium with weathering waters, by subtracting 0-80 % of unweathered siliciclastic detritus with an average  $\delta^{18}$ O crustal value of +6.5 ‰ (Table S-3). Such a procedure was used by Bindeman et al. (2018) in their global shale inversion. Then we employed a mathematical inversion of measured  $\delta^{18}$ O and  $\delta^{17}$ O values of our samples and computed a weathering product (Fig. 3, Table S-3), by using the modern meteoric water line (MWL) equation  $\delta^{17}O =$  $0.528 \times \delta^{18}$ O + 0.033. As we have two fractionation equations for  $1000 ln \alpha^{18} O_{shale-water}$ ,  $1000 ln \alpha^{17} O_{shale-water}$ , and the MWL equation, we are able to obtain solutions for  $\delta^{18}O_{water}$  $\delta^{17}O_{water}$  and temperature (see Table S-3 for further details of these computations). We obtain  $\delta^{18}$ O values of weathering waters of  $-18.9 \pm 2.3$  % (bulk sample) and  $-20.9 \pm 4.8$  % (weathering product), values found in polar regions today. Computed temperatures are 37-41 °C.



**Figure 3** Triple oxygen isotope diagram showing shale-water fractionation lines connected to various parental meteoric waters (MWL, present day meteoric water line; Surma *et al.*, 2021) that participated in weathering. Note that Delfkom Formation shales and diamictites plot around  $-18 \pm 2.3$  ‰ meteoric water and have  $\delta^{18}$ O values lower than any other shales in the geologic record (data of Bindeman *et al.*, 2018). Curved arrow indicates the effect of subtracting a detrital component in the samples (with crustal  $\delta^{18}$ O of +6.5) to compute a "pure weathering product" (Table S-3).

As Archaean seawater may have been lower in  $\delta^{18}$ O (*e.g.*, Bindeman, 2021), we additionally performed computations assuming Archaean seawater with  $\delta^{18}$ O of -5 ‰, generating a MWL equation of  $\delta^{17}$ O =  $0.528 \times \delta^{18}$ O + 0.078, having higher  $\Delta^{'17}$ O values *per* lower  $\delta^{18}$ O in seawater (*e.g.*, Sengupta and Pack, 2018). Under this assumption, with a meteoric water line higher in  $\Delta^{'17}$ O,  $\delta^{18}$ O values of weathering waters are -26 to -28 ‰ at 6-8 °C.

The computed temperatures reflect the conditions during isotopic closure, during the last equilibrium between the weathering waters and sediment, possibly at the time of expulsion of pore waters during compaction, leading to a reduction in porosity and hydrologic impermeability (Bindeman, 2021). We consider it was then that most oxygen atoms from the hydrosphere were taken up by the bulk of the silicates and their precursors analysed here. The rocks carry no textural evidence of percolation of post-diagenetic fluids, however the effects of subsequent metamorphism and tectonic uplift, namely dehydration of rocks to potential re-hydration, on bulk isotope values of rocks are considered in the Supplementary Information and produce <1 ‰ shifts in  $\delta^{18}$ O values but affect  $\delta$ D and [H<sub>2</sub>O] significantly, potentially explaining "reset"  $\delta$ D values.

Assuming no major change between 2.95 and 2.90 Ga in the degree of continentality and elevation of the sedimentary source terrain, the isotopic data are consistent with deposition of the Delfkom Formation under cool climatic conditions with continental weathering involving low  $\delta^{18}$ O meteoric waters. Palaeomagnetic data constrain the Kaapvaal Craton to mid to high latitudes at the time of deposition of the Pongola Supergroup (de Kock et al., 2021). Climatic cooling may be linked to drift of the Kaapvaal Craton towards a pole. Alternatively, climatic cooling was a global phenomenon pending verification on different crustal blocks. Stabilisation of the Singhbhum and Kaapvaal cratons at ~3.1 Ga (Hofmann et al., 2022) and the Pilbara Craton at ~2.9 Ga (Hickman, 2023) allowed for subaerial emergence, enhanced continental weathering, and the drawdown of atmospheric CO2, providing suitable conditions for the development of continental glaciers. In addition, muted S-MIF signatures reported from Pongola strata may hint to atmospheric oxidation and destabilisation of greenhouse methane (Ono et al., 2006). However, there is no intracratonic record for the 2.90 to 2.87 Ga time interval apart from the Kaapvaal Craton, necessitating a search for glacial deposits in Archaean greenstone successions that formed around that time, but under deeper water conditions. The presence of continental ice sheets may explain well developed sedimentary cyclicity recorded in the Pongola Supergroup (Beukes and Cairncross, 1991) due to glacio-eustatic sea-level changes.

