Geochronological constraints on stratigraphic correlation and oceanic oxygenation in Ediacaran-Cambrian transition in South China

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Abstract

The continuous late Ediacaran-early Cambrian deep-water successions of South China archive the complete evolution of seawater chemical condition in deeper ocean during this critical time interval. However, the geochemical data from these poorly fossiliferous and condensed successions lack high-resolution stratigraphic constraints, hampering their interpretation for the spatio-temporal evolution of the sweater chemistry in this time interval. Here we report a new SIMS and CA-ID-TIMS zircon U-Pb age 545.76 ± 0.66 Ma (total uncertainty) of an ash bed at the lower Liuchapo Formation in the deep-water Longbizui section in western Hunan Province. The new age suggests that the lower and the middle-upper parts of the Liuchapo Formation in deep water facies can be correlated to the lower Dengying Formation and the upper Dengying–lower Zhujiaqing formations in shallow water facies, respectively. This correlation implies that the equivalent horizon of the Ediacaran-Cambrian boundary in the deep water facies in South China is likely located near the base of a widespread negative $\delta^{13}C_{org}$ excursion at the upper Liuchapo Formation. The compilations of Fe-speciation, Mo, and U data, based on our new geochronological framework, indicate that the deep ocean was characterized by widespread anoxic, ferruginous water, with intermittent euxinic water impinged on the middle-lower slope in Ediacaran-Cambrian transition, and significant oxygenation events occurred in 535–520 Ma. And the compilations do not support the ca. 540 Ma oceanic oxygenation event.

Keywords: Zircon U-Pb age, Ediacaran, Cambrian, Liuchapo Formation, oceanic oxygenation, South China

1. Introduction

The Ediacaran-Cambrian transition witnessed the most remarkable reorganization of biology and ecology in Earth history. Stratigraphic successions spanning this critical period are well developed and exposed in South China, including strata preserved in different sedimentary settings ranging from platform interior via slope into deep basin (Zhu et al., 2003). Sedimentary sequences of slope-to-basinal environments are more continuous than those of shallow-water settings, providing a complete record of the deep ocean changes during this time interval. However the deep-water sequences are condensed, and less constrained by age-diagnostic biostratigraphic markers and radiometric ages, making the stratigraphic subdivision and correlation ambiguous. The poorly age-calibrated stratigraphy leads to inconsistent understandings about the ocean redox conditions based on sets of chemical data (e.g., Wille et al., 2008; Jiang et al., 2009; Chen et al., 2015a; Sahoo et al., 2016).

To achieve a better understanding of geochronological framework of Ediacaran-Cambrian transition in deep-water settings in South China, we contribute new high-precision geochronological constraint using SIMS and CA-ID-TIMS zircon U-Pb dating for the lower Liuchapo Formation in the Longbizui section, western Hunan Province. Together with published organic carbon isotope, iron speciation data, redox sensitive trace elements, radiometric ages, and scarce fossil records, our new data provide: (1) tie-point for regional and global stratigraphic correlation; (2) new clue to the placement of equivalent horizon of the Ediacaran-Cambrian boundary in the deep-water settings in South China; (3) time scale to calibrate the deep water conditions and oceanic oxygenation events in late Ediacaran-early Cambrian.

