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Re–Os geochronology of black shales from the Neoproterozoic Doushantuo Formation, Yangtze platform, South China

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ABSTRACT

In South China, the Doushantuo Formation represents 90% of the time interval of the Neoproterozoic Ediacaran Period (635–542 Ma). However, subdivision and correlation of strata in this formation is limited by sporadic occurrences of fossils of uncertain age and a scarcity of radiometric time constraints. In order to obtain Re–Os ages and initial $^{187}Os/^{188}Os$ (Os_i) data, black shale samples from the Doushantuo Formation (Yangtze Platform, South China) were analyzed using the CrO_3-H_2SO_4 digestion technique. A Re–Os date of 595 ± 22 Ma (Os_i = 0.85 ± 0.18, MSWD = 29, n = 7) was obtained for black shale samples from the basal part of the fossil-bearing Doushantuo Member 4 ("Miaohe Member") at Jiulongwan section, Three Gorges area, South China. A subset of these samples define a more precise isochron age of 591.1 ± 5.3 Ma (Os_i = 0.874 ± 0.038, MSWD = 1.3, n = 4). We interpret the high MSWD of 29 and larger uncertainties for the 595 ± 22 Ma date to reflect heterogeneity of the Os_i of samples related to temporal change of $^{187}Os/^{188}Os$ ratio of seawater when the sedimentary rocks were deposited. Taking 591.1 ± 5.3 Ma as the age for the base of the Doushantuo Member 4, together with the age of a tuff bed on the top of Member 4 (551.1 ± 0.7 Ma, zircon U–Pb dating, Condon et al., 2005), a minimum time difference of 35 m.y. between the base and top of Member 4 is obtained. This estimate suggests very low sedimentation rates during black shale deposition (∼0.4 mm/ka). The time difference of 35 m.y. also represents a minimum duration of the Shuram–Wonoka $\delta^{13}C$ excursion in South China. Black shale samples from Doushantuo Member 2 at Baiguoyuan section yield an imprecise date of 592 ± 68 Ma (Os_i = 0.534 ± 0.057, MSWD = 77) due to limited spread in $^{187}Re/^{188}Os$ ratio of the samples and a relatively large sampled stratigraphic interval (∼6 m). If deposition occurred in water masses with access to the open ocean, Os_i of the hydrogenous fraction from these organic matter rich sedimentary rocks may record the Os isotopic composition of coeval seawater. Thus, combined with previously published Re–Os data, the highly radiogenic initial $^{187}Os/^{188}Os$ ratio of 0.874 ± 0.038 derived from Re–Os isochron for the base of Doushantuo Member 4, and even more radiogenic values near the top of Member 4 (1.08–1.17, calculated at 551 Ma) indicate a dramatic increase of the flux of ^{187}Os into the ocean during the late Ediacaran. The enhanced ^{187}Os flux can only result from enhanced continental weathering and oxidation rates during that period.

1. Introduction

The Ediacaran marks the final geological period of the Proterozoic eon between the termination of the global Marinoan glaciation at ∼635 Ma and the beginning of the Cambrian at 542 Ma. The Ediacaran Earth experienced major biological changes, including radiation of complex multicellular life such as globally distributed Ediacaran-type soft-bodied animals (Xiao et al., 1998; Xiao et al., 2002; Brasier and Antcliffe, 2004; Zhou et al., 2007; McCall, 2006 and reference therein). Ediacaran strata record dramatic changes in atmosphere and seawater chemistry, presumably caused by a major rise in atmospheric oxygen and oxidation of the deep ocean (Derry et al., 1992; Fike et al., 2006; Canfield et al., 2007; Halverson and Hurtgen, 2007; Scott et al., 2008). Stable isotope studies suggested an expanded sulfur reservoir in the Ediacaran ocean and decoupling of carbonate and organic carbon isotopes accompanied by the largest negative $\delta^{13}C_{carb}$ excursion in Earth history (Fike et al., 2006; Le Guerroué et al., 2006; Halverson and Hurtgen, 2007; Jiang et al., 2007a; McFadden et al., 2008). Strontium isotopes from the Ediacaran successions showed an overall increasing trend throughout this period and $^{87}Sr/^{86}Sr$ ratio as high as ∼0.7090 has been documented (Jacobsen and Kaufman, 1999; Halverson et al.,

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2007, 2010; Sawaki et al., 2010). These prominent changes characterize the Ediacaran Period as a unique time interval in Earth's history.