### Acknowledgements

AH is supported by the DST-NRF Centres of Excellence CIMERA and Palaeosciences (Grant 86073) and thanks AngloGold-Ashanti for access to drill core samples. INB is supported by US-NSF grant 1822977. We thank Hartwig Frimmel for review. This article is dedicated to the memory of Nic Beukes, who kindly provided the PNG core logs.

Editor: Romain Tartèse

### Additional Information

**Supplementary Information** accompanies this letter at https:// www.geochemicalperspectivesletters.org/article2319.





© 2023 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0

License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at https://www.geochemicalperspectivesletters.org/copyright-and-permissions.

Cite this letter as: Hofmann, A., Bindeman, I.N. (2023) Earth's first glaciation at 2.9 Ga revealed by triple oxygen isotopes. *Geochem. Persp. Let.* 26, 20–24. https://doi.org/10.7185/geochemlet.2319

### References

- BEUKES, N.J., CAIRNCROSS, B. (1991) A lithostratigraphic-sedimentological reference profile for the Late Archaean Mozaan Group, Pongola Sequence: application to sequence stratigraphy and correlation with the Witwatersrand Supergroup. South African Journal of Geology 94, 44–69. https://journals. co.za/doi/10.10520/AJA10120750\_593
- BINDEMAN, I.N. (2021) Triple Oxygen Isotopes in Evolving Continental Crust, Granites, and Clastic Sediments. *Reviews in Mineralogy and Geochemistry* 86, 241–290. https://doi.org/10.2138/rmg.2021.86.08
- BINDEMAN, I.N., BEKKER, A., ZAKHAROV, D.O. (2016) Oxygen isotope perspective on crustal evolution on early Earth: A record of Precambrian shales with emphasis on Paleoproterozoic glaciations and Great Oxygenation Event. *Earth and Planetary Science Letters* 437, 101–113. https://doi.org/10.1016/j. epsl.2015.12.029
- BINDEMAN, I.N., ZAKHAROV, D.O., PALANDRI, J., GREBER, N.D., DAUPHAS, N., RETALLACK, G.J., HOFMANN, A., LACKEY, J.S., BEKKER, A. (2018) Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. *Nature* 557, 545–548. https://doi.org/10.1038/s41586-018-0131-1
- DE KOCK, M.O., LUSKIN, C.R., DJEUTCHOU, C., WABO, H. (2021) Chapter 12 -The Precambrian drift history and paleogeography of the Kalahari craton. In: PESONEN, L.J., SALMINEN, J., ELMING, S.-Å., EVANS, D.A.D., VEIKKOLAINEN, T. (Eds.) Ancient Supercontinents and the Paleogeography of Earth. Elsevier, Netherlands, 377–422. https://doi.org/10.1016/B978-0-12-818533-9.00019-9
- EICKMANN, B., HOFMANN, A., WILLE, M., BUI, T.H., WING, B.A., SCHOENBERG, R. (2018) Isotopic evidence for oxygenated Mesoarchaean shallow oceans. *Nature Geoscience* 11, 133–138. https://doi.org/10.1038/s41561-017-0036-x
- GASCHNIG, R.M., RUDNICK, R.L., MCDONOUGH, W.F., KAUFMAN, A.J., VALLEY, J.W., HU, Z., GAO, S., BECK, M.L. (2016) Compositional evolution of the upper continental crust through time, as constrained by ancient glacial diamictites. *Geochimica et Cosmochimica Acta* 186, 316–343. https://doi.org/10. 1016/j.gca.2016.03.020
- GUMSLEY, A., OLSSON, J., SÖDERLUND, U., DE KOCK, M., HOFMANN, A., KLAUSEN, M. (2015) Precise U-Pb baddeleyite age dating of the Usushwana Complex, southern Africa – Implications for the Mesoarchaean magmatic and sedimentological evolution of the Pongola Supergroup, Kaapvaal Craton. *Precambrian Research* 267, 174–185. https://doi.org/10.1016/j.precamres. 2015.06.010
- HEARD, A.W., AARONS, S.M., HOFMANN, A., HE, X., IRELAND, T., BEKKER, A., QIN, L. DAUPHAS, N. (2021) Anoxic continental surface weathering recorded by the 2.95 Ga Denny Dalton Paleosol (Pongola Supergroup, South Africa). Geochimica et Cosmochimica Acta 295, 1–23. https://doi.org/10. 1016/j.gca.2020.12.005
- HICKMAN, A.H. (2023) Archean Evolution of the Pilbara Craton and Fortescue Basin. Modern Approaches in Solid Earth Sciences, v. 24, Springer Nature, Cham. https://doi.org/10.1007/978-3-031-18007-1
- HOFMANN, A., JODDER, J., XIE, H., BOLHAR, R., WHITEHOUSE, M., ELBURG, M. (2022) The Archaean geological history of the Singhbhum Craton, India – a proposal for a consistent framework of craton evolution. *Earth-Science Reviews* 228, 103994. https://doi.org/10.1016/j.earscirev.2022.103994
- LUSKIN, C., WILSON, A., GOLD, D., HOFMANN, A. (2019) The Pongola Supergroup: Mesoarchaean Deposition Following Kaapvaal Craton Stabilization. In: KRÖNER, A., HOFMANN, A. (Eds.) The Archaean Geology of the Kaapvaal Craton, Southern Africa. Springer Nature, Cham, 225–254. https://doi. org/10.1007/978-3-319-78652-0\_9

