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SHRIMP U-Pb zircon age of tuff at the bottom of the Lower Cambrian Niutitang Formation, Zunyi, South China

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A SHRIMP U-Pb zircon geochronology study of the tuff at the bottom of the Lower Cambrian Niutitang Formation at Songlin, Zunyi, South China yielded a mean $^{206}Pb/^{238}U$ age of 518±5 Ma. It is significantly younger than the Re-Os ages of 537—542 Ma for the overlying polymetallic Ni-Mo-PGE-rich layer in the basal Niutitang Formation at Songlin, suggesting that the Re-Os ages might represent that of the original magma chamber for the Ni-Mo-PGE-rich layer rather than the formation age of the strata. The intra-basinal stratigraphic correlation also implies that the absolute age of the Chengjiang biota should be younger than 518±5 Ma. Our new result, together with the SHRIMP U-Pb zircon age for the K-bentonite in the Zhongyicun member of the Zhujiaqing Formation at the Meishucun section, Yunnan Province, provides a temporal constraint for the Lower Cambrian of the Yangtze Platform in South China.

Lower Cambrian, Niutitang Formation, tuff, SHRIMP, zircon, Chengjiang biota, polymetallic Ni-Mo-PGE-rich layer

The wide-spread outcrops of the early-Cambrian sequences over the Yangtze Platform in South China represent an important window for studying the Cambrian bio-radiation, the secular paleo-seawater isotope variations, the ore-forming events of terminal Neoproterozoic-Cambrian times, and in particular, for investigating the Cambrian subdivision and global correlation[1−9]. Since the last century, these sequences have been studied from a number of different aspects, and paleontological studies have acquired many unique findings[10−19]. The geochronological research, on the other hand, is still lagging behind. Up to now, there is only one high-precision, reliable U-Pb zircon age for the early Cambrian strata at the Meishucun section, Yunan Province, South China[20−22]. Global correlations for the Lower Cambrian strata and biological events have thus been hampered by the lack of good geochronological constraints. The existence of two biogeographic realms during early Cambrian[23] and the lithofacies change made stratigraphic correlations over long distances even harder. Therefore, high-precision ages are urgently needed for the Lower Cambrian of the Yangtze Platform, South China.

The extensive occurrences of a polymetallic Ni-Mo-PGE-rich layer[24,25] in the Lower Cambrian black shale series (the basal Niutitang Formation in Guizhou and Hunan Provinces and its lateral equivalents) within the Yangtze Platform apparently represents one of the major ore-forming events in early Cambrian. Previous study[26] suggested that the Chengjiang biota[10−19] in the Kun-

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ming, and the Zunyi biota in the Songlin region, Zunyi, are lateral equivalents. As the Ni-Mo-(PGE)-rich layer is stratigraphically below both of them, it has been used as a critical geochemical marker for correlating the Lower Cambrian successions on the Yangtze Platform[27]. We recently discovered a bed of tuff ca. 2 m below the Ni-Mo-PGE-rich layer in the basal Niutitang Formation at Songlin, Zunyi, Guizhou Province. In this study we dated the zircon grains in the tuff using the Sensitive High Resolution Ion Microprobe (SHRIMP) U-Pb method. The result not only provided a constraint on the absolute age for the Ni-Mo-PGE-rich layer, but also enabled us to evaluate the absolute age of the Chengjiang biota through regional stratigraphic correlation.

The objectives of this study are: (1) to provide a SHRIMP U-Pb zircon age constraint for the tuff unit in the basal Niutitang Formation in Zunyi, South China, and to discuss the genetic model of the polymetallic Ni-Mo-PGE-enriched layer based on both the new SHRIMP U-Pb zircon age and previous Re-Os datings of the polymetallic Ni-Mo-PGE-enriched layer; (2) to constrain the absolute age of the Chengjiang biota, and (3) to construct a preliminary temporal framework for the Lower Cambrian in South China, using both the SHRIMP U-Pb zircon age obtained in this study and that by Jenkins et al.[22] for the Lower Cambrian on the Yangtze Platform, and compare that with the internationally accepted age for the Precambrian-Cambrian boundary[28].

