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A trace element and Pb isotopic investigation into the provenance and deposition of stromatolitic carbonates, ironstones and associated shales of the ~3.0 Ga Pongola Supergroup, Kaapvaal Craton

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Abstract

Major and trace element, and Pb isotopic data for chemical and clastic sedimentary rocks of the Mesoarchaean Pongola Supergroup are employed to infer aspects of the provenance and depositional environment, including ambient seawater composition. Stromatolitic carbonates of the Nsuze Group were formed in a tidal-flat setting, whereas ironstones of the Mozaan Group were deposited in an outer-shelf setting during marine transgression. Geochemical criteria, employed to test for crustal contamination and diagenetic/metamorphic overprinting, demonstrate that carbonates and ironstones preserved their primary chemical signature. In comparison to other documented Precambrian stromatolites, shale-normalised REE+Y patterns for Nsuze carbonates show pronounced enrichment in middle REE, but lack strong elemental anomalies (La, Gd, Y) that are diagnostic for derivation from open marine waters. In contrast, normalised REE+Y for ironstones exhibit distinct positive La, Gd and Y anomalies. Both rock types are devoid of normalised Ce anomalies and show only minor enrichment in Eu, suggesting deposition in anoxic environments (with respect to the Ce^{3+}/Ce^{4+} redox couple) accompanied by minor high-temperature hydrothermal input. Trace element geochemical data are most consistent with deposition of Nsuze carbonates in a shallow-water epicontinental basin with restricted but variable exchange to the open-ocean and dominant fluvial input, whereas ironstone precipitated in a deeper-water, epicontinental sea. Estuarine fractionation and organic complexation due to microbial activity is possibly indicated by MREE enrichment of the carbonates, also consistent with a restricted environment.

Shales belonging to the Mozaan Group are characterised by high concentrations of Al and K relative to Ca, Na and Sr, indicative of pronounced in-situ weathering, coupled with K-metasomatism. The provenance is mixed, comprising (ultra)-mafic and granitic source rocks.

Pb isotope regression for Nsuze carbonates documents a widespread, tectono-thermal or fluid percolation event at around 2.4 Ga. Two-stage modelling of Pb isotope data, in association with published Sr and Nd isotope data, requires a source for

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Nzuse carbonates that was derived from evolved continental crust with an elevated U/Pb ratio (μ-value) and an approximate crustal residence time of ~100–600 Ma.

1. INTRODUCTION

Archaean chemical sedimentary rocks, including carbonates and banded iron formation, provide important information on the physico-chemical conditions on the Earth surface in general, and the hydrosphere in particular (e.g., Hofmann and Bolhar, 2007; Hofmann et al., 2014). Clastic sedimentary rocks, especially shales, on the other hand, hold clues to provenance and the influence of weathering processes, thus providing constraints on atmospheric conditions in the past (e.g., Wronkiewicz and Condie, 1987; Bolhar et al., 2005a). Since secondary processes, such as metamorphism, can strongly overprint primary geochemical signatures, only the best-preserved rocks should be relied on to unravel conditions in the distant past. For the Mesoarchaean time period (3.2–2.8 Ga), the best preserved supracrustal rocks can be found in South Africa, represented by the Pongola and Witwatersrand supergroups deposited on continental crust of the Kaapvaal Craton. Although metamorphism at greenschist-facies grade affected the Pongola Supergroup, textures, structures and composition of the volcano-sedimentary succession are generally well preserved (Beukes and Cairncross, 1991; Wilson et al., 2013). Several important studies on the Pongola Supergroup have recently emerged using trace element and isotope geochemistry to unravel aspects relating to seawater composition, continental weathering and oxygenation of the early atmosphere. For instances, relative fluxes of solutes from mid-oceanic ridge versus continental weathering were investigated by Alexander et al. (2008), based on REE and Nd isotopes of Mozaan ironstones. More recently, Delvigne et al. (2012) employed a combination of REE+Y data, Ge/Si ratios and Si isotopes to infer a common parental water reservoir of mixed freshwater and open ocean seawater for precipitation of both Fe- and Si-rich layers in Mozaan ironstones. Mo and Cr isotopic data obtained from Mozaan ironstones and a palaeo-weathering horizon within the Nsuze Formation were used to place the timing of oxygenic photosynthesis in the Kaapvaal Craton at around 2.95–3.0 Ga (Crowe et al., 2013; Planavsky et al., 2014), 450–700 myr before the Great Oxidation Event at 2.5–2.3 Ga (Bekker et al., 2004).

