Earth and Planetary Science Letters 430 (2015) 43–53

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

A redox-stratified ocean 3.2 billion years ago

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ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 22 July 2015
Accepted 10 August 2015
Available online xxxx
Editor: H. Stoll

Keywords:
banded iron formation
uranium
Fe isotopes

ABSTRACT

Before the Great Oxidation Event (GOE) 2.4–2.2 billion years ago it has been traditionally thought that oceanic water columns were uniformly anoxic due to a lack of oxygen-producing microorganisms. Recently, however, it has been proposed that transient oxygenation of shallow seawater occurred between 2.8 and 3.0 billion years ago. Here, we present a novel combination of stable Fe and radiogenic U–Th–Pb isotope data that demonstrate significant oxygen contents in the shallow oceans at 3.2 Ga, based on analysis of the Manzimnyama Banded Iron Formation (BIF), Fig Tree Group, South Africa. This unit is exceptional in that proximal, shallow-water and distal, deep-water facies are preserved. When compared to the distal, deep-water facies, the proximal samples show elevated U concentrations and moderately positive δ^{56}Fe values, indicating vertical stratification in dissolved oxygen contents. Confirmation of oxidizing conditions using U abundances is robustly constrained using samples that have been closed to U and Pb mobility using U–Th–Pb geochronology. Although redox-sensitive elements have been commonly used in ancient rocks to infer redox conditions, post-depositional element mobility has been rarely tested, and U–Th–Pb geochronology can constrain open- or closed-system behavior. The U abundances and δ^{56}Fe values of the Manzimnyama BIF suggest the proximal, shallow-water samples record precipitation under stronger oxidizing conditions compared to the distal deeper-water facies, which in turn indicates the existence of a discrete redox boundary between deep and shallow ocean waters at this time; this work, therefore, documents the oldest known preserved marine redox gradient in the rock record. The relative enrichment of O_2 in the upper water column is likely due to the existence of oxygen-producing microorganisms such as cyanobacteria. These results provide a new approach for identifying free oxygen in Earth's ancient oceans, including confirming the age of redox proxies, and indicate that cyanobacteria evolved prior to 3.2 Ga.

1. Introduction

The timing of oxygenation of the world's oceans and atmosphere has long been a topic of debate. A long-standing proposal embraced by many studies is that a step-wise oxygenation of the planet occurred, with the first rise in O_2 taking place between 2.4 and 2.2 billion years ago (Ga), a time referred to as the Great Oxidation Event (GOE), and a second rise approximately 0.6 billion years ago to nearly present-day levels (Holland, 1984). The world before the GOE is thought to have been largely anoxic, where O_2 sinks out-paced O_2 sources. Recent studies, however, have called into question this strictly step-wise increase in planetary O_2 levels, instead proposing transient increases in atmospheric oxygen before the GOE as far back as 3.0 Ga (Anbar et al., 2007; Crowe et al., 2013). Kasting (1992) predicted accumulation of O_2 in the shallow oceans, termed "oxygen oases", before the GOE, but such environments would be limited to the photic zone through high biological primary productivity. Recent work has shown that oxygen oases could have been pervasive in the shallow ocean in the Archean under an essentially anoxic atmosphere (Olson et al., 2013). Geologic evidence for oxygen oases and a redox-stratified ocean has been difficult to find, especially from the earlier parts of the Archean, although this is changing. Planavsky et al. (2014), for example, used Mo isotope data from iron formations in the Pongola Basin (Kapvaal Craton, South Africa) to infer free oxygen in the oceans at 2.95 Ga, and Riding et al. (2014) used REE variations in platform carbonates at Steep Rock (Superior Craton, Canada) to in-

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http://dx.doi.org/10.1016/j.epsl.2015.08.007

