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Cerium anomaly variations in Ediacaran–earliest Cambrian carbonates from the Yangtze Gorges area, South China: Implications for oxygenation of coeval shallow seawater

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ABSTRACT

The late Neoproterozoic ocean witnessed the naissance of animals which is believed to have been stimulated by an increase in oxygen levels in the ocean. However, apart from the emergence of animal fossils, little supporting evidence has been found for the rise of oxygen in shallow seawater. Here we present Ce anomaly data, a redox proxy with a higher reduction potential than many other redox proxies, for carbonates from well-preserved marine successions (the Doushantuo Formation, Dengying Formation and lower Yanjiahe Formation of the Ediacaran Period, and the upper Yanjiahe Formation of early Cambrian) on the Neoproterozoic Yangtze Platform in the Yangtze Gorges area, in order to constrain the redox evolution of the shallow marine environment. Calculated Ce anomalies were screened, using the following criteria: Al < 0.35% and Fe < 0.45% in bulk rock, Th < 0.5 ppm, Sc < 2 ppm, ΣREE < 12 ppm and Y/Ho > 36 in acetic-acid-leached carbonate, to target samples that preserve primary seawater REE features and Ce anomalies. The samples satisfying this screening show seawater-like REE distribution patterns in leached carbonates and may have recorded Ce anomalies of the seawater from which the carbonates precipitated. These data show that the Doushantuo Formation has Ce/Ce* values between 0.92 and 0.71, the Dengying Formation between 0.90 and 0.40, and the Yanjiahe Formation between 0.52 and 0.72. The Ce/Ce* values of the Doushantuo Formation suggest that shallow waters during the Doushantuo stage (635–551 Ma) were anoxic to suboxic. From the bottom to the top of the Dengying Formation, Ce/Ce* values decrease systematically, which cannot be explained by a change in depositional depth of the carbonate but suggests that the shallow waters became more oxygenated during the Dengying stages (from 551 Ma to Ediacaran–Cambrian boundary). These results may provide direct evidence for an increase in oxygen levels in the shallow marine environment during the Ediacaran Period.

1. Introduction

Increasing geochemical evidence suggests that oxygenation of Earth's surface occurred in two main steps. The first is thought to have taken place between 2.45 and 2.2 Ga (Bekker et al., 2004; Bekker and Kaufman, 2007), involving a significant increase in atmospheric oxygen concentrations and oxygenation of the surface ocean (e.g. Holland, 1984, 2006; Bekker et al., 2004). The second step appears to have occurred during the late Neoproterozoic (800–542 Ma) (e.g. Des Marais et al., 1992; Canfield and Teske, 1996; Fike et al., 2006; Canfield et al., 2007; Shields-Zhou and Och, 2011), leading to intermittent oxygenation of the deep ocean during that period (Canfield et al., 2008). However, details of this Neoproterozoic oxidation event remain unclear.

Sulfur isotope and carbon isotope records from the Huqf Supergroup in the Sultanate of Oman (635–548 Ma) indicate three stages of oxidation (Fike et al., 2006), whereas sulfur isotope and carbon isotope records from the Doushantuo Formation at Jiulongwan section in South China (635–551 Ma) indicate only one oxidation stage that occurred during deposition of the third member of the Doushantuo Formation (McFadden et al., 2008), corresponding to the second stage in Oman, both of which show a prominent negative carbon isotope excursion. The first oxidation stage in Oman has not been found in the Doushantuo Formation; the time span of the Doushantuo Formation does not cover the third stage in Oman.

Mo contents increase abruptly in sulfidic black shales of the fourth member, the Miaohe Member of the Doushantuo Formation, deposition of which ended at 551 Ma, whereas Mo contents of sulfidic black shales of the Datangpo Formation (663 Ma) in South

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China are the same as those in older Proterozoic strata. This Mo increase in the Miaohe Member has been taken to indicate that the deep ocean became oxygenated between 663 and 551 Ma (Scott et al., 2008).

Extensive studies of iron speciation in sedimentary rocks deposited at different water depths and locations during 850–530 Ma (Canfield et al., 2007, 2008; Shen et al., 2008; Jiang et al., 2009) show that shallow waters were typically well-oxygenated, whereas waters below mean storm wave base were commonly, or at least regionally, anoxic and ferruginous in the interval from the Sturtian glaciation to early Cambrian, with a few periods of anoxic sulfidic deep water ca. 750 Ma found from the Chuar Group at Grand Canyon in the United States and around 540 Ma found from the earliest Cambrian Niutitang Formation on the Yangtze Platform in China. These iron speciation studies also imply oxygenation of the deep ocean during the middle Ediacaran Period (580–560 Ma), but show that this deep ocean oxygenation was not global and that anoxic conditions could also be present.

