Earth and Planetary Science Letters 486 (2018) 70–83

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Two-step deoxygenation at the end of the Paleoproterozoic Lomagundi Event

Frantz Ossa Ossa [a,*], Benjamin Eickmann [a,b], Axel Hofmann [a], Noah J. Planavsky [c], Dan Asael [c], Florent Pambo [d], Andrey Bekker [e,a]

[a] Department of Geology, University of Johannesburg, 2092 Johannesburg, South Africa
[b] Department of Geosciences, University of Tübingen, 72074 Tübingen, Germany
[c] Department of Geology & Geophysics, Yale University, New Haven, CT 06511, USA
[d] Direction Mine, COMILOG SA, BP 27-28 Moanda, Gabon
[e] Department of Earth Sciences, University of California, Riverside, CA 9252, USA

ARTICLE INFO

Article history:
Received 4 August 2017
Received in revised form 12 January 2018
Accepted 14 January 2018
Available online xxxx
Editor: D. Vance

Keywords:
Paleoproterozoic
Lomagundi Event
eukaryotes
deoxygenation
Francevillian Group

ABSTRACT

The ca. 2.1 Ga Francevillian Group of Gabon was deposited in the aftermath of the Great Oxidation Event (GOE) and records the Lomagundi Event (LE), which is the most pronounced and long-lived carbon isotope excursion in the geologic record. Moreover, the sedimentary succession contains putative evidence for the earliest appearance of macro-eukaryotes. An emerging paradigm is that the end of the LE was accompanied by a deoxygenation event that preceded the apparent stability of environmental and redox conditions as well as the carbon cycle characteristic of the Mesoproterozoic. However, the processes that led to deoxygenation some 300 to 200 Ma after the beginning of the GOE are not well understood. Here we present a multi-proxy stable isotope (δ^{34}S, Δ^{33}S, Δ^{36}S, δ^{98}Mo, $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$, and $\delta^{18}O_{carb}$) study of the Francevillian Group. We suggest that sedimentation of the lower part of the Francevillian Group took place during the LE in oxygenated shallow waters with elevated sulfate concentrations. Two episodes of anoxic water shoaling during deposition of the upper Francevillian Group correspond with broader marine deoxygenation and a contraction of the seawater sulfate reservoir. This shoaling of anoxic conditions may be linked to intense submarine hydrothermal and volcanic activity that led to sedimentary manganese deposits. We propose that increased concentrations of aqueous, hydrothermally sourced reductants drove oxygen consumption during the first deoxygenation event and established a sulfidic oxygen-minimum zone at the margin of the shallow shelf. Carbonates with positive $\delta^{13}C_{carb}$ values characteristic of the LE precipitated during this first stage of deoxygenation. The second deoxygenation, separated from the previous event by a period of well-oxygenated conditions, was marked by a stronger contraction of the seawater sulfate reservoir and coincided with the end of the LE. During this time, widespread euxinic conditions were established in shallow (above storm wave base) marine environments. The presence of a shallow-water redoxcline points to a generally low-oxygen atmosphere–ocean system. Further, the negative co-variation between δ^{34}S and δ^{13}C values in sediments of the Francevillian Group and other sedimentary successions of similar age worldwide suggests that the inferred two-step deoxygenation corresponding to the end of the LE reflects global rather than local events that likely occurred between ~2.1 and 2.05 Ga ago.

1. Introduction

The disappearance of mass-independent fractionation of sulfur isotopes (S-MIF) in the sedimentary record between ca. 2.43 and 2.31 Ga marks the Great Oxidation Event (GOE); a permanent rise of atmospheric oxygen level above $\sim 10^{-5}$ of the present atmospheric level (PAL) (Bekker et al., 2004; Gumsley et al., 2017; Luo et al., 2016; Pavlov and Kasting, 2002). The mechanisms that triggered O_2 rise at the Earth's surface and its timing remain, however, controversial. The Earth is traditionally envisioned to have undergone a two-step increase in pO_2 at the beginning and the end of the Proterozoic Eon (e.g., Lyons et al., 2014). However, an emerging view supported by a number of geochemical proxies points to transient oxygenations of the atmosphere–ocean system before the Archean–Proterozoic transition (e.g., Lyons et al., 2014

* Corresponding author.
E-mail address: ossaf@uj.ac.za (F. Ossa Ossa).

https://doi.org/10.1016/j.epsl.2018.01.009

and references therein), preceding dramatic atmospheric oscillations between ∼2.43 and 2.31 Ga ago and remarkable deoxygenation at end of the ∼2.22–2.06 Ga Lomagundi Event (LE; cf. Bekker and Holland, 2012; Gumsley et al., 2017; Kipp et al., 2017; Lyons et al., 2014; Planavsky et al., 2012; Scott et al., 2014).