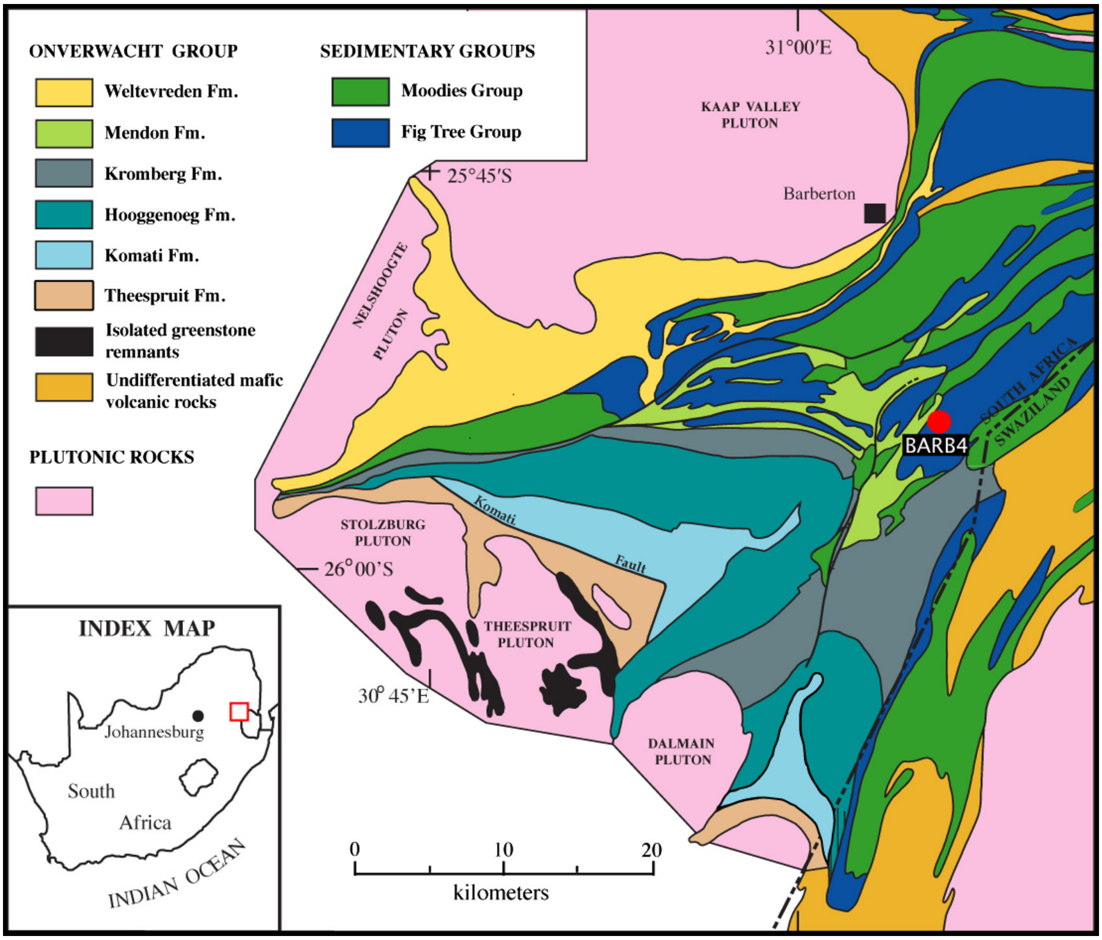

Fig. 1. Geologic map of the southwestern half of the Barberton greenstone belt showing the location of the BARB4 core drill site. Map is modified from Lowe (2013).

fer a redox-stratified ocean at 2.8 Ga. In contrast, using combined U–Pb and Fe isotope data on the 3.4 Ga Marble Bar Chert jasper (Pilbara Craton, Australia), Li et al. (2013a) argued that the oceans at that time were essentially anoxic. Although there is an emerging view that intermittent rises in oxygen likely occurred prior to the GOE (Lyons et al., 2014), little is known about the potential transitions in oxygen contents in seawater that may have occurred over the 400 Myr between deposition the Marble Bar Chert and sedimentary rocks in the Pongola Basin.

Iron-rich chemical sedimentary rocks, including jaspers and Banded Iron Formations (BIFs) formed by oxidation of reduced iron, Fe(II), in an aqueous environment, and therefore have been prominent lithologies targeted for studies of the redox conditions of the oceans and atmosphere throughout the Archean and into the Proterozoic (Johnson et al., 2003; Rouxel et al., 2005; Planavsky et al., 2012; Li et al., 2013a). Iron isotope compositions of early Archean jaspers and BIFs are enriched in the heavy isotopes relative to bulk crust (high $^{56}Fe/^{54}Fe$ ratios, or positive $\delta^{56}Fe$ values), which is interpreted to reflect partial oxidation of a reduced iron pool, indicating very low oxygen contents (Dauphas et al., 2004; Czaja et al., 2013; Li et al., 2013a). The concentrations of redox sensitive elements in BIFs, such as uranium (U), which is enriched in the oceans in its oxidized U(VI) form, have been used to argue for low O_2 contents in the oceans prior to the GOE (Partin et al., 2013). A key issue that has been largely ignored, however, is the fidelity of redox proxies in terms of post-depositional mobilization through younger fluid–rock interactions, alteration, or metamorphism. It is possible, for example, that inferences of high oxygen contents in the early Archean may reflect later fluid circulation under relatively oxidized (post-GOE) conditions; for example, using ^{238}U–^{206}Pb and ^{235}U–^{207}Pb geochronology, Li et al. (2012) showed that oxidation and U enrichment in the 3.4 Ga Apex Basalt (Pilbara Craton, Australia) occurred in the Phanerozoic and therefore does not provide a constraint on redox conditions in the early Archean as previously proposed. In this contribution, we present combined U–Th–Pb geochronology and stable Fe isotope results from the 3.23 Ga Manzimnyama BIF of the Fig Tree Group (Barberton greenstone belt, South Africa). Samples are from the BARB4 diamond-drilled scientific core, and include high-Fe and low-Fe cherts that record distinct depositional conditions which allow evaluation of redox conditions from deep- and shallow-ocean environments, respectively. Deep Archean seawater is generally thought to have been anoxic (Kamber et al., 2014), however, if oxygen was being produced by oxygenic photosynthesis, this production would likely happen in shallow water (photic zone) where cyanobacteria would thrive. Thus, the preservation of distinct deep- and shallow-water faces allows us to compare anoxic deep waters with potentially more oxygen enriched shallow waters. The unique combination of stable isotope compositions of redox-sensitive elements, and U–Th–Pb geochronology, allows us to distinguish primary signals from later fluid–rock interaction processes, which is critical for confidently inferring redox conditions in the oceans in the early Archean.

2. Geologic background and samples

The Manzimnyama BIF is part of the Fig Tree Group in the Barberton greenstone belt, South Africa (Fig. 1). The unit has also been described as a jasper or jasperlite, a term used for hematite–chert lithologies. The Barberton greenstone belt is a