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Iron isotopes constrain biogeochemical redox cycling of iron and manganese in a Palaeoproterozoic stratified basin

Harilaos Tsikos [a,*], Alan Matthews [b], Yigal Erel [b], John M. Moore [a]

[a] *Geology Department, Rhodes University, Grahamstown 6140, South Africa*
[b] *Institute of Earth Sciences, Hebrew University of Jerusalem, Israel 91904, Israel*

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ABSTRACT

The Hotazel Formation in the uppermost stratigraphic portion of the Neoarchaean–Palaeoproterozoic Transvaal Supergroup of southern Africa is an unusual sedimentary sequence of banded iron-formation (BIF) intercalated with three manganese-rich layers. As such, it is a succession that holds great potential to offer a unique view of one of the most dramatic transitions in early Earth history — the switch to a full oxidative cycle in shallow oceans at *ca.* 2.3 Ga. We present iron isotope results from BIF and Mn-rich samples collected across the entire Hotazel sequence, with a view to constraining processes of biogeochemical redox cycling for both metals close to the transition from a reducing to an oxidizing ocean–atmosphere system. The recorded de-coupling of Fe- and Mn reduction during anaerobic organic carbon cycling in the Hotazel strata, suggests that manganese became an important electron acceptor in stratified marine environments of the Palaeoproterozoic during periods of increased primary manganese precipitation relative to iron. Very low δ^{57}Fe values registered across the entire Hotazel sequence and especially in manganese-rich samples (-2.4 to -3.5‰) signify deposition of iron and manganese in a terminal, stratified aqueous reservoir that was depleted in the heavy iron isotopes. These isotopic signatures, in conjunction with the unusual endowment of the Hotazel sequence in manganese, are interpreted to have evolved by Rayleigh distillation processes during protracted deposition of Mn-poor BIFs as preserved in the lower stratigraphic portion of the Transvaal Supergroup (Kuruman and Griquatown BIFs). The unique end-member geochemical and isotopic characteristics of the Hotazel rocks may therefore constitute a potential link between the widespread deposition of BIF during the Neoarchaean and Palaeoproterozoic, and the postulated rise in atmospheric oxygen levels around 2.3 Ga ago.

1. Introduction

Iron and manganese are two of the principal electron acceptors in the Phanerozoic oceanic biogeochemical cycle and are commonly discussed together in the literature due to their broad similarities in terms of both geochemistry and microbiology (Canfield et al., 2005). The massive deposition of iron as banded iron formations (BIF) in the Neoarchaean and Palaeoproterozoic (2.7–2.2 Ga) also suggests that redox cycling of iron essentially has been active throughout Earth's history. Consequently, major research emphasis has been placed on the role of iron as a key redox proxy for the evolution of oxygen in the atmosphere–ocean system of the early Earth (Bekker et al., 2004; Rouxel et al., 2005; Kump 2005, 2008; Anbar et al., 2007; Kaufman et al., 2007; Kump and Barley, 2007; Lyons, 2007). Most BIFs, however, contain manganese at levels no higher than 0.5 wt.% on average (Klein, 2005). Accordingly, there has been limited discussion of manganese as a direct biogeochemical tracer of stratified marine environments of the Neoarchaean and Palaeoproterozoic, particularly in terms of biological *versus* abiotic processes of manganese oxidation in primary depositional environments and anaerobic reduction of high-valence sedimentary precursors during early diagenesis. An explanation for the very low levels of manganese recorded in most classic BIF sequences was previously sought in terms of low rates of Mn photo-oxidation relative to Fe (Anbar and Holland, 1992). More recently, emphasis has shifted towards biologically-driven iron oxidation pathways (Konhauser et al., 2007).

In this paper, we address the potential significance of manganese as a proxy of biogeochemical redox cycling and atmosphere–ocean evolution during Precambrian BIF deposition. Our approach is based on the use of iron isotope data obtained from the Hotazel Formation, a Palaeoproterozoic BIF succession in South Africa that contains the most voluminous sedimentary deposit of manganese on the Earth's continents, in the form of three discrete sedimentary layers (Laznicka, 1992). Previous research has demonstrated the potential of iron isotopes in tracking metal cycling during deposition and diagenesis of BIFs on a variety of temporal scales (Rouxel et al., 2005; Johnson et al.,

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* Corresponding author.
E-mail address: h.tsikos@ru.ac.za (H. Tsikos).

