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Supplementary Information for

Limited oxygen production in the Mesoarchean ocean

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Supplementary Text

Lithofacies and geochemistry of the Mozaan Group.

Our study focuses on well-preserved shales from the Mozaan Group, Pongola Supergroup. The Pongola Supergroup is a Mesoarchean volcano-sedimentary succession deposited ca. 2.98–2.85 Ga on the southeastern margin of the Kaapvaal Craton, South Africa (1, 2). It crops out in northern KwaZulu-Natal, Mpumalanga, and Swaziland (Fig. S1), and a significant portion of it was deposited in the same sedimentary basin as the Witwatersrand Supergroup (3). It includes two major stratigraphic units: (1) the volcano-sedimentary Nsuze Group in the lower part, and (2) the unconformably overlying sedimentary Mozaan Group composed of marine sandstone, shale, and minor BIF (3, 4). Samples were collected from drill cores TSB07-26 and PNG2 in the White Mfolozi Inlier and Nongoma areas, respectively (Figs. S1, S2). Samples from the White Mfolozi Inlier were collected across 97 m of the Ntombe Formation (Mozaan Group). The stratigraphy and data are presented in Fig. S2, Tables S1 and S2, and in Fig. 1A. Detailed petrographic analysis shows that these rocks experienced greenschist facies metamorphism and no evidence for high fluid-rock post-depositional alteration was found in the samples selected for this study (5), suggesting that isotopic compositions recorded by these samples capture the primary signals of the depositional environment. A 23 meter-thick dolerite sill of likely Mesozoic age is present at the contact between the Ntombe Formation and the underlying Sinqeni Formation. The upper part of the Sinqeni Formation in contact with this dolerite sill is composed of a thick sandstone unit of the Kwaaiman Member, which records upward deepening from an intertidal to subtidal environment (4). Except for baking of the host rock over a relatively short interval, no influence of the sill on the sedimentary succession was observed (5).

The 97 m of the Ntombe Formation intersected by the studied drill core are represented by three upward-deepening sequences. The lower 32 m-thick sequence I of the Ntombe Formation (97 to 65 m interval in the core) is characterized by dark- to light-grey and green shales and siltstones interbedded with fine- to very fine-grained dark- to light-grey sandstones (Fig. S2). Sedimentary structures in shale and siltstone beds include planar and current ripple lamination, lenticular and wavy bedding, load casts, and desiccation cracks. Sandstone beds show current ripple lamination, normal graded bedding, load casts, and mud-drapes that are locally reworked and form intraclasts (Figs. S2). These features suggest that the sediments of the lower sequence were deposited in an intertidal to shallow subtidal environment. Mn content in this section fluctuates between 0.5 and 4.4 wt.% (Fig. 1, Table S1), which is considerably higher than the average Mn content of 0.07 wt.% for shales of the Pongola Supergroup (6). The

$\delta^{15}N$ values of extracted kerogen ($\delta^{15}N_{ker}$) and bulk sediments ($\delta^{15}N_{bulk}$) vary between −2.8 and +5.2‰ and between −3.4 and +1‰ (Air-N_2), respectively, whereas $\delta^{13}C_{org}$ values vary between −30.4 and −25.8‰, and −29.2 and −25.7‰ (VPDB), respectively, for extracted kerogen and bulk sediments (Table S2; Fig. 1).

The sedimentary succession between 65 and 54 m depth, defined here as sequence II, is represented by interbedded dark- to medium-grey shales showing wavy bedding, lenticular bedding, load casts, and fluid escape structures. It was likely deposited in the deeper part of the basin (relative to sequence I), probably from deeper subtidal to fair-weather wave base settings. No evidence for subaerial exposure was observed in this interval. The average Mn content decreases upward from 2.5 to 0.1 wt.%, while water depth indicators suggest deepening. The $\delta^{15}N_{ker}$ ranges between −4.7 and +1.6‰, while the only measured $\delta^{15}N_{bulk}$ value is −0.3‰. $\delta^{13}C_{org}$ values show a slight decrease upsection, from −29.3 to −31.7‰ for both bulk sediments and extracted kerogen.

The upper 54 m of the studied interval, termed sequence III, are characterized by dark- to medium-grey shale and siltstone with intercalations of lithologies similar to those stratigraphically immediately below. In addition, very fine-grained grey to light-grey sandstone, normally grading to shale, having sharp contacts with the underlying shales, and resembling tempestite or turbidite deposits, suggests a deepening of the depositional environment, probably to between storm and fair-weather wave bases. Mn concentrations in sequence III sediments are ≤0.1 wt.%, while $\delta^{15}N_{ker}$ values are near-to-zero and $\delta^{13}C_{org}$ values are as low as −38.1‰. In the White Mfolozi Inlier, $P_{(ppm)}/Al_{(wt.\%)}$ ratios vary between 16 and 41, which is less than the average value of 87 for the upper crust (7), and is consistent with low P bioavailability under globally ferruginous oceanic conditions (8). The Mo/Al and U/Al ratios in this area decrease from shallow-water to deeper-water with only a few values from sequence I being higher than those for the upper crust (7) (Table S1). This is consistent with minimal oxidative weathering of the continents at this time (e.g., 9, 10).

Although not strictly correlative, the deeper-water chemostratigraphic equivalent of sequence III in the Nongoma area is between 2300 and 1500 m depth in drill core PNG2, where offshore-deposited shales (11, 12) have $\delta^{15}N_{ker}$ and $\delta^{13}C_{org}$ values near to 0‰, and as low as −37‰, respectively (Table S2, Fig. 1B). However, the section of the Nongoma area between 1500 and 900 m depth in drill core PNG2 (corresponding to the transition from the Ntombe Formation to the Thalu Formation) deposited near storm wave base (11), probably during an episode of sea-level fall, has similar $\delta^{13}C_{org}$ values (with an average of ~ −30‰) to sequence II. The two high $\delta^{15}N$ values up to 35‰ likely reflect post-depositional/metamorphic alteration by circulating fluids (Table S2, Fig. 1B). Although Mn concentrations in these two samples are only 0.3 wt.%, these are slightly higher than those typical of the underlying interval, which are similar to those in sequence III (≤0.1 wt.%; Table S1, Fig. 1B). In the distal Nongoma area, U/Al and Mo/Al ratios are below average values for the upper crust (7), whereas average P/Al ratios are slightly above the average value for the upper crust (87; ref. 7) (Table S1). TOC contents for samples from all sequences are below 0.7 wt.% (Table S2), partly due to organic matter remineralization through microbial respiration below the water-sediment interface (5, 12) that contributed to carbonate precipitation, but also potentially because of low organic productivity in the Mesoarchean oxygen oases with limited P supply.

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