- MARTIN, D.M., STANISTREET, I.G., CAMDEN-SMITH, P.M. (1989) The interaction between tectonics and mudflow deposits within the main conglomerate formation in the 2.8–2.7 Ga Witwatersrand Basin. *Precambrian Research* 44, 19–38. https://doi.org/10.1016/0301-9268(89)90074-0
- NESBITT, H.W., YOUNG, G.M. (1982) Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* 299, 715–717. https://doi.org/10.1038/299715a0
- ONO, S., BEUKES, N.J., RUMBLE, D., FOGEL, M.L. (2006) Early evolution of atmospheric oxygen from multiple-sulfur and carbon isotope records of the 2.9 Ga Mozaan Group of the Pongola Supergroup, Southern Africa. *South African Journal of Geology* 109, 97–108. https://doi.org/10.2113/gssajg.109. 1-2.97
- OSSA, F.O., HOFMANN, A., WILLE, M., SPANGENBERG, J.E., BEKKER, A., POULTON, S.W., EICKMANN, B., SCHOENBERG, R. (2018) Aerobic iron and manganese cycling in a redox-stratified Mesoarchean epicontinental sea. *Earth and Planetary Science Letters* 500, 28–40. https://doi.org/10.1016/j.epsl.2018.07.044
- PAPRIKA, D., HOFMANN, A., AGANGI, A., ELBURG, M., XIE, H., HARTMANN, S. (2021) Age of the Dominion-Nsuze Igneous Province, the first intracratonic Igneous Province of the Kaapvaal Craton. *Precambrian Research* 363, 106335. https://doi.org/10.1016/j.precamres.2021.106335
- SENGUPTA, S., PACK, A. (2018) Triple oxygen isotope mass balance for the Earth's oceans with application to Archean cherts. *Chemical Geology* 495, 18–26. https://doi.org/10.1016/j.chemgeo.2018.07.012
- SHEPPARD, S.M.F., GILG, H.A. (1996) Stable isotope geochemistry of clay minerals: "The story of sloppy, sticky, lumpy and tough" Cairns-Smith (1971). Clay Minerals 31, 1–24. https://doi.org/10.1180/claymin.1996.031.1.01
- SIAHI, M., HOFMANN, A., HEGNER, E., MASTER, S. (2016) Sedimentology and facies analysis of Mesoarchaean carbonate rocks of the Pongola Supergroup, South Africa. *Precambrian Research* 278, 244–264. https://doi.org/10.1016/ j.precamres.2016.03.004
- SURMA, J., ASSONOV, S., STAUBWASSER, M. (2021) Triple Oxygen Isotope Systematics in the Hydrologic Cycle. *Reviews in Mineralogy and Geochemistry* 86, 401– 428. https://doi.org/10.2138/rmg.2021.86.12
- VON BRUNN, V., GOLD, D.J.C. (1993) Diamictite in the Archean Pongola Sequence of southern Africa. Journal of African Earth Sciences 16, 367–374. https://doi. org/10.1016/0899-5362(93)90056-V
- WIEBOLS, J.H. (1955) A suggested glacial origin for the Witwatersrand conglomerates. Transactions of the Geological Society of South Africa 58, 367–382. https:// journals.co.za/doi/10.10520/AJA10120750\_2097
- YOUNG, G.M., VON BRUNN, V., GOLD, D.J.C., MINTER, W.E.L. (1998) Earth's Oldest Reported Glaciation: Physical and Chemical Evidence from the Archean Mozaan Group (~2.9 Ga) of South Africa. *The Journal of Geology* 106, 523–538. https://doi.org/10.1086/516039
- ZEH, A., WILSON, A.H. (2022) U-Pb-Hf isotopes and shape parameters of zircon from the Mozaan Group (South Africa) with implications for depositional ages, provenance and Witwatersrand–Pongola Supergroup correlations. *Precambrian Research* 368, 106500. https://doi.org/10.1016/j.precamres. 2021.106500