1 Geological settings

The tectonic setting for the terminal Neoproterozoic-Early Cambrian Yangtze Platform is still unclear. Sedimentological studies suggest that the paleogeography of the Yangtze Platform during this geological interval can be divided into three zones (i.e., the platform interior, the transitional zone, and the slope to deep basin zone) from northwest to southeast, extending along a NE-SW strike[25,27]. Rock successions in the platform interior zone mainly consist of dolomite and phosphorite while those on the slope and deeper basins are mostly composed of cherts. The distribution and characteristics of fossil material in different zones are also different. In general, rocks on the shallow platform are richer in fossil record than those of the deep-water facies[25,27].

One of the two sections involved in this study is the Jianpoding section, which is adjacent to Zhongnan Village of Songlin Town, 25 km west of Zunyi City in Guizhou Province. It is located within the Early Cambrian platform interior zone (see details in Figure 1 of Zhu et al.[27]). The Precambrian-Cambrian sequences in the Songlin area have already been described in detail in the literature[29,30]. The topmost Precambrian succession in this region is the Dengying Formation dolomite, which is disconformably overlain by the Lower Cambrian Niutitang Formation (Figure 1B), and the contact is marked by a weathered ferriferous clay bed (< 2 cm thick). The basal Niutitang Fomation consists of phosphorites with a thickness of ca. 25 cm. The immediately overlying strata consist of, in ascending order, jarosite altered lava, tuff, laminated black shales, and carbonaceous cherts with phosphatic nodules. They are in turn overlain by carbonaceous shales intercalated with carbonaceous carbonate rocks. The polymetallic Ni-Mo-PGE-enriched layer is just above this basal Niutitang Formation succession. The tuff found in this study is stratigraphically ca. 2 m below the Ni-Mo-PGE-rich horizon. The K-bentonite found by Luo et al.[29] is immediately near the tuff and needs further investigation.

The polymetallic Ni-Mo-PGE-enriched layer is overlain by a thick (ca. 25 m) organic-rich carbonaceous shale and silty shale unit. The recently discovered Zunyi biota[25,26] was preserved in the silty shales, and has been considered equivalent to the Chengjiang biota in the Kunming region, Yunnan Province. The horizon hosting the Zunyi biota is stratigraphically ca. 30 m above the studied tuff unit at the basal Niutitang Formation. In the Songlin area, the polymetallic Ni-Mo-PGE-rich layer is usually ca. 10 cm thick, but there are locally up to 200 cm thick podiform bodies.

For comparison, we also plotted the well exposed Precambrian-Cambrian sequences in Kunming, Yunnan Province (Figure 1A), which is about 500 km southwest of the study region. The succession in Yunnan is well documented, and most studies there have focused on the Meishucun section in Jinning County[31−35], which is a former global stratotype candidate section for the Precambrian-Cambrian boundary. Figure 1 shows that the two successions are highly correlatable. At present, the Precambrian-Cambrian boundary in the Kunming region is often placed at the base of the Zhongyicun Member of the Zhujiaqing Formation[27], but it has not reached a general consensus[3,31−33,36,37]. One of the reasons is the disconformity between the Zhujiaqing Formation and