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2003, 2008a,b; Heimann et al., 2010). The strikingly inter-layered nature of the Hotazel Fe–Mn sequence and presence of iron as a common component in both the host BIF and the manganese-rich layers, provide a unique archive for examining the biogeochemical cycling of both metals in a common depositional palaeoenvironment using iron isotope geochemistry. The unusually large volume of manganese-rich sediment and very low iron isotope values across the entire Hotazel sequence recorded in this study, suggest that manganese must have been, at least transiently, an important component in mechanisms of redox cycling in Neoarchaean–Palaeoproterozoic stratified basins. The geochemical and isotopic signatures of the Hotazel deposits are assessed in the context of BIF depositional models, biological evolution, and the history of atmosphere–ocean oxygenation in the early Earth.

2. Geological background

The Hotazel Formation is an inter-layered succession of BIF and manganese-rich sedimentary rock in the stratigraphically uppermost segment of the Palaeoproterozoic Transvaal Supergroup in the Northern Cape Province of South Africa (Fig. 1A). The lower part of the Transvaal Supergroup in this area (Ghaap Group) spans the age bracket 2.64–2.45 Ga (Pickard, 2003; Beukes and Gutzmer, 2008) and is dominated by a thick succession of largely dolomitic carbonates at the base (Campbellrand Subgroup), overlain by the several hundred meter thick BIF of the Kuruman–Griquatown Formations (Klein and Beukes, 1989; Beukes and Klein, 1990; Beukes et al., 1990; Beukes and Gutzmer, 2008). Stratigraphically above the latter, a glacial diamictite unit known as the Makganyene Formation (Polteau et al., 2006) marks the base of the upper portion of the Transvaal Supergroup (the Postmasburg Group; Fig. 1A). The Makganyene diamictite is overlain by a sequence of basaltic andesites belonging to the Ongeluk Formation, with characteristic pillowed structures in its upper portions suggesting sub-aqueous extrusion at least in part.

The Hotazel Formation occurs under a *ca.* 40 m-thick blanket of Tertiary sand and calcrete in an area of approximately 400 km^2 known as the Kalahari manganese field (Fig. 1A,B). It consists of three laterally continuous manganese layers inter-bedded with BIF that lie stratigraphically above the Ongeluk Formation and below Fe-bearing carbonate rocks of the Mooidraai Formation (Fig. 2). The BIF portions of the Hotazel succession are characterised by typically mm- to cm-scale laminated assemblages that are dominated by micro-crystalline quartz and magnetite in roughly equal modal proportions (Fig. 2). Diagenetic carbonates (ankerite, calcite) constitute the next most important species in terms of modal abundance, whereas Fe silicates (mainly greenalite, minnesotaite and stilpnomelane) occur in much smaller modal amounts. This mineralogy suggests only very shallow burial metamorphic overprint (essentially below 200 °C) in the Hotazel sediments (Gutzmer and Beukes, 1996; Tsikos et al., 2003). The inter-bedded manganese-rich layers are dominated by variable relative proportions of very fine-grained braunite and hematite, as well as considerable amounts (up to 40% modal on a hand-specimen scale) of manganiferous carbonate (kutnahorite and lesser manganoan calcite) in the form of mm-scale laminae and diagenetic ovoids (Gutzmer and Beukes 1996; Tsikos et al., 2003).

