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PROMINENT LOWER CAMBRIAN K-BENTONITES IN SOUTH CHINA: DISTRIBUTION, MINERALOGY, AND GEOCHEMISTRY

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ABSTRACT: **The Lower Cambrian on the Yangtze Block in South China is valuable for understanding the early evolution of life, the global biogeochemical cycles, and the major changes of the ocean. However, both the placement of the Precambrian–Cambrian boundary in South China and the correlation of the Lower Cambrian across the Yangtze Block are still in controversy, which hinders the global correlation of the Lower Cambrian and understanding of environmental changes of the paleo-ocean. Discovery of K-bentonites in the Lower Cambrian in South China will facilitate clarifying the above-mentioned problems. In this study, systematic field investigations and mineralogical and geochemical studies were conducted on Lower Cambrian K-bentonites in South China. The field investigations have shown that the widespread K-bentonites occur in two important stratigraphic levels: the middle Zhujiaqing Formation and the basal Shiyantou Formation and their lateral equivalents. Biostratigraphically, the older K-bentonite bed is preserved in the *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone and the younger K-bentonite in the poorly fossiliferous interzone. Geochemical studies reveal that the Lower Cambrian K-bentonite samples are plotted in the fields of trachyte, trachyandesite, rhyodacite (dacite), and rhyolite in a plot of Nb/Y against Zr/TiO_2, suggesting that the K-bentonites are most probably derived from felsic magmas with sub-alkaline to alkaline nature. Compared with the K-bentonite in the basal Shiyantou Formation and its equivalent sequence, the K-bentonite in the middle Zhujiaqing Formation and its correlative succession is characterized by lower Zr and Nb concentrations. Volcanic eruptions recorded by the two K-bentonite beds may have taken place during an interval of tectonic transformation, and the source volcanoes were probably located in the east margin of the Ganze–Songpan Block. Correlation results of the two important Lower Cambrian K-bentonite beds indicate that a previous viewpoint considering the polymetallic Ni-Mo layer in the lowermost Niutitang Formation as the Precambrian–Cambrian boundary in South China is inappropriate. Combined with available geochronological data, the boundary should be placed in the sequence beneath the K-bentonite in the middle Zhujiaqing Formation and its correlative stratigraphic level.**

INTRODUCTION

The widespread outcrops of the Lower Cambrian sequences (equivalent to the Nerreneuvian and second series of the internationally new subdivisions of the Cambrian) on the Yangtze Platform in South China are unique for understanding the early evolution of life and the paleoenvironment of the ocean. Therefore, research on the sequences has been carried out by numerous workers and significant progress has been made. However, a number of scientific problems urgently need to be clarified for the Lower Cambrian strata in this region. Firstly, although several schemes for the placement of the Precambrian–Cambrian (PC/C) boundary in South China have been proposed by geologists, they have not reached a general consensus (Hsu et al. 1985; Shen and Schidlowski 2000; Zhu et al. 2001; Zhu et al. 2003; Steiner et al. 2007; Wille et al. 2008; Zhou et al. 2008; Jiang et al. 2009; Li et al. 2009; Wen et al. 2009; Zhu et al. 2009). Secondly, the regional correlation across different facies of the successions is still uncertain due to the scarce fossil records in the Lower Cambrian of the deep-water facies on the Yangtze Block, which hampers understanding of environmental changes of the paleo-ocean (Chen et al. 2009; Chang et al. 2012; Fan et al. 2013). The presence of a K-bentonite is valuable not only to obtain the U-Pb age but also to resolve the problem of stratigraphic correlation. Therefore, discovery of K-bentonites in the Lower Cambrian in South China will undoubtedly facilitate resolution of the above-mentioned problems. Previous studies discovered several K-bentonite beds in the Lower Cambrian from eastern Yunnan Province (Zhang et al. 1997). Among them, two widespread K-bentonites with considerable thickness are recognized from the middle Zhujiaqing Formation and the base of the Shiyantou Formation. However, reports on the Lower Cambrian K-bentonites in regions other than eastern Yunnan Province (especially in deep-water deposits) of the Yangtze Block are sporadic, which is an enigma to geologists. Recently, we have discovered K-bentonites from other areas on the Yangtze Block that can be correlated with the K-bentonites in the two important horizons in eastern Yunnan Province. In the present study, the data on the distribution, mineralogy, and geochemistry of the K-bentonites in the two significant horizons are presented. On the basis of these data, information on the nature of the source magmas and the tectonic settings of the source volcanoes of the K-bentonites was obtained. Further, a stratigraphic correlation scheme across various facies based on the K-