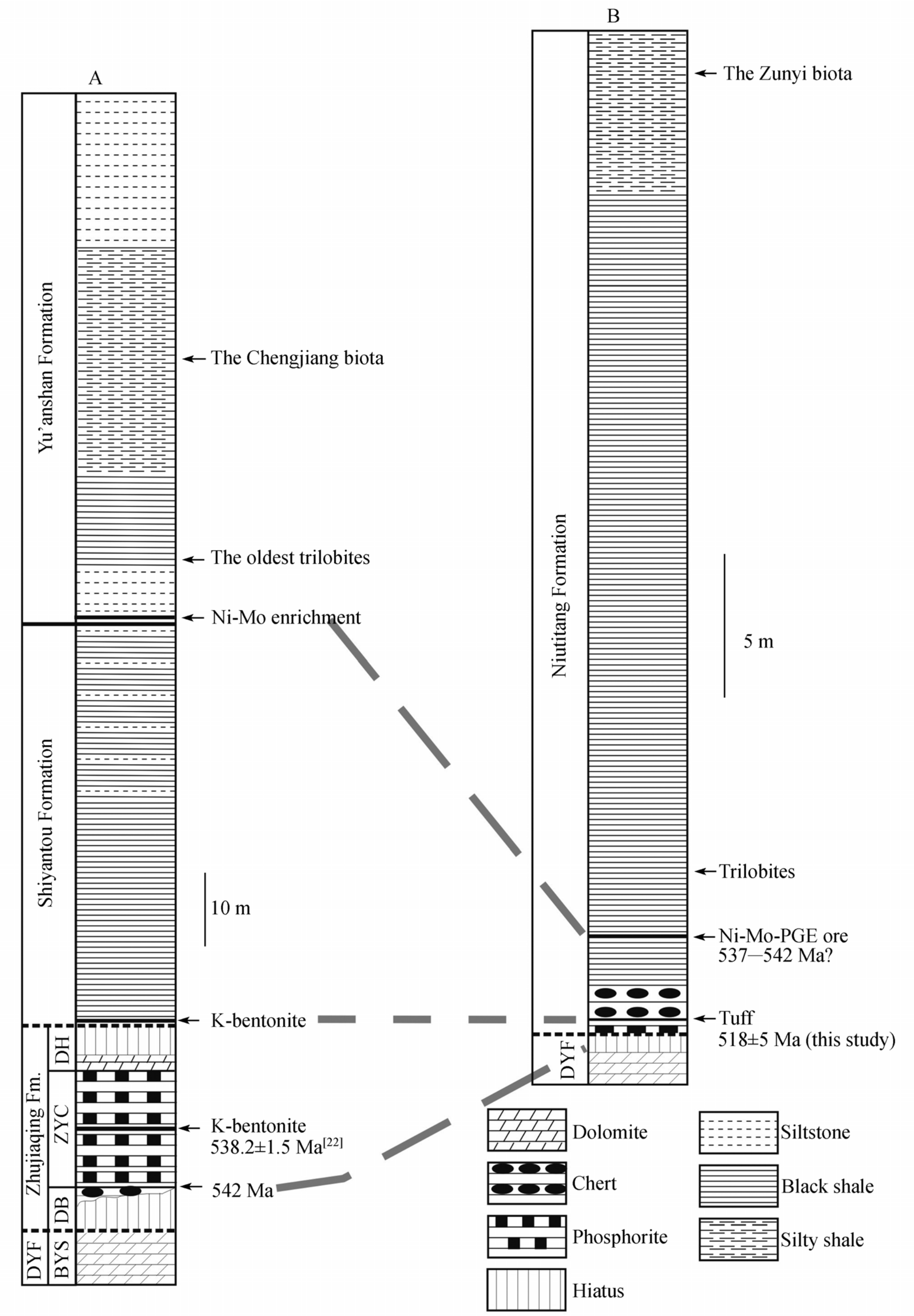

Figure 1 Stratigraphic columns of the Precambrian-Cambrian sequences in the Kunming (A) and Zunyi (B) regions. DYF, DH, ZYC, DB, and BYS denote the Dengying Formation, and the Dahai, Zhongyicun, Daibu, and Baiyanshao Members, respectively.

the underlying Dengying Formation, which makes carbon isotope chemostratigraphic studies difficult. From bottom to top, the Zhujianqing Formation can be subdivided into three members: the Daibu Member, the Zhongyicun Member, and the Dahai Member, which consist dominantly chert and dolomite, phosphorite, and dolomite, respectively. A K-bentonite layer was found in the middle Zhongyicun Member (Bed 5), and it has a SHRIMP U-Pb zircon age of 538.2 ± 1.5 Ma[20−22]. The overlying Shiyantou Formation comprises mostly black shales, and at its base, a 10-cm-thick K-bentonite layer[38]. The Yu'anshan Formation that overlies the

