New U–Pb age from the basal Niutitang Formation in South China: Implications for diachronous development and condensation of stratigraphic units across the Yangtze platform at the Ediacaran–Cambrian transition

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1. Introduction

The Ediacaran–Cambrian (E–C) transition witnessed the great biological innovation characterized by the replacement of Ediacaran soft-body animals by Cambrian-type shelly fauna (e.g., Narbonne, 2005, 2010) and dramatic ocean geochemical changes including large carbonate carbon isotope (813C) excursions (e.g., Maloof et al., 2010), sulfur isotope variations (e.g., Schröder et al., 2011). The casual link between these events, however, remains uncertain and requires further investigation, particularly the time and synchrony of biological and geochemical events.

Owing to the relatively good preservation, the Ediacaran-early Cambrian succession in the Yangtze platform of South China plays important roles in exploring the relationship between biological evolution and paleoenvironmental changes. In the last decade, enormous paleontological (e.g., Qian, 1999; Shu et al., 1999, 2001, 2003a, 2003b, 2006; Zhang et al., 2002, 2003, 2004; Steinier et al., 2007; Dong et al., 2009; Liu et al., 2011) and geochemical (e.g., Shen and Schidlowski, 2000; Goldberg et al., 2007; Ishikawa et al., 2008; Wille et al., 2008; Wen et al., 2011) data have been obtained from the early Cambrian strata in this region, but stratigraphic correlation among shallow- to deep-water facies has been difficult due to facies-dependent fossil preservation and the lack of radiometric age data in general. Existing radiometric ages from the lower Cambrian strata were mostly obtained from shallow-water facies and show significant discrepancy. U–Pb age dating from the basal Cambrian units in eastern Yunnan Province yielded ages of 538.2 ± 1.5 Ma (Jenkins et al., 2002), 539.4 ± 2.9 Ma (Compton et al., 2008), and 536.7 ± 3.9 Ma (Zhu et al., 2009), confirming their proximity with the E–C boundary. However, much younger ages of 532.3 ± 0.7 Ma (Jiang et al., 2009), 518 ± 5 Ma (Zhou et al., 2008), and 521 ± 5 Ma (Xu et al., 2011) were obtained from the basal Niutitang Formation in Guizhou Province; the base of this unit has been traditionally considered as the E–C boundary. These age differences raise questions about the diachrony of stratigraphic units across the early Cambrian Yangtze platform and compel for...
additional age constraints, particularly in deep-water sections
where biostratigraphic data are very limited.

In this paper, we report a U–Pb SHRIMP age of a tuffaceous bed
from the basal Niutitang Formation in Taoying, Guizhou Province.
Paleogeographically, the Taoying area was located in the slope
environment of the early Cambrian Yangtze platform (Fig. 1A and
B and Fig. 2). In combination with existing ages and biostrati-
graphic data, we discuss the possible E–C boundary in deep-water
sections, diachronous development and condensation of early
Cambrian stratigraphic units, and the depositional age of the poly-
metallic (Ni–Mo–PGE) ore deposits across the Yangtze platform.

2. Geological setting and sample section

It has been inferred that the E–C Yangtze platform inherited
from a late Neoproterozoic rifted basin that was initiated at the
southeastern side of the Yangtze block at ca. 820–830 Ma (Wang
and Li, 2003; Zhao et al., 2011). Several lines of evidence including
the stratal thickness, spatial distribution of facies and the lack of
major tectonic events and igneous activity indicate that the E–C
succession was deposited in a passive continental margin setting
(Jiang et al., 2006a, 2011). During the latest Ediacaran and earliest
Cambrian, shallow-water carbonate deposits of the Dengying and
Yanjiahe formations (and their correlative units) dominated the
northwest part of the Yangtze platform and changed basinward
into deep-water mudstone/shale and cherts of the Liuchapo For-
mation (Fig. 1A; Wang, 1985; Zhu et al., 2003; Steiner et al.,
2007). Overlying the Dengying and Yanjiahe formations, the black
shale-dominated Niutitang Formation and its correlative units
(including Shiyantou Formation in Yunnan, Guojia Formation
in Sichuan, Shuijingtuo Formation in Hubei, and Xiaoyanxi Formation
in Hunan; Fig. 1C) cover the majority of the early Cambrian
Yangtze platform, representing a major sea-level transgression.
The exact time and number of transgressive–regressive cycles
across the E–C transition are still uncertain, largely due to the dif-
ficulties of establishing a precise stratigraphic framework across
the Yangtze platform.