2. Geological background and sampling

The South China Block was formed by amalgamation of Yangtze and Cathaysia blocks (Fig. 1) along the Sibao orogen in Neoproterozoic (e.g., Li et al., 2002, 2009a; Zhou et al., 2002). The paleogeography of South China Block was divided into platform interior, transitional zone, and slope-deep basin in late Ediacaran-early Cambrian (Fig. 1), as the water deepened from the northwest to the southeast on the passive continental margin (Zhu et al., 2003). The Ediacaran-Cambrian transitional strata were extensively developed and well exposed in South China, especially in the Yangtze Block. They consist mainly of carbonate rocks (Dengying and Zhujiaqing formations) in the shallow water settings and cherts (Liuchapo, Laobao, and Piyuancun formations) in the deep water settings (Zhu et al., 2003, 2007). The studied section, Longbizui section, is located in the western Hunan Province. Paleogeographically it was within the lower slope setting. This section records sediment from early Marinoan Glaciation to early Cambrian and its upper part consists of, from bottom to top, Liuchapo and Niutitang formations. This section has been well described in Wang et al. (2012a), Guo et al. (2013), Cremonese et al. (2014), and Och et al. (2016). For the convenience of interpretation, the stratigraphic depth is following Wang et al. (2012a). The Liuchapo Formation measures ca. 70 meters thick and is composed of chert with intercalated siliceous shale (Fig. 2). The overlying Niutitang Formation is about 75 meters thick and consists of black shale and siltstone with its base marked by rich phosphatic nodules. The sample for zircon U-Pb dating, 14GZLCP01, was collected about 20 meters above the base of Liuchapo Formation in the Longbizui section (Fig. 2). It comes from a 5-cm-thick light blue clay-rich bed, and is dominated by very fine-grained clay, with a few crystalloclast (quartz) and vitric fragment (Fig. 3), supporting a volcanic pyroclastic origin. In this instance, the age defined by zircons would be the depositional age of the ash bed.

3. Zircon U-Pb dating methods

Separated zircon crystals were mounted in an epoxy resin together with zircon standards 91500, Plešovice and Qinghu. Measurements of U, Th and Pb isotopes were conducted using a Cameca 1280HR SIMS at Institute of Geology and Geophysics, Chinese Academy of Sciences. A single electron multiplier was used in ion-counting mode to measure secondary ion beam intensities by peak jumping. Analyses of standard zircon grains were interspersed with those unknown grains. The error of the U/Pb calibration curve fitted by the standard zircon Plešovice was propagated to the unknowns. U-Th-Pb ratios were determined relative to the Plešovice standard zircon (Sláma et al., 2008), and the absolute abundances were calibrated to the standard zircon 91500 (Wiedenbeck et al., 1995). Measured Pb isotopic compositions were corrected for common Pb using the ^{204}Pb-method. Corrections are sufficiently small to be insensitive to the choice of common Pb composition, and an average of present-day crustal composition is used for the common Pb correction assuming that the common Pb is largely surface contamination introduced during sample preparation. Data reduction was carried out using the Isoplot/Exv. 4.15. Detailed SIMS zircon U-Pb analytical and calibration methods are described by Li et al. (2009b). In order to monitor the external uncertainties of SIMS U-Pb measurements, analyses of zircon standard Qinghu were interspersed with unknowns. 6 analyses yielded a weighted mean ^{238}U-^{206}Pb age of 159.5 ± 1.5 Ma (MSWD = 1.8, 2σ), identical within errors to the reported age of 159.5 ± 0.2 Ma (Li et al., 2013a).

Zircons of the youngest ^{238}U-^{206}Pb age population were micro-drilled off from the SIMS mount for CA-ID-TIMS analysis. Zircons were annealed in a muffle furnace at

900°C for ~60 hours in quartz beakers before being transferred to 3 ml Hex Savillex beakers. After ultrasonic bath and rinsing by 30% HNO_3, zircons were transferred to 300 µl Teflon PFA microcapsules, leached in ~5:1 mix of 29M HF + 30% HNO_3 for 12 hours at 180°C. Then the acid solution was removed, and zircons were rinsed again by 30% HNO_3 and 6M HCl before spiking with the mixed EARTHTIME ^{205}Pb–^{233}U–^{235}U tracer (Condon et al., 2015). The single zircons were dissolved in ~ 120 µl of 29M HF with a trace amount of 30% HNO_3 at 220°C for 60 hours. After converting the dried fluorides into chlorides in 3M HCl at ~180°C overnight, U and Pb were separated using standard HCl-based anion-exchange chromatographic procedures on 0.05 ml PTFE columns. Pb and U were loaded together on a single Re filament in a silica-gel/phosphoric acid mixture, and analysed using NIGL's Thermo-Electron Triton Thermal Ionisation Mass-Spectrometer. Pb isotopes were measured by peak-hopping on a single SEM detector. U isotope measurements were made in static Faraday mode or on a single SEM detector, based on the uranium content. Age calculations and uncertainty estimation were made using the Tripoli and ET_Redux.