Shiyantou Formation consists mainly of black shales, with the Chengjiang biota preserved in a silty shale unit at the middle part of the formation. Steiner et al.[25] observed a Cr-Ni enrichment at the base of the Shiyantou Formation. Work by Zhu et al.[27], however, indicates that the Ni-Mo anomaly should lie within the black shales in the Yu'anshan Formation. The finding of Zhu et al. was confirmed by our field investigations. We also found that the Ni-Mo-rich layer belongs to the bottom of the Yu'anshan Formation.

2 Sampling and analytical method

The Songlin region has a gentle dome structure, with Precambrian sequences at its center surrounded by successions of the basal Niutitang Formation and other early Paleozoic sediments. The tuff unit at the basal Niutitang Formation outcrops at the Jianpoding, Heishapo, and Xiaozhuliushui sections in the southwestern portion of the Songlin dome. As the tuff is relatively soft and loose, the surface layer of the outcrop is easy for weathering and contamination by detrital materials. To avoid such problems, digging work was carried out to collect fresh tuff at the Jianpoding section. A total of 25 kg of fresh tuff sample was collected.

Zircons from sample (labeled JFD) were separated using conventional heavy liquid and magnetic techniques. Subsequently, more than 200 zircon grains were hand-picked under a binocular microscope. Representative zircons were mounted in an epoxy resin disc, and then polished and coated with gold film. Zircon U-Pb dating for sample JFD was performed using the Sensitive High-Resolution Ion Microprobe (SHRIMP) at Curtin University of Technology, Australia, and 23 zircon grains were analyzed. Details of the analytical procedures were described by Compston et al.[21]. TEMORA standard zircon was used for calibrating U/Pb isotopic ratios. The data were reduced using the Squid v. 1.02 and Isoplot/Ex v. 2.49 programs[39,40], and ^{204}Pb was used for common Pb correction. The uncertainties of the isotope analyses are cited as 1σ, and the weighted mean age is quoted at 95% confidence level.

3 Results

The SHRIMP dating results are shown in Table 1. Ex-

Table 1 SHRIMP zircon U-Pb isotopic analyses of the Jianpoding tuff[a)]