The basal part of the Niutitang Formation and its correlative
units contain an organic-rich polymetallic sulfide layer with unus-
ual enrichment of Ni, Mo, and platinum group element (PGE) that
have been locally mined as metallic ores (Mao et al., 2002; Jiang
et al., 2006b; Lehmann et al., 2007). The extreme enrichment of
redox-sensitive elements (Ni, Mo, V, U, Cr, and PGE) and large
Mo isotope change across the Ni–Mo–PGE sulfide layer have been
interpreted as recording a major ocean anoxic event at the E–C
boundary (Lehmann et al., 2007; Wille et al., 2008). More recent
U–Pb ages of 532.3 ± 0.7 Ma (Jiang et al., 2009) and 536.3 ±
5.5 Ma (Chen et al., 2009) from tuffaceous beds below the
Ni–Mo–PGE sulfide layer and Re–Os age of 521 ± 5 Ma (Xu et al.,
2011) from the metallic sulfide layer itself, however, indicated that
the depositional age of Ni–Mo–PGE enriched sulfides should be
much younger than the E–C boundary.

The study section (Taoying section) is located in northeastern
Guizhou Province, South China, about 4 km southeast of the
Taoying town. Paleogeographically, this area was within the slope environment of the Yangtze platform (Fig. 2A). Well-exposed outcrop consists of, in ascending stratigraphic order, the Doushantuo Formation, the Liuchapo Formation and the lower Niutitang Formation (Fig. 2B). The upper Doushantuo Formation is characterized by organic-rich black shale containing abundant macroscopic algae of the Wenghui biota (Zhao et al., 2004; Wang et al., 2008; Tang et al., 2008). This formation is conformably overlain by approximately 30-m-thick black cherts of the Liuchapo Formation that host \textit{Horodyskia} and \textit{Palaeopascichnus} fossils, which have been also found in the Jiumen section in Guizhou Province (Dong et al., 2008). Overlying the Liuchapo Formation is the pyrite-rich black shale of the Niutitang Formation. The lower part of the Niutitang Formation contains a laterally discontinuous phosphorite layer and an unusually metal-enriched layer (Fig. 3A) that is typical of the polymetallic sulfide layer seen in other sections across the Yangtze platform. Trace elemental analysis (unpublished data) indicates that redox-sensitive elements Ni, Mo, V are extremely enriched in this interval (unpublished data); (B) Field photograph of the tuffaceous bed at the base of the Niutitang Formation. Hammer for scale is 30 cm long. (C) Representative zircon grains that yield concordant age show clear oscillatory zones under cathodoluminescence (CL). Circles show the position of the SHRIMP beam spots; (D) Representative zircon grains that have discordant ages.

Taoying town. Paleogeographically, this area was within the slope environment of the Yangtze platform (Fig. 2A). Well-exposed outcrop consists of, in ascending stratigraphic order, the Doushantuo Formation, the Liuchapo Formation and the lower Niutitang Formation (Fig. 2B). The upper Doushantuo Formation is characterized by organic-rich black shale containing abundant macroscopic algae of the Wenghui biota (Zhao et al., 2004; Wang et al., 2008; Tang et al., 2008). This formation is conformably overlain by approximately 30-m-thick black cherts of the Liuchapo Formation that host \textit{Horodyskia} and \textit{Palaeopascichnus} fossils, which have been also found in the Jiumen section in Guizhou Province (Dong et al., 2008). Overlying the Liuchapo Formation is the pyrite-rich black shale of the Niutitang Formation. The lower part of the Niutitang Formation contains a laterally discontinuous phosphorite layer and an unusually metal-enriched layer (Fig. 3A) that is typical of the polymetallic sulfide layer seen in other sections across the Yangtze platform. Trace elemental analysis (unpublished data) indicates that redox-sensitive elements Ni, Mo, V are highly enriched in this interval. A 10-cm-thick, greenish grey tuffaceous bed (Fig. 3B) is present just below the polymetallic layer. So far, no biostratigraphic data is available for the Niutitang Formation in this section.
3. Analytical procedure and result