Possible reasons for the inconsistency of these data may lie in the different depositional depths for contemporaneous samples and different responses to redox changes for different proxies. One approach to resolve this problem and to constrain the secular and spatial redox state of the Neoproterozoic ocean is by analysis of samples representing different depths and ages and of multiple proxies. This is difficult to achieve in practice though. Efforts in this direction have been made to some extent. For example, Canfield et al. (2008) analyzed iron speciation for samples of various depths and ages, and obtained the generally accepted secular and spatial redox scenario that was mentioned above for the Neoproterozoic. Li et al. (2010) studied sulfur isotopes and iron speciation for the Doushantuo Formation (635–551 Ma) at sections representing different depositional environments from inner shelf through slope to deep basin, along the southern margin of the Yangtze Platform, South China. Their results indicate that anoxia prevailed throughout the deposition of all sampled shallow-water strata, with a metastable mid-water-column sulfidic zone located between the inner shelf and the shelf margin and sandwiched between ferruginous shallower and deeper seawaters. Although Li et al. (2010) did not observe the oxygen-rich surface layer, they still inferred a thin layer of oxygenated surface water above the anoxic ferruginous and sulfidic water masses. Their model seems to reconcile some spatially irregular redox conditions that were proposed previously; but does not evaluate the secular evolution of oxygen levels in the Ediacaran ocean.

The oceanic response to changes in atmospheric oxygen concentration should be reflected in redox changes in both shallow and deep waters. However, more factors affect the redox state of the deep marine environment than affect the shallow water realm. The oxygen level of shallow waters should directly (but not necessary linearly) correlate with the redox state of the atmosphere, regardless of whether the basin is open or restricted with respect to the ocean. For example, the oxygen concentration in shallow waters of the modern Black Sea is similar to that of the modern open ocean although their deepwater oxygen concentrations are markedly different (Chester, 1990; Luther et al., 1991).

Different proxies may respond to different redox ranges, with elements having a lower reduction potential responding earlier to environmental gradual oxygenation than those with a higher reduction potential as the lower reduction potential redox proxies would retain their high valence state unchanged during further oxygenation. For example, the mid-Ediacaran (580–560 Ma) oxygenation event in the deep ocean that can be ascertained from iron speciation data (Canfield et al., 2008) is not apparent in iron speciation changes in samples from shallower waters. As a consequence, higher reduction potential proxies are needed to trace oxygenation events in the atmosphere and shallow water marine realms of this time period.

In this paper, we investigate cerium (Ce) anomalies because Ce has a relatively high reduction potential (de Baar et al., 1988), and apply this proxy to evaluate the redox evolution of shallow shelf facies in the Yangtze Gorges area, South China, during the period from 635 to the earliest Cambrian. Using Ce anomaly data we are able to show that from 635 to 551 Ma (Doushantuo Formation depositional interval), oxygenation indicated by other proxies is not reflected in Ce anomaly data, probably because redox changes had not reached the threshold necessary for Ce to respond. More importantly, we reveal a substantial enhancement in the negative Ce anomaly from 551 to the earliest Cambrian, which coincides with the occurrence of Ediacaran macroscopic multicellular animals (Wang et al., 2002).

2. Brief background of carbonate Ce anomaly as a seawater redox proxy

Cerium (Ce) can exist in either trivalent or tetravalent forms depending on the redox conditions. In modern oxygenated seawater, trivalent Ce is oxidized to its tetravalent form by the mediation of manganese oxide and/or bacteria (Byrne and Sholkovitz, 1996; Tanaka et al., 2010). The tetravalent Ce is prone to be adsorbed and sequestered by Mn-oxides and hydroxides (Elderfield et al., 1981; Bau et al., 1996), or the trivalent Ce absorbed on the Mn-oxides and hydroxides is preferentially oxidized to tetravalent Ce (Tachikawa et al., 1999), and thus Ce is more insoluble in seawater than other rare earth elements (REE) that can only exist in trivalent form. Consequently, Fe–Mn sediments have relative enrichments in Ce, exhibiting positive Ce anomalies, with oxygenated seawater exhibiting correspondingly negative Ce anomalies (Bau et al., 1996). The magnitude of the negative Ce anomaly in seawater is related to dissolved oxygen concentration. For example, in modern fully oxygenated deep oceans, the dissolved REE load exhibits the most negative Ce anomalies (~0.06–0.16: Byrne and Sholkovitz, 1996), whereas in suboxic and anoxic waters Ce anomalies are weaker or absent due to the reductive dissolution of settling Mn- and Fe-rich particles (German et al., 1991). Therefore, Ce anomalies can be used to trace oxygenation changes in seawater, although such changes are complicated by depth-related factors in shallow and stratified waters (see Section 5.3.1 below).

REE in many kinds of marine precipitates such as skeletal carbonates (e.g., Palmer, 1985; Sholkovitz and Shen, 1995) and phosphate (e.g., Wright et al., 1987) are susceptible to diagenetic alteration. Nevertheless, Webb and Kamber (2000) demonstrated that original seawater REE patterns may be retained in ancient marine non-skeletal carbonates. They found that microbialites incorporate more REEs in proportion to seawater levels than coexisting skeletal carbonate. The relatively high REE concentrations observed in limestones and regarded as diagenetic enrichments by Scherer and Seitz (1980) and Shaw and Wasserburg (1985) are therefore consistent with REE contents of microbial carbonates and do not necessarily indicate diagenetic alteration. Their studies revealed that REE patterns of Permian limestones from the paleo-Pacific region (Panthalassa) are very similar to those of modern Pacific seawater, and that Precambrian limestones (stromatolites) also retain seawater REE signatures. Nothdurft et al. (2004) also found that a variety of different ancient limestone components, including microbialites, some skeletal carbonates (stromatoporoids), and cements, record seawater-like REE signatures. Their results suggested that limestones should retain important aspects of the REE geochemistry of the waters from which they precipitated, provided that the limestone samples are relatively free of terrigenous contamination and major diagenetic