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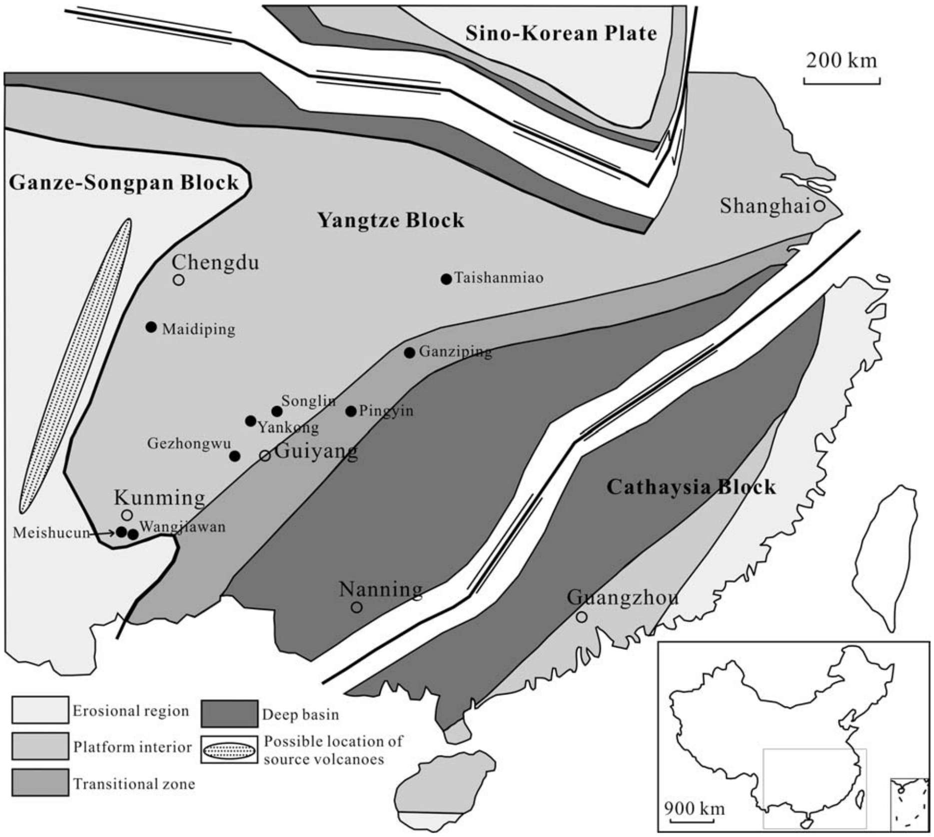

FIG. 1.—Sketch-maps showing the paleogeography of the Yangtze Block during the Ediacaran–Cambrian transition and sampling localities for this study.

bentonites helps to refine the placement of the PC/C boundary in South China.