 $$\ensuremath{\mathbb{C}}\xspace$  2023 The Authors Published by the European Association of Geochemistry

# Earth's first glaciation at 2.9 Ga revealed by triple oxygen isotopes

## A. Hofmann, I.N. Bindeman

### **Supplementary Information**

The Supplementary Information includes:

- > Methods
- Supplementary Tables S-1 to S-3
- ➢ Supplementary Figures S-1 to S-5
- Supplementary Information References

### Methods

Major element contents of powdered samples were determined using a Panalytical MagiX PRO X-ray fluorescence spectrometer housed at the University of Johannesburg's SPECTRUM analytical facility on fusion discs. USGS and GSJ standard reference samples were used for calibration (Table S-2). Detection limits are conservatively estimated at 0.05 wt. %. CIA values were determined using the procedure of Nesbitt and Young (1982), with CaO corrected for apatite content only as samples lack carbonate.

Raman analyses were carried out on thin sections using a WITec alpha300R confocal laser Raman microscope configured with a frequency-doubled Nd-YAG laser (wavelength 532 nm) at the Department of Geology, University of Johannesburg. Raman spectra and maps were collected using a 20× Nikon objective. A laser power of 4 mW was used to prevent thermal degradation of magnetite. Beam centering and Raman spectra calibration were performed before spectral acquisition using a Si standard (111).