Three packages of sample (AP-29.0) were collected from the tuffaceous bed in the basal Niutitang Formation. Zircons were hand picked from heavy mineral concentrates under binocular microscope. The representative grains, together with the several standard zircons TEM (417 Ma) (Black et al., 2003), were mounted in epoxy and polished to approximately half of their thickness. Prior to dating, zircon grains were photographed under transmitted and reflected lights. Cathodoluminescence (CL) images were used to observe the internal structure of grains in order to choose the well-preserved spot for dating. The U, Th and Pb isotope compositions were analyzed using SHRIMP II at the Ion Microprobe Analysis Center of the Academy of Geological Sciences in Beijing, China, following the procedure described in Williams (1998). The data were processed using the SQUID and ISOPLOT programs of Ludwig (2001, 2003). The uncertainties in isotope ratios are 1σ, and the weighted mean ages are quoted at 95% confidence level after 208Pb correction.

Zircon grains extracted from sample AP-29.0 are euhedral to subeuhedral (Fig. 3C and D), with sizes mostly in the range of 50–100 μm. Some of them have clear oscillatory zones (Fig. 3C) indicative of contemporaneous volcanic origin. Sixteen zircons were chosen for dating and their isotope data are shown in Table 1. Among the analyzed grains, 10 zircons gave a narrow age range from 510–530 Ma, yielding a weighted mean 206Pb/238U age of 522.7 ± 4.9 Ma, with mean square of weighted deviates (MSWD) of 1.6 (Fig. 4A and B). Three zircons (AP-2.1, AP-3.1 and AP-5.1; Fig. 3D) gave discordant ages of 576 Ma, 546 Ma and 548 Ma, respectively. These ages are older than the main group and the E–C boundary age of 542.0 ± 0.3 Ma (Amthor et al., 2003). Thus we interpret that they may have an inherited origin. Zircon AP-4.1 has significantly younger age of 448 Ma, which is most likely affected by the fracture on zircon surface. The remaining two grains

<table>
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<tr>
<th>Spot</th>
<th>206Pb (%)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>232Th/238U</th>
<th>206Pb/238U</th>
<th>±1σ (%)</th>
<th>±1σ (%)</th>
<th>±1σ (%)</th>
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<td>AP-2.1</td>
<td>2.27</td>
<td>810</td>
<td>535</td>
<td>0.68</td>
<td>66.7</td>
<td>0.0569</td>
<td>1.7</td>
<td>0.735</td>
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<td>AP-3.1</td>
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<td>732</td>
<td>410</td>
<td>0.58</td>
<td>56.6</td>
<td>0.0593</td>
<td>1.4</td>
<td>0.723</td>
<td>2.0</td>
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<tr>
<td>AP-4.1</td>
<td>0.89</td>
<td>425</td>
<td>542</td>
<td>0.54</td>
<td>49.9</td>
<td>0.0784</td>
<td>1.2</td>
<td>0.778</td>
<td>1.8</td>
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<tr>
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<td>0.25</td>
<td>1934</td>
<td>1014</td>
<td>0.54</td>
<td>148</td>
<td>0.0657</td>
<td>0.7</td>
<td>0.743</td>
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<td>1409</td>
<td>754</td>
<td>0.55</td>
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<td>0.0608</td>
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<td>934</td>
<td>0.50</td>
<td>137</td>
<td>0.0621</td>
<td>0.9</td>
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<td>1376</td>
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<td>376</td>
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<td>1.0</td>
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<td>576</td>
<td>0.43</td>
<td>101</td>
<td>0.0600</td>
<td>0.9</td>
<td>0.701</td>
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<td>-</td>
<td>2250</td>
<td>1220</td>
<td>0.56</td>
<td>150</td>
<td>0.0653</td>
<td>0.7</td>
<td>0.701</td>
<td>1.5</td>
</tr>
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</table>

Notes: 1. Errors are 1σ; Pb and Pb/C3 indicate the common and radiogenic portions, respectively.
2. Error in standard calibration was 0.40% (not included in above errors but required when comparing data from different mounts).
4. Those data with symbol # are rejected from mean-age calculation and are not show in concordia plot (Fig. 4).