Geological Setting

During the Ediacaran–Cambrian transition, the Yangtze Block evolved to a passive continental margin and was surrounded by deep basins to the north and southeast (Fig. 1). Previous paleogeographical studies show that the major part of the Yangtze Block 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 (Steiner et al. 2001; Zhu et al. 2003; Steiner et al. 2007; Chen et al. 2009). The PC/C transitional sequences in the three zones vary in facies due to the different water depth of their sedimentary environments. Successions in the platform interior consist mainly of carbonates whereas those in the deep-water environment (the transitional zone, and the slope to deep basin zone) are composed mostly of carbonaceous cherts. The distribution and characteristics of fossil materials in these zones are also different. Generally, strata on the shallow platform are richer in fossils than those of the deep-water facies. In the platform interior, the typical PC/C transitional sequences include, in ascending order, the Dengying Formation, the Zhujiaqing Formation, and the Shiyantou Formation. The Dengying Formation is composed mainly of dolostones and is unconformably overlain by successions marked by a paleokarst contact. In turn, the Zhujiaqing Formation consists of phosphorites and dolostones and is unconformably overlain by the Shiyantou Formation, which is mostly black shale. In the deep-water zones, the PC/C transition is continuous and consists of the Laobao Formation (or the Liuchapo Formation) and the overlying Niutitang Formation. The Laobao Formation is composed mainly of cherts, and its major part can be correlated with the Dengying Formation in the shallow platform interior. However, at least the upper boundaries of the two lithological units are diachronous inasmuch as the top of the Dengying Formation is generally erosional. Up to now, the placement of the PC/C boundary in the shallow-water region is still debated due to the hiatus within the PC/C transitional sequences. Although some workers have tentatively suggested that the PC/C boundary in the deep-water facies should be within the Laobao Formation (or the Liuchapo Formation) (Zhu et al. 2003; Chen et al. 2009), the placement of the boundary is still unclear because of the scarce fossil records in the successions.

Distribution of the K-Bentonites

In outcrop, K-bentonites in the Lower Cambrian on the Yangtze Block have different colors (white, blackish gray, and yellow) which are distinct from their adjacent strata (phosphorites, black shales, cherts, and dolostones). Due to their clay-rich nature, they feel slippery and waxy when wet. Accelerated weathering of the K-bentonites causes them to be recessed into the outcrop face and to have sharp contacts with their enclosing sequences (Fig. 2).

The Lower Cambrian K-bentonites that have already been recognized crop out in the shallow-water platform interior and in the deep-water transitional zone of the Yangtze Block (Fig. 1). Representative Lower Cambrian K-bentonite sections in the platform interior include the Meishucun, Wangjiawan, Maidiping, Gezhongwu, Yankong, Songlin and Taishanmiao sections. The Meishucun section is located in Jinning County of Yunnan Province. It is a former global stratotype candidate section for the PC/C boundary. At this section, a K-bentonite locally up to 2.6 m and two ca. 10 cm K-bentonite beds occur in the middle Zhujiaqing Formation (bed 5) and the bottom of the Shiyantou Formation (bed 9), respectively. The Wangjiawan section also lies in Jinning County and is about 23 km southeast of the Meishucun section. Lithostratigraphic units of this section are highly similar to those of the Meishucun section. A 20 cm K-bentonite and an approximately 10 cm K-