Measurement of <sup>17</sup>O values relied on 1–2 mg of material after drying them under vacuum at 200 °C overnight in a vacuum oven. The oxygen from the samples was extracted by a 35 W MIR-10 Laser, using BrF<sub>3</sub>-laser fluorination line coupled with a MAT253 mass spectrometer at University of Oregon, USA (Bindeman *et al.*, 2022). The extracted O<sub>2</sub> was purified by first cryogenic purification, then via boiling Hg, and then frozen on the first 5A molecular sieve held at LN2 temperatures. We then used a home-built GC-based purification system and passed O<sub>2</sub> in the flow of He (10 mL/min) through 5A 8-ft-long column. This separates O<sub>2</sub> from NF<sub>x</sub> components causing molecular interferences on mass 33. Gas was then frozen on the second molecular sieve loop by LN2 and further purified by an ethanol-dry ice slush at -114 °C to further remove any molecules interfering with mass 33 (e.g., NF). The gas was then frozen on a zeolite finger in front of the mass spectrometer and expanded into bellows; it was analysed in dual inlet mode for 3 cycles of eight repetitions each against gas from the University of Washington, calibrated relative to VSMOW. A set of international (SCO, UWG-2) and in-house standards comprising of chert (KFKS, Miller *et al.*, 2020) were used to calibrate the raw values with respect to the VSMOW scale. Typically, long-term mantle (SCO) value we obtain is  $\Delta'^{17}O_{0.528} = -0.037$  ‰ and we adjusted measured values downward by 10–20 ppm  $\Delta'^{17}O$  to match the theoretical values of standards, and this amount of adjustment stayed constant for two years across different sessions, likely reflecting



differences in calibration of solid standards among different labs, as well as values of accepted working reference gas standard. The analytical precision of the silicate standards was  $\pm 0.2$  % for  $\delta^{18}$ O and  $\pm 0.01$  % for  $\Delta'^{17}$ O.

In a different set of runs, we loaded 2–4 mg of powdered samples into Ag cups and dried them overnight at 200 °C in a vacuum oven to drive away any absorbed water.  $\delta^2$ H ( $\delta$ D) of bulk samples and amount of water was analysed by TCEA method, following the protocol in Hudak *et al.* (2022). We used a glassy carbon reactor and crucibles were held at 1450 °C in a He flow. Analyses were performed in a continuous flow mode and the data was reduced with respect to concurrently run water and slid standards (USGS mica and water welded in Ag tubes). Precision for  $\delta$ D is ±1–3 ‰ and 0.02–0.03 ‰ for [H<sub>2</sub>O]tot.

# Using bulk chemical composition of analysed rocks for correct $1000 \ln \alpha^{18} O_{shale-water}$ , $1000 \ln \alpha^{17} O_{shale-water}$ fractionation equations

We used  $1000 \ln \alpha^{18} O_{\text{shale-water}}$ ,  $1000 \ln \alpha^{17} O_{\text{shale-water}}$ , *vs. T* parametrisations as employed in Bindeman *et al.* (2018). Briefly, it finds the "bulk shale"- water curve based on estimated proportions of quartz (highest fractionation factor) *vs.* illite (lowest fractionation factor) by a linear combination of  $A/T^2 + B/T$  equations, where coefficients are  $A = 4.28 \times 10^6$  and B = -3500 for quartz (from Sharp *et al.*, 2016) and  $A = 3.8257 \times 10^6$  and B = -5661 for illite (reapproximated for low-T using two parameters after Zheng (1993) as in Bindeman *et al.* (2018). We used a parameter Q that ranges from 0 (100 % illite, most mafic shales) to 0.2 (20% quartz, 80% illite, most silicic shales in this database) to find  $1000 \ln \alpha^{18} O_{\text{shale-water}}$  fractionation equation for each sample.  $1000 \ln \alpha^{17} O_{\text{shale-water}}$  in this work was set to follow curvature for quartz as other minerals plot insignificantly above and below  $\Delta^{17} O vs. \delta^{18} O$  fractionation curves based on theoretical calculations (Schauble and Young, 2021).

