ARTICLE IN PRESS

Geoscience Frontiers xxx (2017) 1–18

HOSTED BY
ELSEVIER

Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Research paper

Redox history of the Three Gorges region during the Ediacaran and Early Cambrian as indicated by the Fe isotope

Yusuke Sawaki [a,*], Miyuki Tahata [a], Tsuyoshi Komiya [b], Takafumi Hirata [c], Jian Han [d], Degan Shu [d]

[a] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan
[b] Department of Earth Science and Astronomy Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan
[c] Geochemistry Research Center, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan
[d] Department of Geology and Key Laboratory for Continental Dynamics, Northwest University, Xi'an 710069, China

ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form
17 February 2017
Accepted 22 February 2017
Available online xxx
Handling Editor: C. Spencer

Keywords:
$\delta^{56/54}$Fe
Pyrite
Ediacaran
Cambrian
Three Gorges

ABSTRACT

The Ediacaran–Cambrian transition is characterized by numerous events such as the emergence of large multi-cellular metazoans and surface environmental disturbances. Based on geological evidence, it has been proposed that this transition coincided with the increase in the atmospheric oxygen level that was key to the evolution of life. Even though ancient redox conditions can be inferred from the composition of sedimentary iron mineral species, this method is not necessarily applicable to all rocks. In the Earth system, the cycling of iron is of considerable interest owing to its sensitivity to redox conditions. Information regarding the paleo-oceanic iron cycle is revealed in the iron isotopic composition of iron-bearing minerals. Unfortunately, only limited iron isotopic data exists for Ediacaran- to Cambrian-period oceans.

To circumvent this deficiency, we drilled a fossiliferous Ediacaran to Early Cambrian sedimentary succession in the Three Gorges region, South China. We analyzed the iron isotope ratios ($\delta^{56/54}$Fe) of pyrite grains in the drill cores using laser ablation multi collector inductively coupled plasma mass spectrometry. The results demonstrate large variations in $\delta^{56/54}$Fe, from −1.6 to 1.6‰, and positive iron isotope ratios are observed in many successions. The presence of positive $\delta^{56/54}$Fe in pyrite indicates that the ferrous iron in the seawater was partially oxidized, suggesting that seawater at Three Gorges was ferruginous during the Ediacaran and Early Cambrian periods. However, aggregated pyrite grains in organic carbon-rich black shales at Member 4 of the Doushantuo Formation and the base of the Shuijingtuo Formation yield near-zero $\delta^{56/54}$Fe values; this suggests that the ocean was transiently dominated by sulfidic conditions during these periods. Notably negative $\delta^{56/54}$Fe values, lower than −1‰, can be interpreted as a signature of DIR. The DIR also might contribute in part to the re-mineralization of organic matter during the largest negative carbon isotope anomaly in the Ediacaran.

1. Introduction

The Ediacaran–Cambrian period records one of the most dramatic biological episodes in Earth's history, including the emergence of multi-cellular animals, Ediacaran-type fauna (*Vendobionta*), and possible bilaterians (e.g., Xiao et al., 1998; Chen et al., 2000; Narbonne and Gehling, 2003; Brasier and Antcliffe, 2004). Because large, multi-cellular animals need a certain level of oxygen to maintain their vital functions (Runnegar, 1991), it is thought that the development of life was closely linked to seawater chemistry, especially redox conditions (e.g., Anbar and Knoll, 2002; Catling and Claire, 2005; Payne et al., 2009). Recent sulfur and selenium isotopes indicated that the ocean–atmosphere system was progressively oxidized during the Neoproterozoic (Fike et al., 2006; McFadden et al., 2008; von Strandmann et al., 2015). By contrast, iron speciation analyses demonstrate that the redox conditions in the Ediacaran ocean depended on each sedimentary facies, which

* Corresponding author. Fax: +81 3 5734 3538.
E-mail address: y-sawaki@geo.titech.ac.jp (Y. Sawaki).
Peer-review under responsibility of China University of Geosciences (Beijing).

http://dx.doi.org/10.1016/j.gsf.2017.02.005
1674-9871/

Please cite this article in press as: Sawaki, Y., et al., Redox history of the Three Gorges region during the Ediacaran and Early Cambrian as indicated by the Fe isotope, Geoscience Frontiers (2017), http://dx.doi.org/10.1016/j.gsf.2017.02.005

further indicates no statistically significant changes in the Ediacaran and Early Paleozoic (Johnston et al., 2013; Sperling et al., 2013, 2015). In this study, we constrain the redox conditions recorded in the Ediacaran to Early Cambrian succession in the Three Gorges region because this area has been recognized as a type locality of the Sinian (Ediacaran) System and its succession is fossiliferous.

