Palaeogeography, Palaeoclimatology, Palaeoecology 398 (2014) 132–143

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Rare earth element and Sr–Nd isotope geochemistry of phosphate nodules from the lower Cambrian Niutitang Formation, NW Hunan Province, South China

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ARTICLE INFO

Article history:
Received 29 December 2012
Received in revised form 27 September 2013
Accepted 8 October 2013
Available online 12 October 2013

Keywords:
Phosphate nodules
Rare earth elements
Sr–Nd isotopes
Lower Cambrian
Niutitang
South China

ABSTRACT

Phosphate nodules are widely distributed in the early Cambrian black shale sequence in Yangtze platform, South China. In this study, we carried out X-ray diffraction, major element, rare earth element, and Sr–Nd isotopic studies on phosphate nodules from two PC-C sections in Hunan Province, South China. Two different types of phosphate nodules can be recognized based on REE and Nd isotopic characteristics: type 1 with seawater-like REE patterns, higher εNd(t) values; and type 2 with hat-shaped REE patterns and more negative εNd(t) values. We suggest that the difference in REE patterns and Nd isotopic compositions between the two types reflects changes in pore water geochemistry from seawater-dominated towards diagenetic fluid-dominated conditions during early diagenesis. Positive Eu anomalies are displayed in most samples, and are likely to record not only the anoxic environments but also the involvement of submarine exhalative hydrothermal fluids which prevailed in South China during early Cambrian.

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1. Introduction

Phosphate rocks are widely distributed in ancient and modern marine sediments. At present, phosphogenesis is reported to occur at continental margins and continental shelves in upwelling regions like Peru, Chile, off Namibia, and the Gulf of California (Veeh, 1973; Föllmi, 1996). In contrast, investigations of ancient phosphorite deposits show more variable facies and paleogeographic constellations (Trappe, 1998). Phosphogenesis of marine sediment has been known to take place at or below the sediment–water interface (Paytan and McLaughlin, 2007). Intense biological productivity and low oxygen availability at the sediment–water interface are favorable conditions for the development of phosphogenic environments (Trappe, 1998; Paytan and McLaughlin, 2007). Besides, microbial activities and the reduction of iron-oxyhydroxides may also play important roles in the enrichment of phosphate in pore water (Van Cappellen and Berner, 1988; Jarvis et al., 1994; Krajewski et al., 1994; Schuffert et al., 1998; Schulz and Schulz, 2005).

Previous studies have shown that abundant rare earth elements (REE) can be incorporated into phosphates during their formation (McArthur and Walsh, 1984; Kidder et al., 2003). Removal of REE through early-diagenetic phosphate precipitation may constitute a large output of REE in the oceanic system (Rasmussen et al., 1998). Therefore, the REE contents, the shale-normalized REE patterns, as well as Ce and Eu anomalies of phosphorites may serve as useful indicators for the paleo-seawater or pore water conditions (e.g. McArthur and Walsh, 1984; Shields and Stille, 2001; D.F. Chen et al., 2003; S.-Y. Jiang et al., 2007b). Particularly, there are a large number of studies focusing on the "hat-shaped" patterns of some phosphorites because these patterns may relate to certain geological periods and may indicate changes in the REE geochemistry of seawater in the geological past (McArthur and Walsh, 1984; Jarvis et al., 1994; Ilyin, 1998; Picard et al., 2002; D.F. Chen et al., 2003).

In this study, we carried out X-ray diffraction, major element, rare earth element, and Sr–Nd isotopic analyses of phosphate nodules from the early Cambrian black shale sequence in Hunan Province, South China. This study aims to advance our understanding of the geochemistry of paleo-seawater, and the digenetic processes during phosphogenesis.