In order to derive Q parameters, we used whole rock major element analysis of shales and CIPW norms. Then, we selected fractionation factors for all normative minerals from an online fractionation factor database (<u>http://alphadelta.ggl.ulaval.ca</u>) to compute weighted average mineral-water <sup>18</sup>O fractionation factors. Normative magnetite and corundum in CIPW norms were substituted with goethite and gibbsite as these minerals, as a best approximation, likely represented precursors in the protolith of shales and diamictites. Fractionation factors were later positioned on superimposed illite–water and quartz–water vs. temperature curves and were plotting in between these two endmembers with comparable curvature (cf. Bindeman et al., 2018). We used a meteoric water line equation from Luz and Barkan (2010) for the modern world, to numerically solve a system of two fractionation equations (for <sup>18</sup>O<sub>water</sub>, <sup>17</sup>O<sub>water</sub>) to compute  $\delta^{18}$ O<sub>w</sub> and  $\Delta^{17}$ O<sub>w</sub> and *T* in equilibrium with each sample. Note that an updated MWL from Surma et al. (2021) overlaps with Luz and Barkan (2010) equation in -3 to -30  $\% \delta^{18}$ O range. We used either bulk shale/diamictite values as input parameters, or "computed weathering product, WP" values, which were obtained by subtracting detrital igneous crust from each sample (+6.5 ‰, -0.06 ‰) by relying on CIA. Results of both calculations are shown in Table S-3, providing comparable values of computed equilibrium waters ( $\delta^{18}O_w = -18.9$  % and -20.9 % respectively) and temperature (37.8 °C and 41.2 °C, respectively) of interaction for modern MWL by using bulk or weathering product input parameters. The meaning of the temperature is likely a combination of weathering and diagenetic signatures, and represent diffusional closure of water-rock interaction at ~2.9 Ga. We also present results of calculations for a different value of the mantle (SCO standard) of -0.052 ‰ (Sharp and Wostbrock, 2021) and such assumption result in -20 ‰ water at 32 °C. Sensitivity analysis was performed and results in  $\pm 3$  °C and  $\pm 1.2$  ‰  $\delta^{18}O_w$ difference between identical samples with Q ranging by 0.11.

We then used measured  $\delta^{18}$ O and  $\Delta^{17}$ O values, and an Archaean MWL equation  $\delta^{17}$ O<sub>w</sub> =  $0.528 \times \delta^{18}$ O<sub>w</sub> + 0.078, corresponding to starting seawater value of -5 ‰ (as used in Bindeman, 2021). Results of these calculations give  $-26.3 \ \text{\%} \ \delta^{18}$ O<sub>w</sub> values and 7 °C temperature.

# Effects of dehydration and then hydration on triple O isotopic value of rocks upon greenschist facies metamorphism: preservation of protolithic isotopic values

We consider measured whole-rock parameters  $\delta^{18}$ O,  $\Delta^{17}$ O to be mostly reflecting the original breaking/creation of Si-O and Me-O bonds during weathering/diagenesis (e.g., Savin and Epstein, 1970; Bindeman, 2021) and that metamorphic



cycling would not change them significantly, while  $\delta D$  are affected more. We estimated potential effects of metamorphic devolatilisation on O and H isotopes by assuming a starting concentration of 6 wt. % H<sub>2</sub>O in equilibrium with shale. Water content decreases to 2 wt. % while fractionation factors (tabulated in <u>http://alphadelta.ggl.ulaval.ca</u>) are following the T path, and fluid is removed in a Rayleigh manner. In all cases lighter  $\delta^{18}O$  (heavier  $\Delta^{17}O$ ) water is lost and heavier  $\delta D$  water is lost conforming to the sense of isotope fractionation (Sharp, 2017). Values of  $\delta^{18}O$  increase by 0.4–0.52 ‰ and  $\Delta^{17}O$  decrease by 0.004 ‰ in the residual rock regardless of batch *vs*. Rayleigh process (see Fig. 7 in Bindeman, 2021 for the magnitude of diagenetic changes in a Texas drillcore). Values of  $\delta D$  decrease by ~20 ‰ (Ripley *et al.*, 1992). We did not consider the effects of dehydrogenisation (molecular H<sub>2</sub> loss, leading to heavier  $\delta D$  values; Kyser *et al.*, 1986), nor effects of organic volatilisation.