SIMS and CA-ID-TIMS zircon U-Pb data are given in supplementary Table S1 and Table S2, respectively. Uncertainties of individual analysis are reported at 1σ level in the text. The SIMS weighted mean ^{238}U-^{206}Pb age uncertainties are presented as ± X/Y, where X includes the analytical and U/Pb calibration uncertainties, Y includes X and external reproducibility (1%, 2 SD). The ID-TIMS ^{238}U-^{206}Pb age uncertainties are presented as ± X/Y/Z, where X is the uncertainty arising solely from internal or analytical uncertainty, Y includes X and the tracer calibration uncertainty, and Z includes Y and the ^{238}U decay constant uncertainty.

4. Zircon U-Pb dating results

Most zircons from sample 14GZLCP01 are 80-150 μm in length, and have aspect ratios of 2-4. Most of them are euhedral and prismatic in morphology, with a small portion of rounded grains. They have weakly or no oscillatory zoning under CL images. A total of 35 SIMS U-Pb analyses were conducted on 35 zircons. U and Th contents are between 75 and 1154 ppm, 46 and 570 ppm, respectively, with Th/U ratios of 0.2-1.9, suggesting the magmatic origin. Except eight sets of data from zircons with high common lead and/or discordant, others are considered to be reliable. The main population includes 24 grains, and their ^{238}U-^{206}Pb ages range from 530 ± 6 Ma to 561 ± 6 Ma, yielding a weighted mean ^{238}U-^{206}Pb age of 543.3 ± 2.5/6.0 Ma (2σ, n = 24, MSWD = 1.3, Fig. 4a). Other three grains have older ^{238}U-^{206}Pb ages, namely 654 ± 7 Ma, 887 ± 10 Ma, and 1853 ± 19 Ma, suggesting the xenocrystal origin.

CA-ID-TIMS data corroborate and refine the SIMS results of sample 14GZLCP01. Eight crack- and inclusion- free, texture uncomplicated zircons from the youngest populations of this sample were further dated by CA-ID-TIMS. Except one grain with high common Pb (m-z36, Pbc = 2.78 pg), others yield useful data. The main population includes 5 grains with Th/U ratios of 0.4-1.2. Their ^{238}U-^{206}Pb ages range from 545.35 ± 0.33 Ma to 546.07 ± 0.29 Ma, yielding a weighted mean ^{238}U-^{206}Pb age of 545.76 ± 0.20/0.31/0.66 Ma (2σ, n = 5, MSWD = 1.8, Fig. 4b, c). Other two grains have obvious older ^{238}U-^{206}Pb ages, namely 547.50 ± 0.20 Ma, and 554.53 ± 0.48 Ma, suggesting the xenocrystal origin.

5. Discussion

5.1 Geochronological constraints on regional stratigraphic correlation

The upper Ediacaran–lower Cambrian in South China consists mainly of carbonate rocks in shallow-marine settings and cherts in slope and deep water settings (Zhu et al., 2003, 2007). This succession is represented by Dengying and Zhujiaqing formations in Yunnan Province (Fig. 5) in the shallow-marine settings. The base of Dengying Formation is constrained at 551.07 ± 0.61 Ma (Condon et al., 2005), although other stratigraphic model correlates this ash horizon to the middle of this formation (An et al., 2015). Ash bed from the middle Dengying Formation is dated at 546.3 ± 2.7 Ma (Fig. 5), similar with dates from Namibia and Oman sections, providing geochronological constraint on the Ediacaran fossils (Yang et al., 2017). Based on the chemostratigraphical correlation of the Ediacaran–Cambrian transition between South China and Oman, we speculate that the age for the top of Dengying Formation is ca. 541 Ma (Amthor et al., 2003; Bowring et al., 2007; Li et al., 2013b). Upwardly, ages for the middle and the top of Zhujiaqing Formation are constrained at 535.2 ± 1.7 Ma and 526.5 ± 1.1 Ma, respectively (Compston et al., 2008; Zhu et al., 2009).