A geochemical study, comprising major and trace element, and Pb isotopic, data of marine sedimentary rocks, including stromatolitic carbonates and banded iron formation, as well as a suite of fine-grained clastic sedimentary rocks, from the Pongola Supergroup was conducted in the White Mfolozi Inlier in KwaZulu-Natal in order to better constrain the environment and tectonic setting in which sedimentation took place.

Specifically, REE and isotope geochemistry was used to (i) test if primary geochemical signatures were retained, (ii) to evaluate contributions from hydrothermal, marine and terrestrial sources, (iii) to provide geochronological constraints on the timing of deposition or thermal overprinting and (iv) to characterise source material that was available for weathering at the time of deposition.

2. REGIONAL GEOLOGY

The Archaean Pongola Supergroup is a volcano-sedimentary succession that was deposited ca. 3.0–2.9 Ga ago on continental crust of the south-eastern part of the Kaapvaal Craton (Fig. 1; Gold, 2006). It is lithologically and stratigraphically similar to the Witwatersrand Supergroup, which is well known for its rich gold mineralization. The Pongola and Witwatersrand supergroups are the oldest preserved successions of epicratonic volcanic and sedimentary rocks.

A twofold subdivision of the Pongola Supergroup has been established, namely the lower volcano-sedimentary Nsuze Group and the upper, largely sedimentary Mozaan Group (SACS, 1980; Weilers, 1990; Gold, 2006; Wilson et al., 2013). The succession has been regionally metamorphosed to lower greenschist facies, although higher metamorphic grades have been reported locally (Horvath et al., 2013; Hofmann et al., 2015). The Pongola Supergroup is exposed in a number of erosive inliers and structural remnants that extend for ca. 250 km from Amsterdam in the north to Nkandla in the south (Fig. 1) and that probably once formed part of a single sedimentary basin. The Nsuze Group rests nonconformably on granitoid rocks. Nsuze Group basement includes the Mpuluzi batholith in the Amsterdam area, which has been dated at 3107 ± 4 Ma (U–Pb single zircon; Kamo and Davis, 1994). Mukasa et al. (2013) reported two U–Pb zircon dates for Nsuze Group volcanic rocks: an andesitic flow near the base of the sequence yielded an age of 2980 ± 10 Ma, whilst a rhyolite flow further up in the stratigraphy yielded an age of 2968 ± 6 Ma. Hegner et al. (1994) reported a U–Pb single zircon date of 2985 ± 1 Ma for Nsuze Group lavas, whilst Nhleko (2003) reported a U–Pb SHRIMP zircon date of 2977 ± 5 Ma from a rhyolite flow. Lava flows are rare in the Mozaan Group. Mukasa et al. (2013) obtained a U–Pb zircon age of 2954 ± 9 Ma for an andesite lava flow within the upper part of the sedimentary succession. In contrast, a geochronological study of detrital zircons from the Mozaan Group (Nhleko, 2003) has identified zircons as young as 2902 ± 9 Ma in a sample from near the top of the sequence, suggesting that the date obtained by Mukasa et al. (2013) from the lava flow may reflect the age of a xenocrystic zircon. Emplacement of the Usushwana Complex at 2989.2 ± 0.8 Ma (U–Pb, baddeleyite, Olsson et al., 2012), much earlier than previously assumed (2873 ± 31 Ma, Sm–Nd: Hegner et al., 1984;