



Heterogeneous redox conditions and a shallow chemocline in the Mesoproterozoic ocean: Evidence from carbon–sulfur–iron relationships

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ARTICLE INFO

Article history:

Received 10 September 2014

Received in revised form

25 November 2014

Accepted 30 November 2014

Available online 9 December 2014

Keywords:

Mesoproterozoic

Redox

Iron speciation

Sulfur isotopes

Epeiric seas

ABSTRACT

Oxygenation of Earth's oceans in the Proterozoic was a protracted process that began prior to the Great Oxidation Event (GOE) and culminated in deep ocean ventilation following Neoproterozoic glacial episodes, with both of these major thresholds accompanied by profound changes in the evolution of Earth's biosphere. Our understanding of the redox structure of Mesoproterozoic oceans, however, is considerably less certain. Limited proxy investigations of oceanic redox in the Mesoproterozoic have focused largely on early Mesoproterozoic shelf to basinal settings, with comparatively little attention paid to epeiric sea environments that dominate the late Mesoproterozoic sedimentary record. Here we report multi-proxy shale redox data from epicratonic and pericratonic environments of the 1.1 Ga Atar and El Mreiti Groups, Taoudeni Basin, Mauritania. These strata were deposited across the West African craton during global sea level highstand, and provide insight into the redox structure of Mesoproterozoic epeiric seas. Iron speciation, pyrite sulfur isotope, and trace metal concentration data suggest a shallow chemocline and highly heterogeneous redox conditions, with fundamental heterogeneities in sulfate concentration and the extent and persistence of euxinia between onshore and offshore environments. We suggest that a protracted increase in biospheric oxygenation in the late Mesoproterozoic was accompanied by unstable and heterogeneous redox conditions in shallow, nearshore areas, contributing to the fragmentary pattern of early eukaryotic evolution and diversification.

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1. Introduction

The oxygenation of Earth's surface environments was a protracted process that occurred over nearly two billion years of the Proterozoic Eon (Kah et al., 2004; Canfield, 2005; Och and Shields-Zhou, 2012; Lyons et al., 2014). Sustained oxygenation began at ~2.3 Ga during the Great Oxidation Event, which expanded delivery of oxidative weathering products to the marine system (Holland, 2006; Guo et al., 2009). Persistent deep-ocean ventilation (cf. Kump et al., 2011) did not occur until the end of the Neoproterozoic (Canfield et al., 2007, 2008; Och and Shields-Zhou, 2012; Sahoo et al., 2012), however, and low-oxygen, stratified ocean conditions

were likely widespread until at least the Ordovician (Gill et al., 2011; Zhang et al., 2011; Thompson and Kah, 2012).

Through the Proterozoic, major thresholds of oxygenation were accompanied by dramatic changes in Earth's biosphere, from the initial appearance of eukaryotes in the Paleoproterozoic (Han and Runnegar, 1992; Rasmussen et al., 2008) to the origin and diversification of animals in the terminal Neoproterozoic (Xiao et al., 1998; McFadden et al., 2008). Patterns of biological diversity in the Mesoproterozoic, however, are more complex. Eukaryotic diversity remained limited through much of the Mesoproterozoic (Knoll, 1994), and although a moderate diversity of photosynthetic protists is recorded in early Mesoproterozoic strata (Xiao et al., 1997; Javaux et al., 2003), fossils of unambiguous multicellular eukaryotes do not appear until the late Mesoproterozoic (Woods et al., 1998; Butterfield, 2000, 2001). Furthermore, despite evidence that early eukaryotes were restricted to nearshore settings with abundance and diversity decreasing sharply offshore (Buick and Knoll, 1999; Javaux et al., 2001), molecular evidence suggests that many nearshore environments were devoid of eukaryotic influence (Brocks et al., 2005; Blumenberg et al., 2012).

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Complex patterns of eukaryotic diversity in the Mesoproterozoic may reflect an equally complex redox structure of marine environments. Distal shelf to basinal settings of the Mesoproterozoic appear to have been strongly anoxic, and variably sulfidic (Shen et al., 2002, 2003; Poulton et al., 2004) or ferruginous (Poulton et al., 2010; Planavsky et al., 2011; Scott et al., 2012). Multiple lines of evidence, however—including increased carbon isotopic variability (Kah et al., 1999; Frank et al., 2003), an increase in marine sulfate concentration (Kah et al., 2004), the widespread appearance of marine gypsum (Kah et al., 2001, 2012), and increased oxidative sulfur cycling in marine and terrestrial environments (Johnston et al., 2005b; Parnell et al., 2010)—suggest a moderate increase in biospheric oxygen in the late Mesoproterozoic. Oxygenation may have resulted in increased delivery of bioessential nutrients to the marine system, thereby fostering eukaryotic diversification in nearshore settings (Anbar and Knoll, 2002). Few studies have examined the redox structure of late Mesoproterozoic nearshore environments, however, leaving us unable to directly relate patterns of eukaryotic diversification to redox conditions in nearshore areas where early eukaryotes were most common.

Here we report multiproxy redox data from epicratonic and pericratonic strata of the 1.1 Ga Atar and El Mreiti Groups, Taoudeni Basin, Mauritania, which provide a direct window into shallow ocean redox conditions in the late Mesoproterozoic. These strata were deposited during global sea level highstand when much of the West African craton was flooded with a shallow epeiric sea (Bertrand-Sarfati and Moussine-Pouchkine, 1988; Kah et al., 2012). In this study we examine iron speciation, pyrite sulfur isotopes, and the concentration of redox-sensitive trace metals (Mo, V, Zn, and Mn) in shale deposited across an onshore to offshore depth transect. We then present a detailed reconstruction of the redox structure of

the epeiric sea, and discuss our data within the broader context of Earth's biogeochemical evolution during the Mesoproterozoic.