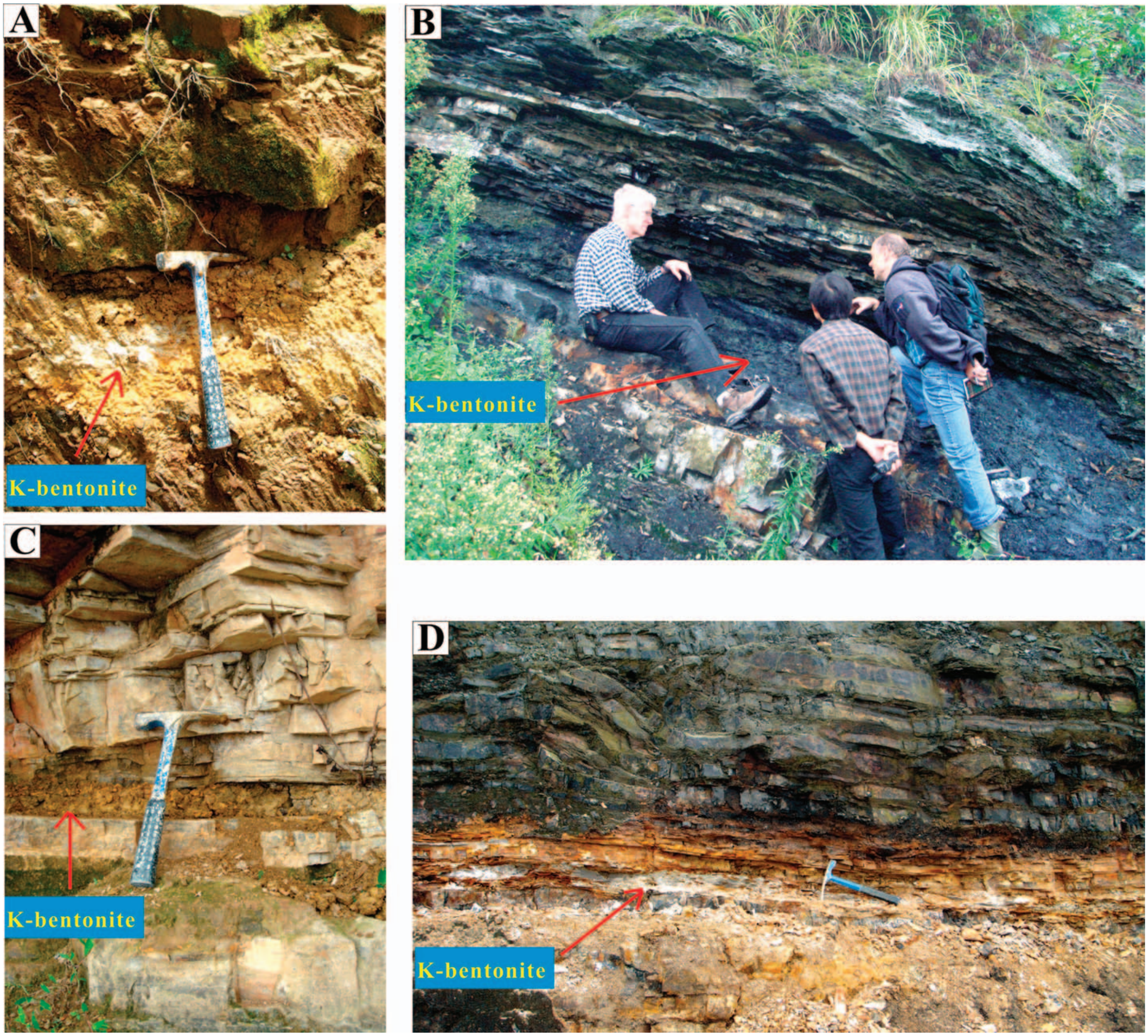

FIG. 2.—Field photos of typical Lower Cambrian K-bentonites in South China. **A)** A light yellow K-bentonite in the base of the Shiyantou Formation at the Wangjiawan section in Yunnan Province. **B)** A blackish gray K-bentonite in the base of the Niutitang Formation at the Songlin section in Guizhou Province. **C)** A brownish yellow K-bentonite in the middle Zhujiaqing Formation at the Wangjiawan section in Yunnan Province. **D)** A grayish white K-bentonite in the top of the Laobao Formation at the Pingyin section in Guizhou Province. The length of the hammer in A, C, and D is 27 cm.

bentonite were discovered near the base of the Shiyantou Formation (Fig. 2A) and the middle Zhujiaqing Formation (Fig. 2C) at the Wangjiawan section, respectively. The Maidiping section, which is also one of the former global stratotype section candidates for the PC/C boundary, is about 10 km southwest of Emeishan City in Sichuan Province. A K-bentonite with a thickness of 5 cm is preserved in phosphorites of the Maidiping Formation at the section. Unfortunately, due to strong weathering of black shales in the basal Jiulaodong Formation, the sequences near the boundary between the Maidiping Formation and the overlying Jiulaodong Formation are covered. However, Zhang and Xu (1994) reported two boundary clay beds near the base of the Jiulaodong Formation, which, based on clay mineralogy and presence of volcanogenic phenocrysts, are considered to be two K-bentonite beds in this study. The Songlin section is about 25 km west of Zunyi City in Guizhou Province. A 15-cm-thick K-bentonite occurs in the base of the Niutitang Formation at the section (Fig. 2B). Both the Gezhongwu section and the Yankong section are located in northern Guizhou Province. Their lithostratigraphic units are correlative with those of the Songlin section (Zhou et al. 2011). We recognized at least one K-bentonite near the base of the Niutitang Formation at the two sections. The Taishanmiao section is ca. 25 km north of Yichang City in Hubei Province. In the base of the Shuijingtuo Formation at the section, two 10-cm-thick K-bentonite beds were discovered.