2. Geological setting

Neoproterozoic–early Cambrian sedimentary rocks are widely exposed on the Yangtze platform in South China. These well developed strata document a series of geological events including sea-level

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0031-0182/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.palaeo.2013.10.002

fluctuation, change in seawater geochemistry, phosphate deposition, oceanic anoxia and bio-radiation of early Cambrian (Steiner et al., 2001; Zhu et al., 2003; G. Jiang et al., 2007; Steiner et al., 2007; Zhu et al., 2007; Canfield et al., 2008; McFadden et al., 2008; Li et al., 2010; Jiang et al., 2011; Pi et al., 2012). Paleogeographic reconstruction reveals that three sedimentary facies can be distinguished from northwest to southeast: carbonate platform, transitional belt, and deep basin (Fig. 1). During this interval, shallow-water carbonate deposits of the Ediacaran Dengying and Yanjiahe Formations (and their correlative units) dominated the northwestern Yangtze platform and changed basinward into deep-water shale and chert dominated Liuchapo Formation. The Cambrian Niutitang Formation (and its equivalent strata) resting on the Dengying Formation/Liuchapo Formation is mainly composed of black shale with abundant fossils like sponges, arthropod body fossils (Steiner et al., 2001; Zhou and Jiang, 2009). A thin Ni–Mo sulfide ore is sporadically distributed in the lowermost few meters of this formation in Yunnan, Guizhou, and Hunan Provinces (Fan et al., 1973; Steiner et al., 2001; Jiang et al., 2006; Lehmann et al., 2007; S.-Y. Jiang et al., 2007a). Abundant phosphate nodules occur below the Ni–Mo sulfide bed and above the hiatus surface (Zhu et al., 2003). Earlier studies reported Re–Os isochron ages of 542 ± 11 Ma (Li et al., 2003), 541 ± 16 Ma (Mao et al., 2002) and 537 ± 10 Ma (Jiang et al., 2003) for this Ni–Mo sulfide ore. The Pb–Pb and Re–Os dating of the host black shale yielded ages of 531 ± 24 Ma (Y.Q. Chen et al., 2003) and 535 ± 11 Ma (S.-Y. Jiang et al., 2007a), respectively. More recent ages include Re–Os age of 521 ± 5 Ma for the polymetallic sulfide layer (Xu et al., 2011), SHRIMP zircon U–Pb ages of 532.3 ± 0.7 Ma (Jiang et al., 2009), 536.3 ± 4.9 Ma (Chen et al., 2009) and 522.7 ± 4.9 Ma (Wang et al., 2012) from volcanic ash layers occurring below the Ni–Mo sulfide ore in Guizhou and Hunan Provinces. Although a number of studies have been focused on geochronology of the Niutitang Formation, the exact age for the phosphate nodules is not clear. As mentioned above, the same, contemporaneous ash bed in Guizhou and Hunan Provinces gave different zircon U–Pb ages, probably indicating lead loss in the analyzed zircon grains, or stratigraphic diachrony and condensation across the early Cambrian Yangtze platform (Wang et al., 2012). Nevertheless, the most precise zircon U–Pb and Re–Os ages still provide an age range between 521 ± 5 Ma and 532.3 ± 0.7 Ma for the phosphate nodules.

The studied Sancha section is located ~25 km to the southeast of Zhangjiajie in Hunan Province, South China (Fig. 1). At this section, the Niutitang Formation disconformably rests on the Dengying Formation following a hiatus. The lowermost part consists of chert, bedded and nodular phosphate, black shale with up to 15% TOC content and Ni–Mo sulfide ore (Steiner et al., 2001). The upper unit consists of black shale with lower TOC content (Steiner et al., 2001) (Fig. 2). The Longbizui section is located in the Guzhang County in western Hunan Province and represents a slope to deep basin setting (Fig. 1). The Niutitang Formation at Longbizui section is mainly composed of black shale and mudstone and overlies the Liuchapo Formation (equivalent