Because of continuous and well exposed Precambrian–Cambrian sections of different paleoenviromental settings and diverse and rich occurrences of fossils, South China plays an important role in global correlation of the Ediacaran rock record and reconstruction of Ediacaran environments. In South China, precise zircon U–Pb dating of volcanic tuff beds from the lower and uppermost Doushantuo Formation has constrained the age of the Doushantuo Formation to between 635.2 ± 0.6 and 551.1 ± 0.7 Ma (Condon et al., 2005).

A number of techniques have been used to constrain the age of sedimentary rocks, including dating interbedded volcanic rocks, bracketing relationships of igneous and metamorphic rocks and dating of detrital and diagenetic minerals (Rasmussen, 2005). However, none of them provide direct depositional ages for sedimentary rocks. In contrast, Re–Os geochronology offers a different approach in that it permits direct dating of deposition of sediments rich in organic matter, like black shale (Cohen et al., 1999; Creaser et al., 2002; Kendall et al., 2004; Selby and Creaser, 2005; Jiang et al., 2007b). Previous studies have shown that the Re–Os system in black shales remains closed during later hydrocarbon maturation, lower greenschist metamorphism and flash pyrolysis associated with igneous intrusions (Creaser et al., 2002; Kendall et al., 2004; Rooney et al., 2010). This method has been successfully applied in recent studies, yielding sub-% level precisions on ages (e.g. Selby and Creaser, 2005; Kendall et al., 2006; Anbar et al., 2007; Xu et al., 2009). Precise and accurate Re–Os ages have also been obtained on syn-sedimentary–early diagenetic pyrite in organic carbon-rich sedimentary rocks (Hannah et al., 2004). Additionally, initial $^{187}Os/^{188}Os$ ratio obtained on Re–Os isochrons of organic matter rich marine sediments provide constraints on temporal variations in $^{187}Os/^{188}Os$ ratio of contemporary seawater (e.g., Ravizza and Turekian, 1989; Cohen et al., 1999). In this study, we present Re–Os data on black shale and associated pyrite nodules of the Ediacaran Doushantuo Formation from sections near Jiulongwan and Baiguoyuan, Three Gorges area, South China with the purpose of obtaining more geochronological and paleoenviromental information about this important time interval in Earth's history.

2. Geological setting and samples

In South China, Neoproterozoic sedimentary successions were deposited on a passive continental margin (the Yangtze Platform) that developed during the breakup of the Rodinia supercontinent (Wang and Li, 2003). Diverse types of sedimentary facies from shallow water to deep basin have been deposited on the South China block during that time interval (Zhu et al., 2003; Jiang et al., 2007b).

In the Three Gorges area (Hubei Province), Ediacaran strata were deposited on the interior of a shallow platform environment (Fig. 1). Overlying the Nantuo diamictite of the Marinoan glaciation, the Ediacaran sedimentary succession in this area consists of the Ediacaran Doushantuo Formation and the overlying upper Ediacaran Dengying Formation. The Doushantuo Formation is further divided into 4 Members in ascending order: Member 1 (cap carbonate), Member 2 (an alternating shale-mudstone-dolostone sequence), Member 3 (dolostone- and limestone- dominated), Member 4 (also called the Miaohe Member black shale) (Wang et al., 1998; Zhu et al., 2003; Sawaki et al., 2010). Abundant multicellular algae, acanthomorph acritarchs and animal embryos have been reported from the Doushantuo Formation in this area (e.g. Zhang et al., 1998; McFadden et al., 2008; Xiao et al., 2002; Zhou and Xiao, 2007). The zircon U–Pb dates of volcanic tuff beds have provided precise age constraints of 635.2 ± 0.6 and 632.5 ± 0.5 Ma for the cap carbonate