If the subsequent dehydrated rock is hydrated upon retrogression, sources of fluids are likely mantle or crustal waters with  $\delta^{18}$ O,  $\Delta^{17}$ O and  $\delta$ D values of ca. +6 ‰, -0.06 ‰ and +60 ± 20 ‰, respectively. Adding 2 wt. % of such water to an assemblage leads to an increase of 0.25 ‰ in  $\delta^{18}$ O, decrease of -0.002 ‰ in  $\Delta^{17}$ O somewhat compensating devolatilisation changes, but causes an increase of up to 50 ‰  $\delta$ D values, respectively. If a heavier (0 ‰) seawater were added it will lead to a heavier value.

### **Supplementary Tables**

**Table S-1**Hydrogen and oxygen isotope data.

**Table S-2**Major element data (anhydrous basis) and CIA from samples of Klipwal Mine. Data of PNG2 samplefrom Ossa *et al.* (2018).

 Table S-3
 Computed temperatures and isotopic values of meteoric waters in equilibrium with samples computed with various assumptions shown.

Tables S-1 through S-3 (.xlsx) are available for download from the online version of this article at <u>https://doi.org/10.7185/geochemlet.2319</u>.



# **Supplementary Figures**



**Figure S-1** Stratigraphic column of the top of the Hlashana Formation and overlying Delfkom Formation in the Klipwal Mine area (modified after von Brunn and Gold, 1993).





**Figure S-2** Results of Raman spectroscopy of shale sample KWA16. (a) Photomicrograph in plane-polarised light; box shows the area shown in (b). (b) Photomicrograph in reflected light; box shows the area of Raman mapping in subsequent images. (c–e) Raman maps showing the distribution of selected minerals. Brighter areas within Raman maps reflect higher intensities of mineral-specific spectra. Abundance of some minerals may be exaggerated due to peak overlaps. (f) Raman spectra of detected minerals.



**Figure S-3** Results of Raman spectroscopy of diamictite sample KWC6. (a) Photomicrograph in plane-polarised light; box shows the area shown in (b). (b) Photomicrograph in reflected light; box shows the area of Raman mapping in subsequent images. (c–g) Raman maps showing the distribution of detected minerals. Brighter areas within Raman maps reflect higher intensities of mineral-specific spectra. Abundance of some minerals may be exaggerated due to peak overlaps. (h) Raman spectra of detected minerals.





Figure S-4Logs of borehole cores PNG 2 and PNG 3. Pongola strata are unconformably overlain by the Permo-Carboniferous Dwyka Group of the Karoo Supergroup.





**Figure S-5** Values of  $\delta^{18}$ O *vs.*  $\delta$ D. Note the lack of correlation between the two isotope systems.

### **Supplementary Information References**

- Bindeman, I.N. (2021) Triple Oxygen Isotopes in Evolving Continental Crust, Granites, and Clastic Sediments. *Reviews in Mineralogy and Geochemistry* 86, 241–290. <u>https://doi.org/10.2138/rmg.2021.86.08</u>
- Bindeman, I.N., Zakharov, D.O., Palandri, J., Greber, N.D., Dauphas, N., Retallack, G.J., Hofmann, A., Lackey, J.S., Bekker, A. (2018) Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. *Nature* 557, 545–548. <u>https://doi.org/10.1038/s41586-018-0131-1</u>
- Bindeman, I.N., Ionov, D.A., Tollan, P.M.E., Golovin, A.V. (2022) Oxygen isotope (δ<sup>18</sup>O, Δ'<sup>17</sup>O) insights into continental mantle evolution since the Archean. *Nature Communications* 13, 3779. <u>https://doi.org/10.1038/s41467-022-31586-9</u>
- Hudak, M.R., Bindeman, I.N., Watkins, J.M., Lowenstern, J.B. (2022) Hydrogen isotope behavior during rhyolite glass hydration under hydrothermal conditions. *Geochimica et Cosmochimica Acta* 337, 33–48. <u>https://doi.org/10.1016/j.gca.2022.09.032</u>
- Kyser, T.K. (1986) Chapter 5. Stable Isotopic Variations in the Mantle. *Reviews in Mineralogy and Geochemistry* 16, 141–164. https://doi.org/10.1515/9781501508936-010
- Luz, B., Barkan, E. (2010) Variations of <sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O in meteoric waters. *Geochimica et Cosmochimica Acta* 74, 6276–6286. <u>https://doi.org/10.1016/j.gca.2010.08.016</u>