The Ediacaran-Cambrian transitional succession in the slope-to-basin settings in South China is represented by the Liuchapo Formation in Hunan-Guizhou areas (Fig. 5). It is more complete without hiatus, condensed, and composed mainly of chert. However, the lack of age-diagnostic biostratigraphic markers and $\delta^{13}C_{carb}$ data make their correlations over the Yangtze Block ambiguous. The Liuchapo Formation is traditionally regarded as the equivalent of Dengying Formation (e.g., Liu et al., 1991), whereas the geochronological dates from upper Liuchapo-lower Niutitang formations demonstrate that the upper Liuchapo Formation should be much younger than previous thought (e.g., Chen et al., 2009; Wang et al., 2012a). In this study, the ash bed from the lower Liuchapo Formation in the Longbizui section is dated at 545.76 ±

0.20/0.31/0.66 Ma, providing the first robust radiometric age for the late Ediacaran successions in deep-water settings in South China. Within errors this new date is identical to the date for the middle Jiucheng Member of Dengying Formation (Yang et al., 2017), indicating that the lower part of Liuchapo Formation in the deep water facies can be correlated to the lower Dengying Formation in the shallow water facies (Fig. 5). Previous geochronological studies reveal that zircon U-Pb ages of ash beds at the uppermost part of the Liuchapo Formation in Ganziping and Pingyin sections are 536.3 ± 5.5 Ma and 536 ± 5 Ma, respectively (Chen et al., 2009; Zhou et al., 2013). The distinct positive $\delta^{13}C_{org}$ excursion (P4, Fig. 2) at lowermost part of Niutitang Formation is comparable to the ZHUCE which equivalent to the Dahai Member in the Xiaotan section of shallow-water facies (Wang et al., 2012a; Cremonese et al., 2013; Guo et al., 2013; Li et al., 2013b). The geochronological constraints and organic carbon isotopes imply that the top of the Liuchapo Formation can be correlated to the middle Zhongyicun Member (near the 535.2 ± 1.7 Ma ash bed) of Zhujiaqing Formation in eastern Yunnan Province. Thus the upper part of Liuchapo Formation is comparable to the upper Dengying-lower Zhujiaqing formations (Fig. 2). This correlation affirms that the Liuchapo Formation straddles Ediacaran and Cambrian periods, and the equivalent horizon of the Ediacaran-Cambrian boundary in the deep water facies in South China is likely located near the base of a widespread negative $\delta^{13}C_{org}$ excursion (e.g., N2 in Longbizui section) at the upper Liuchapo Formation (Fig. 2).

5.2 Deep water conditions and oxygenation in Ediacaran-Cambrian transition

The Ediacaran-Cambrian transition is a key period in the Earth history with major changes in oceanic and atmospheric chemical compositions. Lots of redox sensitive elements and isotopes have been reported from sections in deep-water settings in South China, but the lack of high precision radiometric ages makes their interpretations equivocal. With refined geochronological framework in this study, better understandings about the deep water condition and oceanic oxygenation in Ediacaran-Cambrian transition can be achieved.