The increase in atmospheric oxygen during the GOE caused profound changes in chemical weathering of exposed upper continental crust. For example, oxidation of sulfide minerals during continental weathering led to increased seawater sulfate and content of redox-sensitive elements (e.g., Mo, U, Re, Os, V, and Cr) via riverine input (Bekker and Holland, 2012; Planavsky et al., 2012; Scott et al., 2014). The late stage of the GOE is characterized by the ca. 2.22–2.06 Ga LE (Bekker, 2014; Karhu and Holland, 1996). This event is generally recognized as Earth's most extreme and long-lived carbon isotope excursion in seawater composition due to the burial of unprecedented amounts of organic carbon. It is thought to have been a driver for a further increase in atmospheric oxygen (Karhu and Holland, 1996), giving rise to a proposed oxygen overshoot and enhanced oxidative continental weathering that further increased delivery of phosphate to the oceans (Bekker and Holland, 2012). Controversially, these conditions may have facilitated the emergence of colonial and eukaryotic organisms in the middle Paleoproterozoic oceans (El Albani et al., 2010).

The end of the LE is defined by a marked decrease in $\delta^{13}C_{carb}$ values (Karhu and Holland, 1996), which has been related to a decrease in the relative burial rate of organic matter (OM) possibly coupled to decreased terrestrial phosphate flux (Bekker and Holland, 2012). The end of the LE coincides with anomalous shifts in a number of stable isotope systems. For example, negative $\delta^{13}C_{org}$ excursions are documented from the Upper Zaonega Formation in Karelia, Russia, and the Francevillian Group of Gabon (Canfield et al., 2013; Kump et al., 2011; Qu et al., 2012; Scott et al., 2014). This negative shift in $\delta^{13}C_{org}$ values has been interpreted to reflect a global event controlled by either tectonic uplift and oxidative weathering of organic matter-rich shales deposited during the LE (Kump et al., 2011; Canfield et al., 2013) or a decrease in the terrestrial phosphate flux (Bekker and Holland, 2012). In contrast, Qu et al. (2012) argued for local oil and methane seepage rather than a global process to explain the negative $\delta^{13}C_{org}$ excursion in the Upper Zaonega Formation, triggered by subvolcanic intrusions that acted as a local heat source to induce hydrocarbon generation. The end of the LE is also marked by increasing $\delta^{34}S$ values of carbonate-associated sulfate (CAS), which reflects the isotopic evolution of seawater sulfate and an increase in pyrite burial rates (Planavsky et al., 2012). Furthermore, a rapid contraction of the seawater sulfate reservoir at the end of the LE (cf. Planavsky et al., 2012) was supported by Scott et al. (2014) based on coupled C and multiple S isotope systematics. Scott et al. (2014) suggested that deoxygenation enhanced methane cycling in the water column, which is reflected by a shift to more negative $\delta^{13}C_{org}$ values in the Upper Zaonega Formation. Specifically, low-sulfate conditions could have stimulated methanotrophy at the sediment–water interface and in the water column due to a decrease in methane consumption in sediments by biologically driven anaerobic oxidation of methane coupled to microbial sulfate reduction (MSR), in turn allowing a greater methane flux to the overlying water column (Scott et al., 2014).

In order to provide further insights into marine redox conditions and biological processes in the photic zone during the falling limb of the LE, we present multiple geochemical proxies that include $\delta^{34}S$, $\Delta^{33}S$, $\Delta^{36}S$, $\delta^{98}Mo$, $\delta^{13}C_{org}$, $\delta^{13}C_{carb}$, and $\delta^{18}O_{carb}$ data coupled to total organic carbon (TOC) and total sulfur (TS) contents recorded in organic-rich shales and carbonates of the Francevillian Group of Gabon (see supplementary information for analytical methods). This dataset allows us to compare sedimentary geochemical trends that characterize the end of the LE in the Upper Zaonega Formation with those of the Francevillian Group, and then explore whether these trends correspond to local or global shifts in biogeochemical cycling and redox conditions.