Typical Lower Cambrian K-bentonite sections in the deep-water transitional zone are the Pingyin and Ganziping sections. The Pingyin section is about 22 km northwest of Jiangkou County in Guizhou

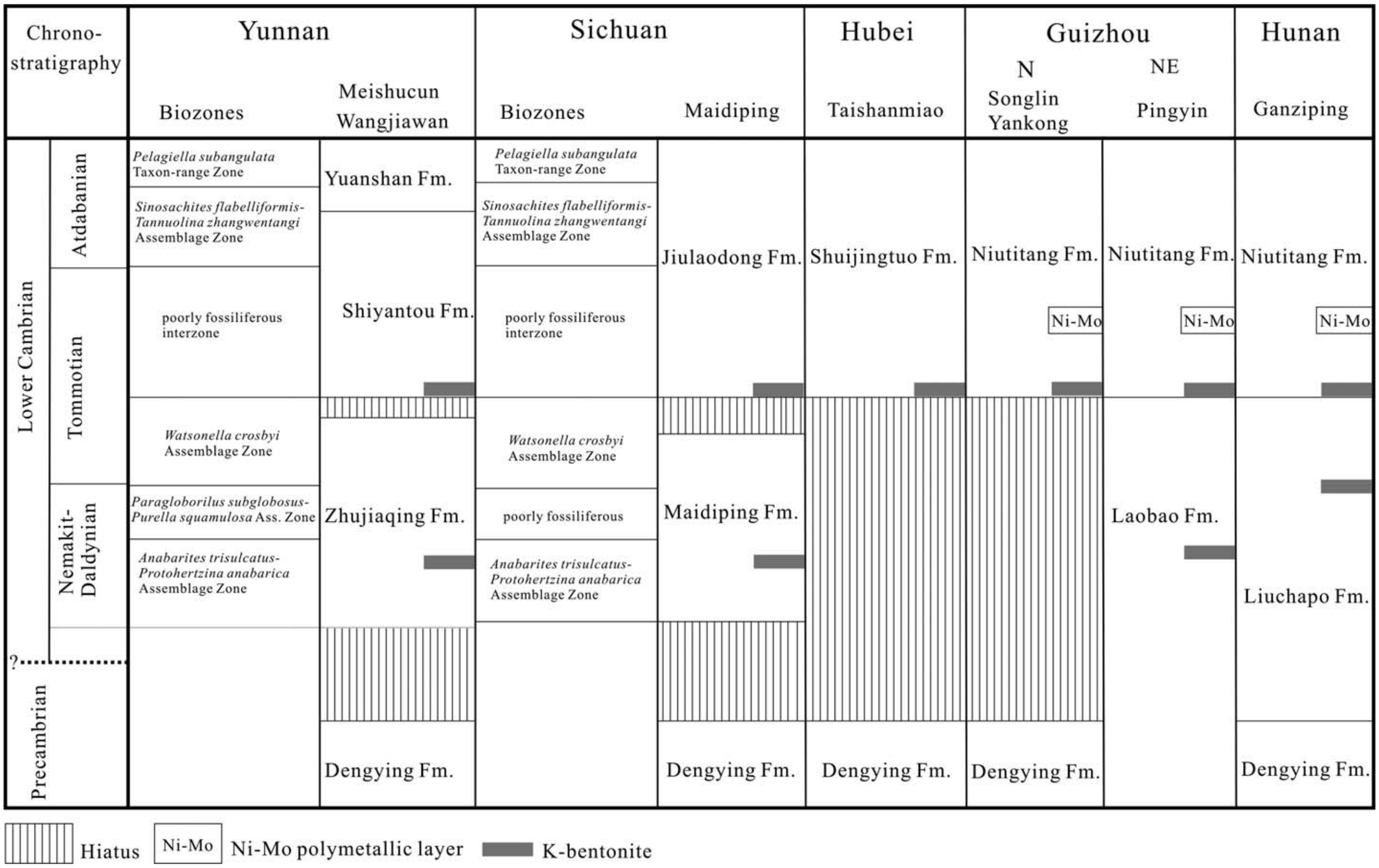

FIG. 3.—Correlation table of Lower Cambrian strata in South China with biozonation based on small shelly fossils.