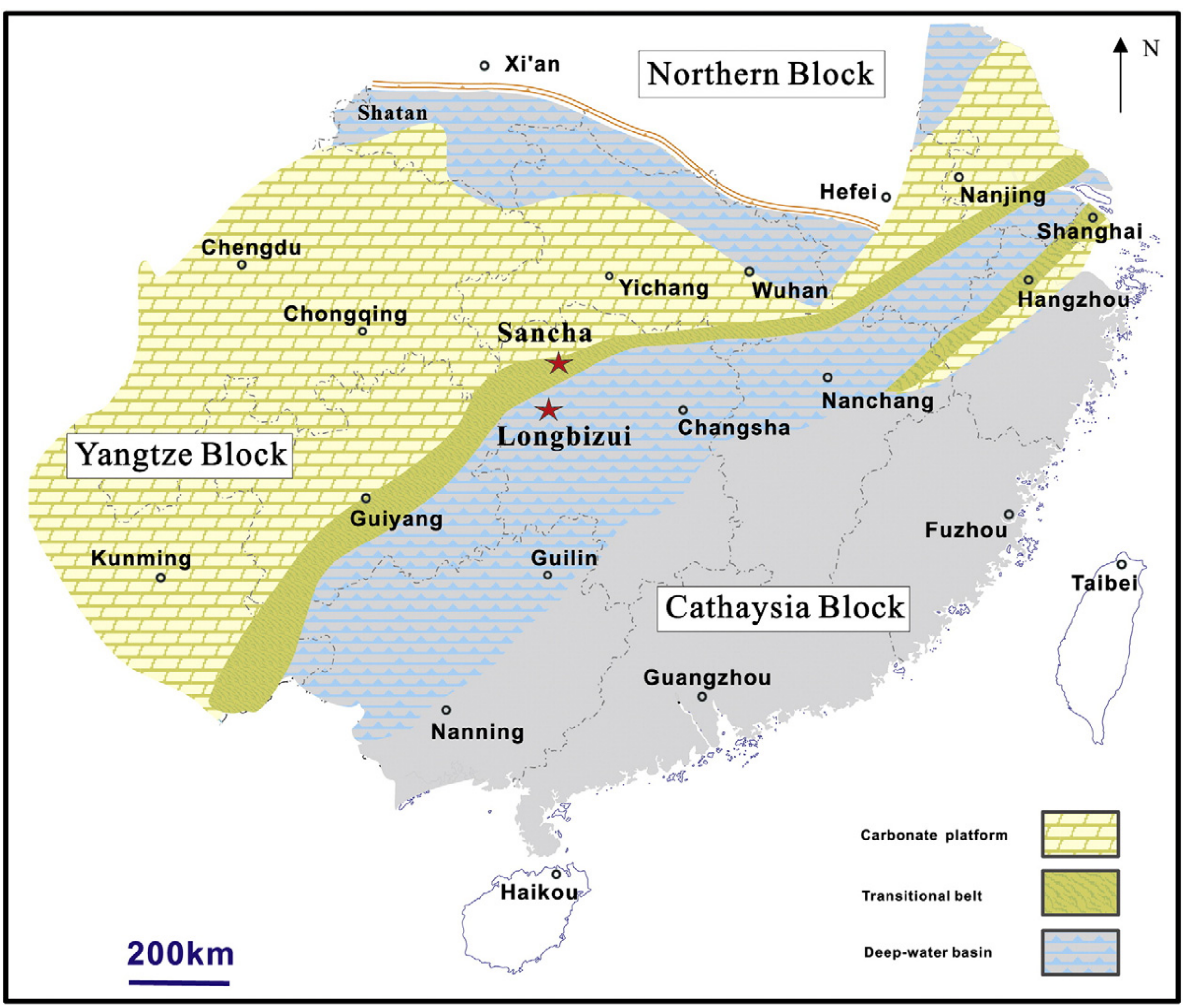

Fig. 1. Palaeo-geographic map of Early Cambrian on the Yangtze platform.

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