2. Geological setting

Sedimentary rocks of the Francevillian basin in the Republic of Gabon are exceptionally well preserved and represent a unique window into the middle Paleoproterozoic (El Albani et al., 2010; Gauthier-Lafaye and Weber, 2003; Ossa Ossa, 2010; Ossa Ossa et al., 2013; Préat et al., 2011). The Francevillian Group was deposited between ∼2200 Ma and 2050 Ma (see SI.1; Bouton et al., 2009; Bros et al., 1992; Horie et al., 2005) and crops out in four sub-basins: the Booué (*Plateau des Abeilles*), Lastoursville, Franceville, and Okondja sub-basins (Fig. 1; Gauthier-Lafaye and Weber, 2003). Five lithostratigraphic formations from the Francevillian A (FA) at the bottom to the Francevillian E (FE) at the top have been described (Fig. 1; Gauthier-Lafaye and Weber, 2003). The FA Formation is characterized by predominantly coarse siliciclastic rocks that were deposited in a fluvial to tidally-influenced deltaic setting (Gauthier-Lafaye and Weber, 2003; Ossa Ossa, 2010; Préat et al., 2011). The FB to FE formations are dominated by marine black shales with intercalations of sandstones, dolostones, and cherts (Gauthier-Lafaye and Weber, 2003; Ossa Ossa et al., 2013; Pambo et al., 2006; Préat et al., 2011). Episodic submarine and subaerial volcanism was active during deposition of the Francevillian Group (Gauthier-Lafaye and Weber, 2003; Préat et al., 2011). Episodic volcanism is thought to have contributed to the formation of sedimentary Mn deposits, hosted in black shale-dominated stratigraphic units (Gauthier-Lafaye and Weber, 2003; Préat et al., 2011).

Our study focuses on black shale/siltstone and carbonate facies of the FB and FC formations from the Franceville and Lastoursville sub-basins (Fig. 1). The FB Formation is subdivided into two members (FB1 and FB2), which are further subdivided into FB1a–c and FB2a–b units (Fig. 1). Overall, the FB Formation consists mainly of deltaic to marine deposits (SI.2; Fig. S1). Facies relationships and sedimentary structures suggest a shifting depositional setting from shallow intertidal to storm wave-influenced deeper-water environments in response to sea-level changes (SI.2; Fig. S1; El Albani et al., 2010; Ossa Ossa, 2010; Ossa Ossa et al., 2013; Pambo et al., 2006). Excellent preservation of the black shale- and siltstone-dominated facies is indicated by the presence of synsedimentary to early diagenetic, smectite-rich clay minerals, indicating sluggish diagenesis and limited post-depositional transformation of minerals during their burial history (Ossa Ossa, 2010; Ossa Ossa et al., 2013). Well-preserved pyritized fossils of putative macro-eukaryotic organisms have been identified in black shales of the FB2b unit (El Albani et al., 2010). These fossils were interpreted as colonial, complex biota living in a well-oxygenated marine environment in shallow water less than ∼60 m deep (El Albani et al., 2010).

The lower part of the FC1 Member is characterized by thick (up to 100 m), dark-gray, beige, and pink dolostone bedsets (Fig. 2). In sandy dolostones, abundant wave and current ripples, tepee structures, mud cracks, cross-bedding and crinkly lamination suggest deposition in an intertidal to subtidal shallow-marine setting with carbonate lagoons and sandy barrier island carbonate shoals (Fig. 2). Fractures in the lower FC1 Member are filled with pyrobitumen, calcite, and pyrite (Fig. 2). The upper part of the FC1 Member is characterized by black shales grading stratigraphically upward into crinkly, microbially laminated beige dolostone with intercalations of dark-gray shale (ribbon dolostone), reflecting open shelf to intertidal deposition (Fig. 2; Préat et al., 2011). The FC2 Member consists of stromatolitic chert, reflecting silicification of microbialites deposited in a tide-influenced,