Province. At this section, a 15-cm-thick K-bentonite (Fig. 2D) and an approximately 5-cm-thick intensely phosphatized K-bentonite occur 2 m below the upper boundary of the Laobao Formation (or Liuchapo Formation) and the base of the Niutitang Formation, respectively. Recently, Wang et al. (2012) discovered a K-bentonite (called a tuffaceous bed by them) in the basal Niutitang Formation at the Taoying section, located several kilometers from the Pingyin section. The Ganziping section is adjacent to Zhangjiajie City (or Dayong City), northwestern Hunan Province. A previous study shows that both the top of the Liuchapo Formation and the bottom of the Niutitang Formation preserve a K-bentonite (known as tuff by the authors) with a considerable thickness (Chen et al. 2009).

The above-mentioned K-bentonites occur in pre-trilobitic Lower Cambrian strata in South China. Steiner et al. (2007) subdivided the pre-trilobitic Lower Cambrian strata in the shallow-water realm of the Yangtze Block into five biozones based on small shelly fossil records. In ascending order the biozones are: *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone, *Paragloborilus subglobosus–Purella squamulosa* Assemblage Zone, *Watsonella crosbyi* Assemblage Zone, poorly fossiliferous interzone, and *Sinosachites flabelliformis–Tannuolina zhangwentangi* Assemblage Zone (Fig. 3). Among them, the *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone plus the *Paragloborilus subglobosus–Purella squamulosa* Assemblage Zone can be correlated with the Nemakit–Daldynian Stage while the *Watsonella crosbyi* Assemblage Zone plus the poorly fossiliferous interzone can be correlated with the Tommotian Stage. In addition, the *Sinosachites flabelliformis–Tannuolina zhangwentangi* Assemblage Zone is equivalent to the base of the Atdabanian Stage. The K-bentonites in the middle Zhujiaqing Formation at the Meishucun and Wangjiawan sections occur in the *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone, and the K-bentonites in the base of the Shiyantou Formation at the two sections belong to the poorly fossiliferous interzone. The K-bentonites within the middle Maidiping Formation and the basal Jiulaodong Formation at the Maidiping section are distributed in the *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone and the poorly fossiliferous interzone, respectively. Both the K-bentonites in the base of the Niutitang Formation at the Songlin, Gezhongwu, and Yankong sections in Guizhou Province and those in the base of the Shuijingtuo Formation at the Taishanmiao section in Hubei Province occur in the poorly fossiliferous interzone. Due to the scarce fossil records, the biostratigraphical position of the K-bentonites in the deep-water realm of the Yangtze Block is still unclear. However, the K-bentonites are below the regionally widespread Ni-Mo polymetallic layer which is under the horizon hosting the oldest trilobites in South China. Thus, we confirm that the K-bentonites recognized in the deep-water region of the Yangtze Block are distributed in the pre-trilobitic strata (Fig. 4).

SAMPLING AND ANALYTICAL METHODS

K-bentonite samples for the present study were collected from the above-mentioned representative sections. Because the K-bentonite beds are usually thin and easily weathered, detrital contamination from country rocks and the strongly weathered portions of the K-bentonites were strictly avoided during sampling. Mineral and chemical analyses were conducted for 17 representative samples of the K-bentonites. For powder diffraction analysis the sample was mixed with water to form a suspension and then allowed to settle for thirty minutes in order to isolate the clay-size material. The suspension was dewatered in a centrifuge and