Spot No.	U (μg·g^{-1})	Th (μg·g^{-1})	^{206}Pb* (μg·g^{-1})	Th/U	Pb$_c$(%)	^{207}Pb*/^{206}Pb*	±%	^{207}Pb*/^{235}U	±%	^{206}Pb*/^{238}U	±%	^{206}Pb/^{238}U Age (Ma)
JFD-1r	142	116	10.1	0.82	1.67	0.0474	7.3	0.533	7.8	0.0815	2.7	505 ± 13
JFD-2r	30	17	2.20	0.55	2.29	0.0476	14	0.542	14	0.0826	3.1	512 ± 15
JFD-3r	45	37	3.05	0.83	0.25	0.0621	10	0.673	11	0.0785	3.0	487 ± 14
JFD-4	42	25	2.96	0.60	2.00	0.0463	6.6	0.518	7.3	0.0812	2.9	503 ± 14
JFD-5	756	415	54.9	0.55	0.08	0.0579	1.2	0.674	2.9	0.0844	2.6	522 ± 13
JFD-6c	1207	708	87.5	0.59	0.25	0.0569	1.1	0.660	2.8	0.0842	2.6	521 ± 13
JFD-7c	1771	891	109	0.50	0.04	0.0577	0.7	0.568	2.7	0.0713	2.6	444 ± 11
JFD-8c	665	361	47.7	0.54	0.02	0.0588	1.1	0.677	2.8	0.0835	2.6	517 ± 13
JFD-9	241	139	18.1	0.58	0.31	0.0557	2.0	0.671	3.3	0.0873	2.6	540 ± 14
JFD-10c	1174	634	84.0	0.54	0.07	0.0581	0.9	0.667	2.8	0.0833	2.6	516 ± 13
JFD-12-1	113	67	8.38	0.59	1.01	0.0479	5.9	0.562	6.5	0.0852	2.7	527 ± 14
JFD-12-2	57	39	4.01	0.68	−0.71	0.0645	5.0	0.732	5.8	0.0823	3.1	510 ± 15
JFD-13	121	77	9.29	0.64	0.75	0.0518	3.8	0.634	4.7	0.0888	2.7	548 ± 14
JFD-14	72	39	5.11	0.54	−0.31	0.0625	3.6	0.709	4.5	0.0823	2.8	510 ± 14
JFD-15	49	31	3.48	0.64	−0.26	0.0653	3.6	0.755	4.6	0.0838	2.9	519 ± 14
JFD-16	158	85	11.5	0.54	−0.02	0.0571	1.9	0.668	3.3	0.0848	2.7	525 ± 13
JFD-17	34	19	2.37	0.57	−0.88	0.0686	7.1	0.783	7.8	0.0827	3.4	512 ± 17
JFD-17c	2185	1098	131	0.50	0.07	0.0569	0.7	0.546	2.7	0.0696	2.6	433 ± 11
JFD-18	46	27	3.23	0.58	−0.50	0.0621	4.7	0.710	5.5	0.0830	2.9	514 ± 14
JFD-19	53	31	3.67	0.59	1.11	0.0509	5.9	0.560	6.7	0.0798	3.1	495 ± 15
JFD-20	192	99	13.7	0.52	−0.18	0.0581	1.7	0.665	3.2	0.0831	2.7	515 ± 13
JFD-21	43	25	3.10	0.58	1.98	0.0506	18	0.567	18	0.0814	3.1	504 ± 15
JFD-22	85	79	5.18	0.93	0.86	0.0621	5.3	0.605	6.0	0.0706	2.8	440 ± 12
JFD-23	838	607	60.4	0.72	0.23	0.0561	1.2	0.648	2.9	0.0837	2.6	518 ± 13

a) Pb$_C$ and Pb* indicate the common and radiogenic portions, respectively; common Pb corrected by ^{204}Pb; the analyses listed in rows filled in 10% grey are those that have been rejected for weighted mean ^{206}Pb/^{238}U age calculation.

cept for two zircon grains (JFD12 and JFD17) where two analyses were conducted on each of them, the other spot analysis was collected from different grains. All analyses have Th/U ratios higher than 0.1 (ranging from 0.50 to 0.83), typical of magmatic zircon. The data were plotted on or near the $^{207}Pb/^{235}U$-$^{206}Pb/^{238}U$ concordia curve (Figure 2). After excluding 7 analyses that we considered as erroneous or outliers, the remaining 17 analyses (including two from the same grain, JFD12) have $^{206}Pb/^{238}U$ ages ranging from 503 ± 14 Ma to 527 ± 14 Ma, which give a weighted mean $^{206}Pb/^{238}U$ age of 518±5 Ma (N = 17, MSWD = 0.37).

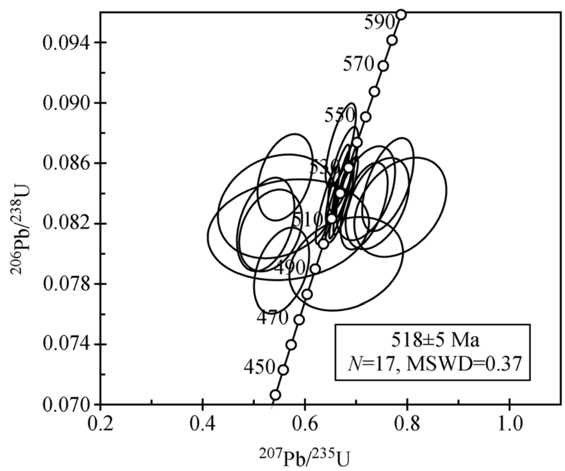

Figure 2 SHRIMP zircon U-Pb concordia diagram for the Jianpoding tuff. Three erroneous analyses are not shown.