Iron undergoes active redox cycling in the seawater and sediments; therefore, iron geochemistry is useful to constrain ancient seawater chemistry (e.g., Raiswell et al., 1988, 2001; Rouxel et al., 2005). The redox conditions in the Three Gorges region from the Ediacaran to the Cambrian have been estimated primarily based on iron speciation analyses (e.g., Li et al., 2010; Fan et al., 2014). These studies showed oscillations in the redox states between ferruginous and sulfidic conditions in the Ediacaran Doushantuo Formation (Fm); however, iron speciation analyses are not always applicable to all rocks. The estimation of ancient redox conditions by iron speciation analyses was originally established from iron mineral species in clastic sediments, including modern oxic and sulfidic clay and shale (Canfield et al., 1996; Raiswell and Canfield, 1998; Poulton and Raiswell, 2002), Phanerozoic shale and mudstone (Raiswell et al., 1988, 2001), and Middle Proterozoic black shale (Shen et al., 2002). This index is calculated from the ratio of iron-bearing highly reactive minerals (Fe_{HR} including pyrite, carbonate, magnetite, and hematite) to total iron (Fe^T), which includes Fe_{HR} and unreactive iron-bearing silicates (Fe_{sil}). Several original studies have pointed out that the target sediments should contain sufficient clastic minerals (Raiswell et al., 1988, 2001); therefore, application of this technique to sediments poor in clastic particles, e.g., carbonate rocks, is not suitable due to the lack of Fe_{sil}. Data reported in previous studies (Li et al., 2010; Fan et al., 2014) showed Fe_{sil} contents in some carbonate rocks lower than 0.5 wt.%. Recently, Clarkson et al. (2014) explored the applicability of the iron speciation method to carbonate rocks and demonstrated that carbonate-rich sediments with low Fe^T (<0.5 wt.%) routinely provide spuriously high Fe_{HR}/Fe^T ratios. Because most carbonate rocks in the Doushantuo Fm have Fe contents less than 0.5 wt.% (Sawaki et al., 2010), the iron speciation method is not appropriate for Ediacaran carbonate rocks in the Three Gorges region. In addition, sequential leaching of whole rock samples, employed in previous studies, cannot avoid altered iron minerals and may be contaminated by detrital reactive iron-bearing minerals.

Iron isotope measurements of iron-bearing minerals is another tool to trace the ancient Fe cycle in seawater (e.g., Rouxel et al., 2005) because biological and non-biological iron isotopic fractionation occurs in nature and in laboratory experiments (e.g., Beard et al., 1999; Welch et al., 2003; Fantle and DePaolo, 2004; Butler et al., 2005; Johnson et al., 2005; Guilbaud et al., 2011; Wu et al., 2012). The iron supplied from river water or hydrothermal circulation ultimately settles as iron-containing minerals via various redox reactions in the water column and sediments. Sedimentary pyrite can also be used to constrain paleo-redox conditions (e.g., Rouxel et al., 2005) because the iron isotope ratio in authigenic pyrite reflects the pyrite formation pathway and the ambient environment. Recently, in situ measurements of iron isotopic ratios of pyrite grains have allowed the detection of iron isotopic variations between individual pyrite grains (Whitehouse and Fedo, 2007; Nishizawa et al., 2010; Yoshiya et al., 2012, 2015a,b). The in situ measurement of iron isotopic ratios in pyrite grains from the Ediacaran to the Early Cambrian allows us to track secular changes in the oceanic iron cycle more precisely because such spatial resolution avoids contamination from detrital grains and altered iron minerals.