Fig. 4. (A) U–Pb concordia diagram for the tuffaceous bed in the Taoying section; Analyses with 1σ error ellipses are plotted as radiogenic ratios after 208Pb correction. Weighted-mean 206Pb/238U dates at a 95% confidence level for the main group of zircon grains show the best estimated age for the dated sample. MSWD – mean square of weighted deviates; (B) 206Pb/238U ages of 10 zircon analyses. Error bars represent 2σ errors.
The exact duration, however, is unknown. Chen et al. (2009) may be early Cambrian (e.g., Chang et al., 2009; Chen et al., 2009). The age of 522.7 ± 4.9 Ma present here is obtained from the basal Niutitang Formation, which is 20 cm above the top of the Liuchapo Formation. No exposure or erosional surface is observed at the Liuchapo/Niutitang boundary in the Taoying section. Thus it is very likely that the majority of the Liuchapo Formation was deposited during the early Cambrian rather than the late Ediacaran and the E–C boundary should be located within the Liuchapo Formation. If the black shale at the top of the Doushantuo Formation in the Taoying section is time equivalent to that of the Doushantuo Formation in the Yangtze Gorges area, which has an age of ca. 551 Ma (Condon et al., 2005; Zhang et al., 2005), the duration of the Liuchapo Formation in deep-water sections may be as long as 30 million years, much longer than the carbonate-dominated Ediacaran Dengying Formation (ca. 551–542 Ma).

4.3. The Ediacaran–Cambrian boundary and stratigraphic correlation

The E–C boundary (542.0 ± 0.3 Ma, Amthor et al., 2003) in South China has been highly debated due to the absence of precise radiometric ages. It is traditionally defined by the first occurrence of small shelly fossils (SSF) (e.g., Chen, 1984; Qian, 1999) and Micrhystridium-like acritarchs (Ding et al., 1992; Yin, 1997; Dong et al., 2009) which is located 10–15 m above the Dengying–Yanjiahe boundary in the Yangtze Gorges area (Fig. 5). However, owing to the lithologically dependent fossil preservation, this idea has been challenged by carbon isotope chemostratigraphy that shows a prominent negative δ13C excursion below the lowest occurrence of SSFs (Zhou et al., 1997; Shen and Schidlowski, 2000; Zhu et al., 2003; Jiang et al., 2007b; Jiang et al., 2012; Ishikawa et al., 2008; Li et al., 2009). In the basinal facies, the first appearance of sponge spicules was usually taken as the base of the Cambrian. Without additional constraints, the stratigraphic correlation between shallow-water platform and deep-water basin has been difficult and in cases, arbitrary.

If the deposition of Liuchapo Formation began at ca. 551 Ma (Condon et al., 2005) and ended at ca. 523 Ma, as discussed above, the E–C boundary in the basinal facies must be located within the Liuchapo Formation. The exact position of the E–C boundary requires additional ages and/or paleontological data, but considering the simple lithology and the lack of obvious stratigraphic discontinuity, it is more likely located at the lower part of the Liuchapo Formation (Fig. 5).

In combination with available absolute ages and biostratigraphic data, regional stratigraphic correlation across the early Cambrian Yangtze platform indicates strong stratigraphic diachrony and condensation (Fig. 5). The late Ediacaran Dengying Formation is only time-equivalent with the lower Liuchapo Formation in the basin; whereas the middle and upper Liuchapo Formation is probably deposited during the Nemakit-Daldynian or lower-middle Meishucunian. In this case, the majority of the Liuchapo Formation should be correlated with the Zhiquaogang Formation in Meishucun section, eastern Yunnan Province, the Kuan-chuanpu Formation in Shatan section, Sichuan Province, and the Yanjiabei Formation in the Yangtze Gorges area. In the Zunyi area represented by the Songlin section in northeastern Guizhou Province, the Kuan-maiton in Meishucun section, eastern Yunnan Province, the Kuan-chuanpu Formation in Shatan section, Sichuan Province, and the Yanjiabei Formation in the Yangtze Gorges area. In the Zunyi area represented by the Songlin section in northeastern Guizhou Province, the Kuan-maiton in Meishucun section, eastern Yunnan Province, the Kuan-chuanpu Formation in Shatan section, Sichuan Province, and the Yanjiabei Formation in the Yangtze Gorges area. In the Zunyi area represented by the Songlin section in northeastern Guizhou Province, the Kuan-maiton in Meishucun section, eastern Yunnan Province, the Kuan-chuanpu Formation in Shatan section, Sichuan Province, and the Yanjiabei Formation in the Yangtze Gorges area.
Tommotian or upper Meishucunian age and is much more widespread across the Yangtze platform. Time equivalent units may include the Shiyantou Formation in Yunnan, the Guojiaba Formation in Sichuan, the Shuijingtuo Formation in Hubei and the Xiaoyanxi Formation in Hunan (Fig. 5).