At the contacts between the BIF and manganese layers, transitional lutitic lithologies develop, dominated by very fine-grained hematite and diagenetic Mn-carbonate (kutnahorite, Mn-calcite, minor Mn-dolomite). The stratigraphic thicknesses of these transitional hematite lutites cannot be precisely defined due to their gradational contacts

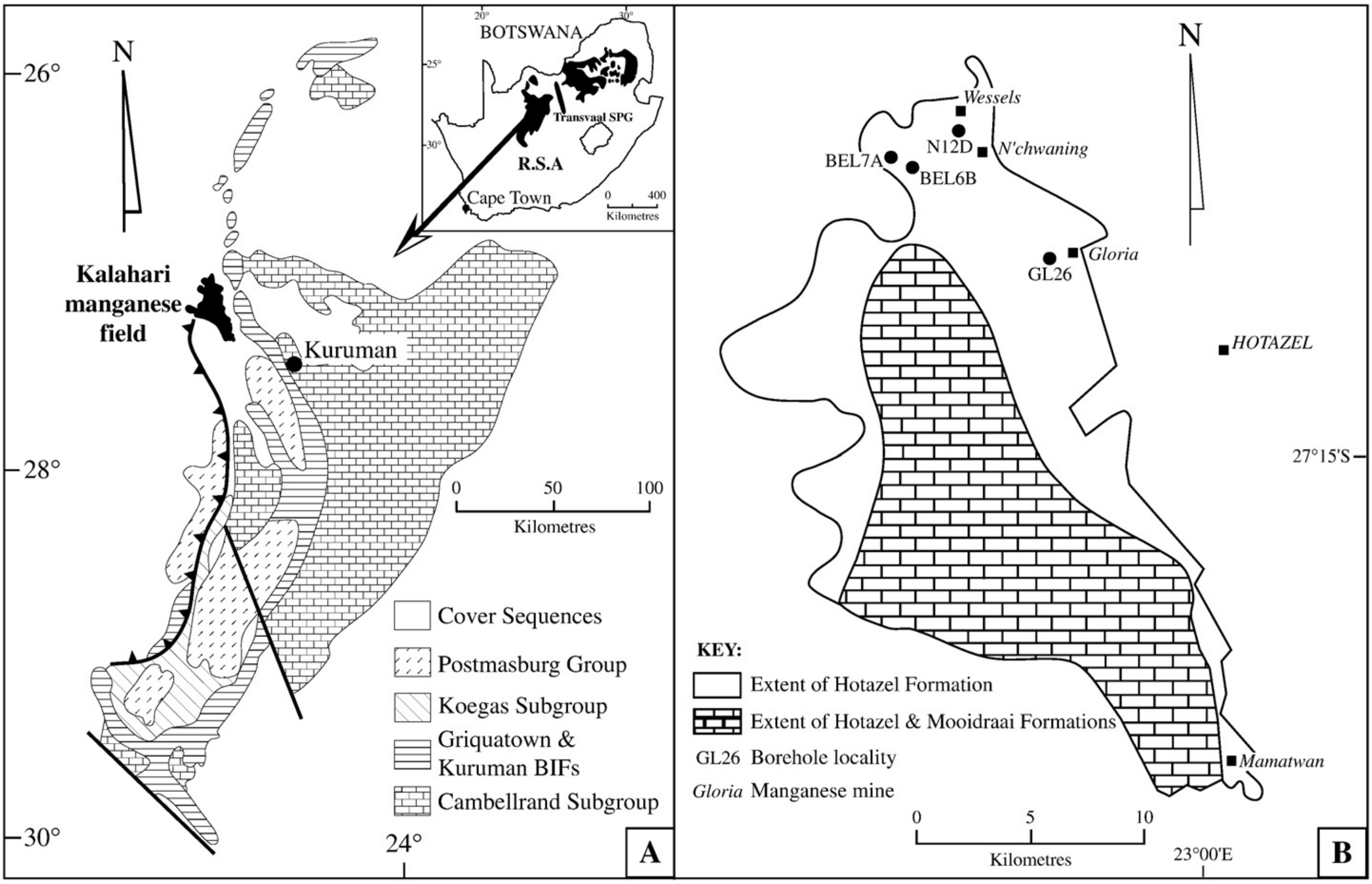

Fig. 1. (A) Geographical distribution of the Transvaal Supergroup in South Africa (inset) and simplified regional geological map of the Transvaal Supergroup in the Northern Cape Province, including the locality of the Kalahari manganese field. (B) Outline of the Kalahari manganese field including mine localities, major structural features and localities of the four drill-cores used in this study.