Speciation of Fe in well-preserved sedimentary rocks can be applied to evaluate the redox chemistry of the marine water column (e.g., Canfield et al., 2008). During period from 551.07 ± 0.61 Ma to ca. 520 Ma, nearly all the Fe_{HR}/Fe_{T} ratios of sediments in slope-basin areas exceed 0.38 (Fig. 6), demonstrating widespread anoxic deep waters (Canfield et al., 2008; Chang et al., 2010; Wang et al., 2012a; Sahoo et al., 2016). Some of Fe_{Py}/Fe_{HR} ratios exceed 0.7 for sediments from lower Liuchapo Formation in the middle-lower slope settings such as Wuhe (Guizhou) (Sahoo et al., 2016) and Longbizui sections (Wang et al., 2012a; Chen et al., 2015a), indicating that intermittent sulfidic water existed in the middle-lower slope area in late Ediacaran period (Fig. 6). The size of the sulfidic water decreased and disappeared at the latest Ediacaran. After that the deep water masses were mainly Fe^{2+}-enriched, until sulfidic water reappeared during 533–520 Ma. The zircon U-Pb age 545.76 ± 0.20/0.31/0.66 Ma for lower Liuchapo Formation is within errors identical to 545.1 ± 1 Ma for the middle Schwarzrand sub-Group of Nama Group in Namibia (Grotzinger et al., 1995), providing a tie-point for the stratigraphic correlation between South China and Namibia. The Nama Group is mainly of shallow-water facies, and its redox is well constrained by Fe-S-C systematics (Wood et al., 2015). Euxinic water was not detected from Nama basins, but persistently anoxic water was detected in deep settings (Wood et al., 2015). Although Fe speciation proxy data usually identify local water column redox conditions, the similar anoxic deep-water conditions detected from South China and Namibia imply that anoxia remained widespread in deep-water during the Ediacaran-Cambrian transitional period.

The persistent anoxic with locally euxinic environments throughout the Ediacaran-Cambrian transition provide an opportunity to track the oceanic oxygenation events using the degree of redox sensitive element (e.g., Mo, U, Re, V, Cr) enrichments. The Mo and U data are compiled based on the new geochronological framework in this study (Fig. 7). And to avoid the effect of basin restriction, only data from slope-basin settings in South China, where the water column was paleogeographically well connected with the open ocean during the Ediacaran–early Cambrian (e.g., Zhang et al., 2015), are included. Compilation of Mo concentrations and Mo/TOC ratios of euxinic sediments in deep-water facies in South China (Fig. 7a) indicates that significant enrichment of Mo occurred in 533–520 Ma, with a minor one at ca. 536 Ma. No enrichment around 540 Ma is presented in Fig. 7a, since euxinic sediments were not recognized from this interval. The onset of U enrichment in sediments requires less reducing conditions than that of Mo (e.g., Algeo and Tribovillard, 2009). Thus U concentrations and U/TOC ratios of sediments deposited under both sulphidic and ferruginous conditions are compiled in Fig. 7b. The profile of U shows similar trend to that of Mo. The period 533–520 Ma with substantial redox sensitive element enrichment suggests the presence of large marine redox sensitive element reservoir and thus a widely oxygenated ocean. However a precise estimation of the times of oxygenation event, and the duration of each event in 533–520 Ma, requires further high precision geochronological studies. Except for a minor enrichment at ca. 536 Ma, the crustal-level Mo and U values of 551–535 Ma anoxic sediments record a prolonged oceanic anoxia. This is different from the compilation in Sahoo et al. (2016), who suggest that a modern-level redox sensitive element enrichment occurred at ca. 540 Ma. Most data forming the ca. 540 Ma enrichment in Sahoo et al. (2016) are from Yuertus Formation in the northern Tarim Basin, Northwest China (Yu et al., 2009). However, the fossil assemblage in the Yuertus Formation demonstrates that it is of Qiongzhusian in age (Qian et al., 2000). If this age estimation is correct, the redox sensitive element enrichment recorded in the lower Yuertusi Formation is equivalent to that in the lower Niutitang Formation in South China. Thus more evidences are needed to support the ca. 540 Ma oceanic oxygenation event.