We carried out on-land drilling of the Ediacaran to Cambrian sedimentary succession in Three Gorges. This sampling methodology allows the effect of secondary alteration and oxidation on the surface to be avoided. Furthermore, the continuous and fossiliferous sequence from the Ediacaran to the Cambrian can be used to constrain the stratigraphic profile of the $\delta^{56/54}$Fe in sedimentary pyrite grains and the redox state of Ediacaran and Cambrian seawater.

2. Geology of the Three Gorges region

2.1. Geological setting and stratigraphy of the drill core samples

Neoproterozoic to Cambrian rocks are widely outcropped in South China; the Three Gorges region is located approximately 30 km west of Yichang along the Yangtze River (Fig. 1a and b). The Sandouping in the southeast of Zigui near Yichang, Hubei Province (Fig. 1b and c), is one of the best-known sections in the Yangtze Gorges region (e.g., Chen, 1987). Above the unconformity in the Huangling granite, the Tonian to Early Cambrian succession comprises the Liantuo, Nantuo, Doushantuo, Dengying, Yanjiahe, and Shuijingtuo Fms, in ascending order (Fig. 2a). As introduced below, these sequences contain many Ediacaran and Cambrian fossils. We carried out on-land drilling in this area from the Nantuo Fm to the Shuijingtuo Fm at three sites (Fig. 1c).

The core collected at Site2 is approximately 130 m long, extending from the basal Liantuo Fm through the Nantuo Fm to the bottom of Member 2 in the Doushantuo Fm (Fig. 2a). The diamictite of the Nantuo Fm corresponds to glacial deposits during the Marinoan glaciation (e.g., Hoffman and Schrag, 2002). A 6 m thick cap dolostone, Member 1 of the Doushantuo Fm, rests on the Nantuo diamictite. Above the cap carbonate, black shale is predominant and intercalated with limestone and dolostone layers. U–Pb zircon dating provides sedimentary ages of 635.2 ± 0.6 Ma for an ash bed within Member 1 and 632.5 ± 0.5 Ma for ash at the bottom of Member 2 (Condon et al., 2005).

The core collected at Site1 is approximately 268 m long, ranging from the lower part of the Doushantuo Fm through the Hamajing Member to the Shibantan Member of the Dengying Fm. The Doushantuo Fm begins with Member 2 (~120 m thick), comprising black shale with thin dolostone layers and small chert nodules (Fig. 2b); continues through Member 3 (~80 m thick), comprising medium- to thick-bedded gray dolostones; and ends with Member 4 (~6 m thick), comprising organic carbon-rich black shale with thin limestone layers. Even though the drill cores at Sites 1 and 2 both contain the lower part of Member 2, it is difficult to compare them exactly due to the absence of key beds. Member 2 contains multiple early diagenetic siliceous nodules with various fossils, such as multi-cellular algae, acanthomorphic acritarchs, filamentous and coccoidal cyanobacteria, and possible sponge gemmules (Yin et al., 2007; Zhou et al., 2007; McFadden et al., 2008; Du et al., 2015). Abundant silicified microfossils, including acanthomorphic acritarchs, were recently reported in chert nodules in Member 3 (Liu et al., 2014). Member 4 is composed of black shale and is extremely enriched in organic carbon (Li et al., 2010; Kikumoto et al., 2014). Member 4 in the Miaohe section contains several species of Miaohe biota, such as *Enteromorphites siniansis*, *Sinospongia chenjunyuani*, and *Sinospongia typica* (Fig. 1b; Xiao et al., 2002). The tuffaceous bed within Member 4 has a U–Pb age of 551.1 ± 0.7 Ma (Condon et al., 2005; Yin et al., 2005; Zhang et al., 2005). The Hamajing Member of the Dengying Fm rests conformably on the Doushantuo Fm; it is composed of wavy layers and stratified dolostones. A black to dark-gray bedded limestone in the Shibantan Member unconformably overlies the Hamajing dolostones. The Shibantan Member contains trace fossils, microbial mats, the algal fossil *Vendotaenia antiqua*, an Ediacaran macrofossil *Paracharnia dengyingensis*, possible Planolites-like trace fossils,