4 Discussion

4.1 Age constraint and genetic model of the Ni-Mo-PGE-rich layer

The ore-forming mechanism for the Ni-Mo-PGE deposit hosted in the black shales at the basal Niutitang Formation is highly controversial[25,31,41−45]. Mao et al.[45] suggested that both elements leached from seafloor mafic-ultramafic rocks by hydrothermal fluids and deep Mo-Re-(Cu) chambers, with the latter serving as both a source of heat and a source for the metal materials, contributed to the mineralization. In a more recent paper, Mao et al.[44] argued for a synsedimentary ore genesis. A hydrothermal origin of this deposit, however, is still favored by most workers[25,41−43], who at the same time emphasize the roles that the hydrothermal fluids played on the mafic-ultramafic rocks and that some of the metal elements were mantle-derived[41−43]. Luo et al.[30] hypothesized recently that the polymetallic Ni-Mo-PGE layer was formed through three different stages, with the last one being a volcanic explosion event that brought the ore-forming materials up from a deep magma chamber. The metal-rich materials were then transported by sea-water and enriched mechanically to form the polymetallic Ni-Mo-PGE deposit. As discussed above, most of the models imply the presence of a deep mafic-ultramafic chamber that is rich in precious metals and other elements during the Precambrian-Cambrian interval.

Some age data have been reported for the polymetallic Ni-Mo-PGE mineralization. Li et al.[41] dated the Ni-MO-PGE ore and reported a Re-Os isochron of 542 ± 11 Ma, which they interpreted as the age for the successions of the Niutitang Formation. In addition, Mao et al.[44] and Jiang et al.[43] reported Re-Os isochrons of 541±16 (2σ) and 537 ± 10 Ma (MSWD = 11.9) for the Ni-MO-PGE ore in Songlin area, Zunyi. They also considered these ages as representing the depositional age of the Niutitang Formation. These ages, however, contradict our SHRIMP zircon U-Pb age of 518±5 Ma (MSWD = 0.37), which we interpret as representing the deposition age for the tuff. As the tuff is ca. 2 m below the polymetallic Ni-Mo-PGE layer, our result implies that the age of the polymetallic Ni-Mo-PGE layer should be younger than 518 ± 5 Ma.

Latest paleontological results show that trilobites occur in the black shales within the Niutitang Formation at the Jianpoding section, which is ca. 2 m above the polymetallic Ni-MO-PGE layer[46], but the layer has not been confirmed as the first appearance datum (FAD) for trilobites. Fortunately, the lowermost trilobites have already been found ca. 8.8 m above the Ni-Mo-rich layer at the base of the Yu'anshan Formation in Kunming area[9,27]. Based on the correlation result of the Ni-Mo-(PGE) layer, it is possible that the tuff we found is overlain by the horizon of the first appearance datum (FAD) for trilobites, and the age of the tuff (518 ± 5 Ma) could be used as a lower age limit for that of the FAD. The agreement of our age with the internationally accepted 521 Ma age estimation for the FAD of trilobites[47] (for details please refer to geological time scale published on website: http://www.stratigraphy.org/chus.pdf) provides additional support to our conclusion. Accordingly, our new SHRIMP U-Pb zircon age also provides a maximum age constraint for the Ni-Mo-PGE-rich layer.