4.4. Uncertainties and future research

The existing age data from the Niutitang Formation and its equivalent units also raise questions on the precision of age dating and the duration of the Liuchapo Formation. In the Zunyi section, zircon grains from almost the same ash bed produced different ages of 532.3 ± 0.7 Ma (Jiang et al., 2009) and 518 ± 5 Ma (Zhou et al., 2008). Considering the better precision of the older age, it is more likely that the younger age (518 ± 5 Ma) was due to the lead loss that commonly resulted in younger ages (e.g., Kooijman et al., 2011). A few zircon grains from the ash bed in this study produced younger ages and there is a possibility that the age of 522.7 ± 4.9 Ma from the Taoying section has also been altered to some degree from lead loss. There is a possibility that most early Cambrian ages from lead loss. This raises the possibility so far (Fig. 5), including 532.3 ± 0.7 Ma (Jiang et al., 2009) and 518 ± 5 Ma (Zhou et al., 2008) ages from Zunyi, northern Guizhou, 522.7 ± 4.9 Ma from Taoying, northeastern Guizhou (this study), and 536.3 ± 5.5 Ma from Ganziping, northwestern Hunan (Chen et al., 2009), were from the same, contemporaneous ash bed widely distributed across the early Cambrian Yangtze platform. The age differences among sections and authors are due to the bean location during SHRIMP U–Pb analyses and the degree of lead loss in analyzed zircon grains. The ages of 538.2 ± 1.5 Ma (Jenkins et al., 2002), 539.4 ± 2.9 Ma (Compston et al., 2008), and 536.7 ± 3.9 Ma (Zhu et al., 2009) from the Meishucun section in eastern Yunnan could be also from the same ash bed as those of Guizhou and Hunan provinces. However, in the Meishucun section, bed 5 and bed 9 bentonites have different age groups from ca. 540 Ma to ca. 526 Ma (Compston et al., 2008). It is uncertain which ash bed is more likely correlatable with the ones in Guizhou and Hunan provinces. Elucidating uncertainties on the potential synchrony of ash beds and age differences across the early Cambrian Yangtze platform requires more precise TIMS age dating of the zircon grains collected from these sections in the same lab following the same procedure.

5. Conclusion

We report a new SHRIMP zircon U–Pb age of 522.7 ± 4.9 Ma from a tuffaceous bed in the basal Niutitang Formation in Taoying, Guizhou Province, South China. This age is significantly younger than the E–C boundary (542 Ma) and suggests that: (1) the polymetallic (Ni–Mo–PGE) layer within the Niutitang Formation has a depositional age of ca. 523 Ma; (2) the paleoceanographic or hydrothermal event recorded by the polymetallic sulfides happened during the early Tommotian stage rather than the Nemakit-Daldynian stage; (3) the Liuchapo Formation in deep-water facies may last as long as 30 million years; (4) the E–C boundary may be located in the lower part of the Liuchapo Formation and the majority of the Liuchapo Formation may have been deposited during the early Cambrian rather than late Ediacaran, and (5) the stratigraphic units across the Yangtze platform at the E–C transi-
tion are strongly diachronous and highly condensed. However, additional study is required in the future to test whether the existing age gaps from the basal Niutitang Formation and its time equivalent units in the Yangtze platform were from the same, contemporaneous ash bed.

Acknowledgements

We are grateful to Mingshuai Zhu and Zhiqing Yang for data analysis and processing. Professor Linzhi Gao is thanked for his valuable comments on the earlier version of the manuscript. We appreciate Dr. Michel Faure and an anonymous reviewer for their constructive comments that helped to improve the manuscript. This research was supported by the Ministry of Science and Technology of China (2011CB808800), the National Natural Science Foundation of China (40972022), and Fundamental Research Funds for the Central Universities (2011YLY018).

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