- Miller, M.F., Pack, A., Bindeman, I.N., Greenwood, R.C. (2020) Standardizing the reporting of Δ'<sup>17</sup>O data from high precision oxygen triple-isotope ratio measurements of silicate rocks and minerals. *Chemical Geology* 532, 119332. https://doi.org/10.1016/j.chemgeo.2019.119332
- Nesbitt, H.W., Young, G.M. (1982) Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* 299, 715–717. <u>https://doi.org/10.1038/299715a0</u>
- Ossa, F.O., Hofmann, A., Wille, M., Spangenberg, J.E., Bekker, A., Poulton, S.W., Eickmann, B., Schoenberg, R. (2018) Aerobic iron and manganese cycling in a redox-stratified Mesoarchean epicontinental sea. *Earth and Planetary Science Letters* 500, 28–40. <u>https://doi.org/10.1016/j.epsl.2018.07.044</u>
- Ripley, E.M., Butler, B.K., Taib, N.I. (1992) Effects of devolatilization on the hydrogen isotopic composition of pelitic rocks in the contact aureole of the Duluth Complex, northeastern Minnesota, USA. *Chemical Geology* 102, 185–197. https://doi.org/10.1016/0009-2541(92)90155-X
- Savin, S.M., Epstein, S. (1970) The oxygen and hydrogen isotope geochemistry of ocean sediments and shales. *Geochimica et Cosmochimica Acta* 34, 43–63. <u>https://doi.org/10.1016/0016-7037(70)90150-X</u>
- Schauble, E.A., Young, E.D. (2021) Mass Dependence of Equilibrium Oxygen Isotope Fractionation in Carbonate, Nitrate, Oxide, Perchlorate, Phosphate, Silicate, and Sulfate Minerals. *Reviews in Mineralogy and Geochemistry* 86, 137–178. <u>https://doi.org/10.2138/rmg.2021.86.04</u>
- Sharp, Z.D. (2017) Principles of Stable Isotope Geochemistry. Second Edition, Prentice Hall, Hoboken. https://doi.org/10.25844/h9q1-0p82
- Sharp, Z.D., Wostbrock, J.A.G. (2021) Standardization for the Triple Oxygen Isotope System: Waters, Silicates, Carbonates, Air, and Sulfates. *Reviews in Mineralogy and Geochemistry* 86, 179–196. <u>https://doi.org/10.2138/rmg.2021.86.05</u>
- Sharp, Z.D., Gibbons, J.A., Maltsev, O., Atudorei, V., Pack, A., Sengupta, S., Shock, E.L., Knauth, L.P. (2016) A calibration of the triple oxygen isotope fractionation in the SiO<sub>2</sub>-H<sub>2</sub>O system and applications to natural samples. *Geochimica et Cosmochimica Acta* 186, 105–119. <u>https://doi.org/10.1016/j.gca.2016.04.047</u>
- Surma, J., Assonov, S., Staubwasser, M. (2021) Triple Oxygen Isotope Systematics in the Hydrologic Cycle. *Reviews in Mineralogy* and Geochemistry 86, 401–428. https://doi.org/10.2138/rmg.2021.86.12
- Thompson, M., Potts, P.J., Webb, P.C., Kane, J.S. (1997) GeoPT A Proficiency Test for Geoanalysis. Analyst 122, 1249–1254. https://doi.org/10.1039/A705095J
- von Brunn, V., Gold, D.J.C. (1993) Diamictite in the Archean Pongola Sequence of southern Africa. Journal of African Earth Sciences 16, 367–374. <u>https://doi.org/10.1016/0899-5362(93)90056-V</u>
- Zheng, Y.-F. (1993) Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. *Earth and Planetary Science Letters* 120, 247–263. <u>https://doi.org/10.1016/0012-821X(93)90243-3</u>