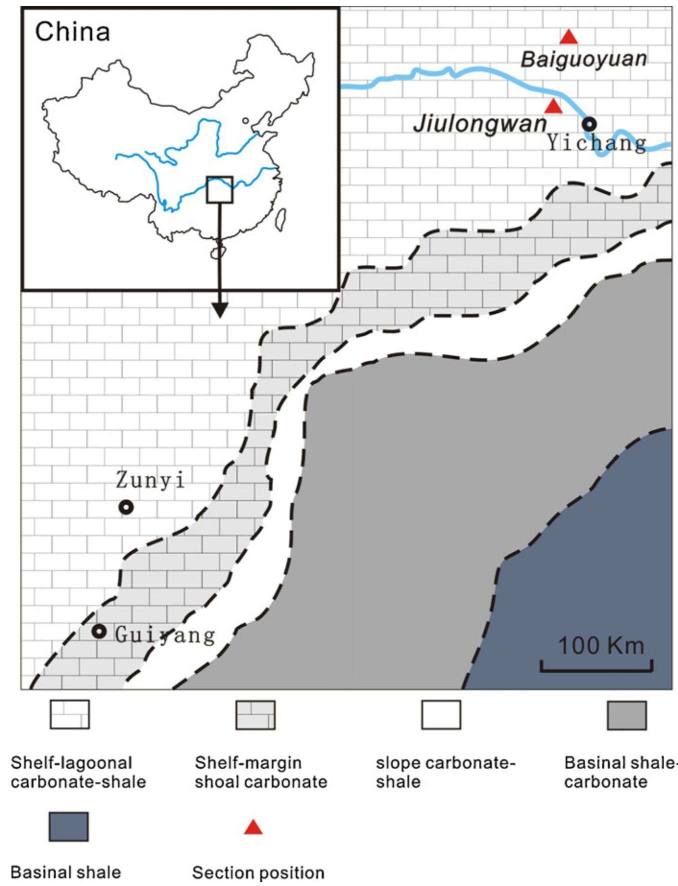

Fig. 1. Paleogeographic reconstruction of the Yangtze Platform during deposition of the middle and upper Doushantuo Formation (Li et al., 2010) in Hubei and Guizhou Provinces.

and the lower part of the Member 2 of the Doushantuo Formation, and 551.1 ± 0.7 Ma for the Doushantuo/Dengying boundary (Condon et al., 2005). In addition to those ages, a zircon U–Pb date of 614.0 ± 7.6 Ma was reported for a volcanic tuff bed occurring below an erosional unconformity at the Wangjiagou section ~50 km NE of the Three Gorges area (Liu et al., 2009). The erosional unconformity is correlated to the middle of Doushantuo Member 2 in the Three Gorges area (Zhu et al., 2007; Zhu et al., 2012).

For the present study, black shale samples of the Doushantuo Formation at Jiulongwan and Baiguoyuan sections were collected (Figs. 1 and 2). The stratigraphy and sedimentary structures of the two sections have been discussed in detail elsewhere (McFadden et al., 2008; Mi et al., 2010). Black shale samples were collected from the ~12 m thick Member 4 at the Jiulongwan section, including 7 lateral samples ~5 to 10 cm thick from the base and 3 samples from the top. In addition, two pyrite nodule samples from black shale sampled close to carbonate concretions that occur less than 0.5 m underneath the 551 Ma old volcanic tuff layer were also studied. Sedimentary layering was observed to deform around the pyrite nodules, indicating they formed before the compaction of sediment. At the Baiguoyuan section, 7 black shale samples were collected from Member 2 of the Doushantuo Formation (Fig. 2). The stratigraphic positions of the samples are listed in Table 1.

3. Analytical methods

The black shale samples were approximately 5 cm × 10 cm × 5 cm (stratigraphic height) in size and pyrite bearing nodules were ~2 cm in diameter. Samples were broken into small chips without metal contact and only fresh pieces were