6. Conclusions

The ash bed from the lower Liuchapo Formation in the Longbizui section in western Hunan Province, South China, is dated at 543.3 ± 2.5/6.0 Ma by SIMS, and is further refined to 545.76 ± 0.20/0.31/0.66 Ma by CA-ID-TIMS. This age suggests that:

(1) The lower and the middle-upper parts of the Liuchapo Formation in the deep water facies can be correlated to the lower Dengying Formation and the upper Dengying–lower Zhujiaqing formations in shallow water facies, respectively. And equivalent horizon of the Ediacaran-Cambrian boundary in the deep water facies in South China is likely located near the base of a widespread negative $\delta^{13}C_{org}$ excursion at the upper Liuchapo Formation.

(2) From late Ediacaran to early Cambrian, the deep ocean was characterized by widespread anoxic, ferruginous water, with intermittent euxinic water impinged on the middle-lower slope, presenting a dynamic redox-stratified ocean. Significant oxygenation events occurred in 535–520 Ma, with a minor one at ca. 536 Ma. Oxygenation event at ca. 540 Ma is not supported by this study.

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Figure captions

Figure 1. Simplified palaeogeographic map of the Yangtze Block during the Ediacaran-Cambrian transition interval (modified after Zhu et al., 2003). The dots represent the cities, and the triangles represent the sections.

Figure 2. Stratigraphy of the Ediacaran-Cambrian transition in South China. Radiometric ages are from Condon et al. (2005), Compston et al. (2008), Zhu et al.

(2009), Yang et al. (2017), and this study. Stratigraphic columns and carbon isotopes of sections are from Zhu et al. (2007), Wang et al. (2012a), Cremonese et al. (2013), and Li et al. (2013b).

Figure 3. (a) Field photo showing the sampling site of the ash bed 14GZLCP01. (b) Photomicrograph of sample 14GZLCP01.

Figure 4. (a) SIMS zircon U-Pb Concordia diagram of sample 14GZLCP01; (b) CA-ID-TIMS zircon U-Pb Concordia diagram; (c) CA-ID-TIMS zircon ^{238}U-^{206}Pb date distribution plot. Vertical bars represent 2σ analytical uncertainty of individual zircon analyses, and the red ones are included in age calculation.

Figure 5. Stratigraphic correlations between sections from deep-water settings, and their comparison with the succession in platform interior in South China. Stratigraphic columns, radiometric ages and fossil distributions are from Condon et al. (2005), Compston et al. (2008), Chen et al. (2009, 2015b), Zhu et al. (2009), Wang et al. (2012b), Zhou et al. (2013), Hofmann et al. (2016), Yang et al. (2017), and this study. DST = Doushantuo Formation, DLT = Donglongtan Member, JC = Jiucheng Member, BYS = Baiyanshao Member, ZYC = Zhongyicun Member.

Figure 6. Iron speciation data of the Ediacaran-Cambrian transition in slope and basin in South China. The green fields represent the euxinic waters. Data are from Canfield et al. (2008), Chang et al. (2010), Wang et al. (2012a), Chen et al. (2015a), and Sahoo et al. (2016).

Figure 7. Compilation of Mo (a) and U (b) data of sediments from Liuchapo and lower Niutitang formations (and their deep-water equivalents) in the deep-water settings in South China. For Mo, only data from euxinic shales are plotted. For U, ferruginous and euxinic shales are plotted. Since the complicated zircon U-Pb ages (ranging from 532.3 ± 1.4 Ma to 518 ± 5 Ma) of the lower Niutitang

Formation (e.g., Zhou et al., 2008; Jiang et al., 2009; Chen et al., 2015b), data from this interval are compiled together, and further high precision geochronological study is required to determine the times and the duration of the redox sensitive trace element enrichments. Data are from Guo et al. (2007), Chang et al. (2010, 2012), Chen et al. (2015a), Wang et al. (2015), Och et al. (2016), and Sahoo et al. (2016).