2. Geologic background

2.1. Taoudeni Basin stratigraphy

The Taoudeni Basin is an extensive (>1,750,000 km²) intracratonic sedimentary basin in present-day Mauritania, Mali, and Algeria (Fig. 1). Basement rocks of the West African craton are exposed to both the north (Reguibat Shield) and south (Leo-Man Shield) of the basin, and consist of deformed Archean amphibolite and quartzo-feldspathic gneiss, along with Paleoproterozoic granitic intrusions (Trompette and Carozzi, 1994; Villeneuve and Corn  e, 1994; Shofield et al., 2006). Initiation of sedimentation in the Taoudeni Basin is marked by siliciclastic strata of the Char (in Mauritania) and Douik (in Algeria) Groups (Benan and Deynoux, 1998; Rahmani et al., 2009), which were deposited during active extension of the basement. The thickness of basal siliciclastic strata varies dramatically from 0 to >400 m in outcrop (Benan and Deynoux, 1998), with even greater thicknesses observed in the subsurface (Rahmani et al., 2009).

A basinwide unconformity marks the boundary between the Char Group and overlying strata of the Atar and El Mreiti Groups, and marks cessation of extensional tectonics and formation of a regional peneplain (Bertrand-Sarfati and Moussine-Pouchkine, 1988; Benan and Deynoux, 1998). Marine transgression and epeiric sea expansion then resulted in deposition of lithologically varied strata of the Atar and El Mreiti Groups, whose facies and thickness were controlled by a combination of eustatic sea level and regional subsidence (Moussine-Pouchkine and Bertrand-Sarfati, 1997; Kah et al., 2009, 2012). In Mauritania, the El Mreiti Group refers

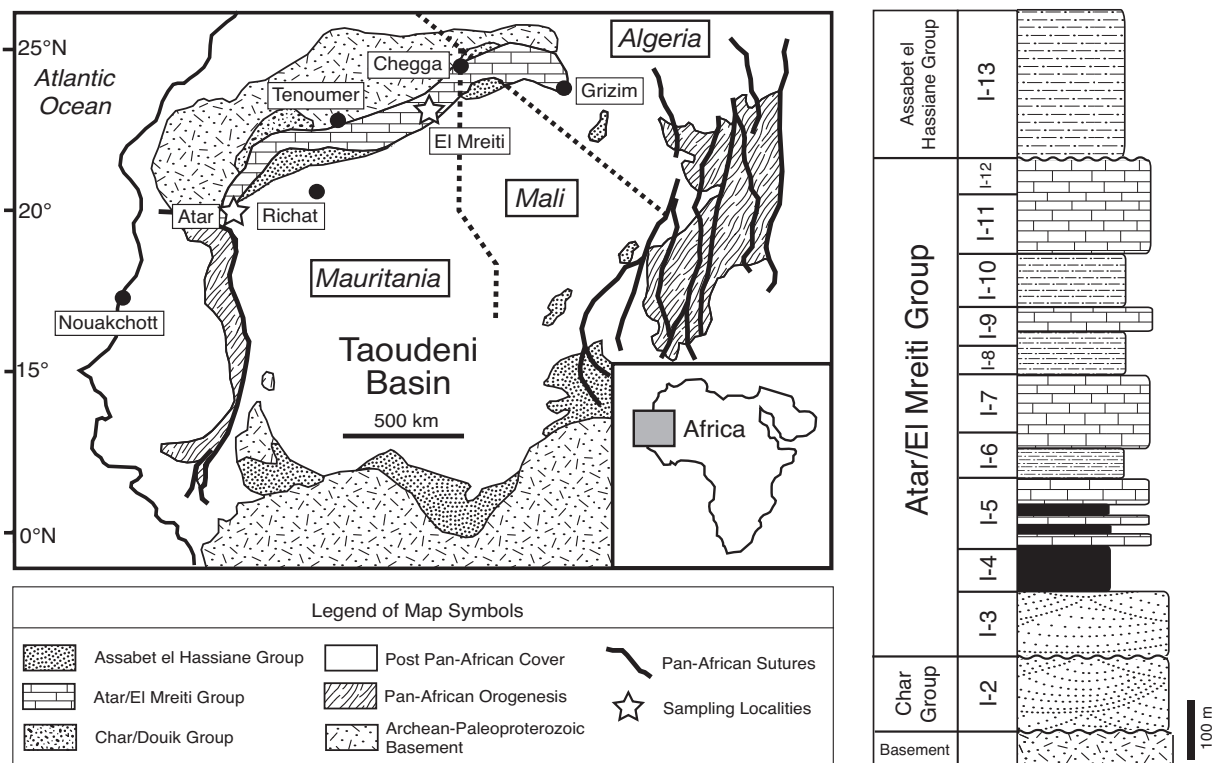


Fig. 1. Map of the Taoudeni Basin, West African craton, and generalized stratigraphy of Proterozoic strata. Strata of the Atar and El Mreiti Groups crop out along a NE–SW transect through Mauritania, northern Mali, and western Algeria. Pericratonic facies occur at both sides of the West African craton—near Atar in the west and near Grizim in the east. Epicratonic facies dominate across the central portion of the craton. Samples for this study come from drill core retrieved north of Atar and west of El Mreiti, Mauritania. The generalized stratigraphic section shown here is characteristic of the better-exposed Atar Group facies, and uses stratigraphic nomenclature of the Atar Group (units I-2 to I-13). Figure modified from Kah et al. (2009, 2012) and Gilleaudeau and Kah (2013a,b).

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