The conflict between the Re-Os ages for the Ni-Mo-PGE layer and the SHRIMP zircon age for the tuff could present a serious problem for elucidating the origin of the polymetallic Ni-Mo-PGE deposit, and needs to be resolved. In the genetic model proposed by Luo et al.[30], the ore-forming materials were brought up from the deep chamber by volcanic explosion and were subsequently transported and enriched mechanically. This implies that the ore-bearing materials (contain Ni, Mo and other metal elements) could be precipitated in the form of fine particulates. In such a case, the Re-Os isotope system of such multi-element particulates might be closed during the cooling processes of the ore-bearing magma. Thus, the Re-Os dating made on the ore formed through a physical conglomeration of the Ni-Mo-PGE-rich particulates could only be used to estimate the age of the original magmas from the deep chamber rather than that of the strata. Such a model can reconcile the discrepancy between the Re-Os ages of the Ni-Mo-PGE ore and our result for the underlying tuff. At the same time, the model also corroborates the existence of a deep magma chamber as implied by numerous studies.

4.2 Constraint on the age of the Chengjiang biota

The well-known Chengjiang biota is preserved in the silty shales of the Yu'anshan Formation in the Kunming area. It provides an extensive fossil record for resolving details of the Cambrian explosion. Despite its significance, the absolute age of the biota, has not been well constrained yet, with so far only a speculated age of ca. 525 Ma[27]. The problem lies in the difficulty in radiometric dating of the sedimentary rocks. Here, we suggest that the age of the Chengjiang biota may be estimated through stratigraphic correlations with the succession in Zunyi. A Ni-Mo-(PGE) layer occurs below both the Chengjiang biota and the Zunyi biota, which are considered to be lateral equivalents[26]. In addition, the Ni-Mo anomaly at the base of the Yu'anshan Formation also correlate with that in the basal Niutitang Formation, with both belonging to the widespread polymetallic Ni-Mo-PGE geochemical marker layer over the Yangtze Platform. As the polymetallic Ni-Mo-PGE-rich layer is underlain by the tuff at the Jianpoding section in Zunyi, the strata (the middle Yu'anshan Formation) that host the Chengjiang biota should be deposited after the tuff unit. Consequently, the age of the tuff (518 ± 5 Ma) from our study should provide a lower age limit for the Chengjiang biota.

The stratigraphic studies have shown that the base of Shiyantou Formation correlates with the base of the Niutitang Formation[25,27]. This is consistent with the discovery of the K-bentonite close to the tuff in the Sonlin area, Zunyi by Luo et al.[29], with whole rock major and trace element analyses (Luo et al. in preparation) suggesting it being an equivalent of the K-bentonite found by Zhang et al.[38] at the base of the Shiyantou Formation in the Kunming area. Considering the presence of > 80 m[31,32] thick shales between the base of the Shiyantou Formation and the horizon preserving the biota (the middle Yu'anshan Formation), we suggest that the previously speculated age of 525 Ma for the Chengjiang biota is possibly somewhat too old.

4.3 Geochronological framework for the Lower Cambrian in South China

At present, the internationally accepted age for the Precambrian-Cambrian boundary is 542 Ma[28]. The position of this boundary in South China, however, is still being highly debated. Zhu et al.[27] suggested that the boundary should be placed at the base of the Zhongyicun Member (probably equivalent to the previous maker B). If that were the case, the absolute age of the Precambrian-Cambrian boundary in South China could be estimated slightly old than 538.2 ± 1.5 Ma, which is the SHRIMP U-Pb zircon age determined by Jenkins et al.[22] for the K-bentonite from the Zhongyicun Member (Bed 5) of the Zhujiaqing Formation at the Meishucun section, Jinning County, Yunnan. The result is consistent with the internationally accepted age of 542 Ma[28], suggesting that the scenario indeed provides a feasible solution for the Precambrian-Cambrian boundary in South China.

The two high precision SHRIMP U-Pb zircon ages available now for the Lower Cambrian in South China can also provide a self-consistent time framework for the Lower Cambrian on the Yangtze Platform (Figure 1). Although reliable absolute ages are still scarce, we expect that more tuff or K-bentonite may be located in the strata in the near future, and precise dating of which will facilitate the subdivision of the Lower Cambrian in the Yangtze Platform and global correlations. Such outcome will undoubtedly improve our understanding of the temporal distribution of the major ore-forming events in South China, temporal variations in stable isotopes, and life evolution in the Early Cambrian.

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