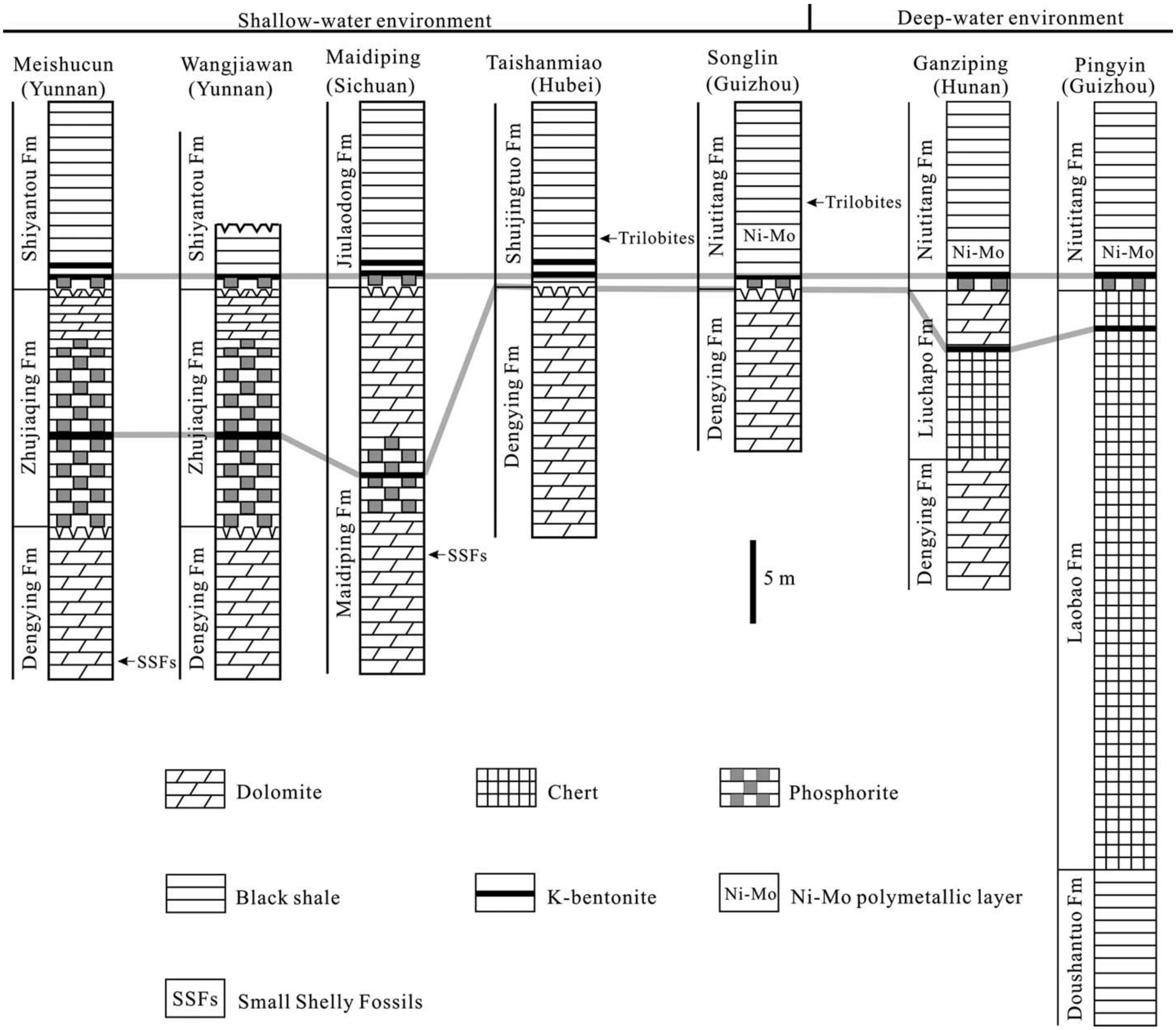

FIG. 4.—Representative sections from the Precambrian–Cambrian transitional strata of the Yangtze Block showing the stratigraphic position and regional correlation of K-bentonite beds.

the resulting paste was smeared in a thin film on a standard petrographic glass slide and allowed to dry. The smear method allows the maximum diffraction effects from the preferred orientation of layer silicates such as clay and mica. Duplicate slides were prepared and treated both with ethylene glycol and heating to 350 degrees C, to test for swelling clays (Moore and Reynolds 1997). Powder diffraction X-ray scans were made over the range of 2–32° 2θ using copper Kα radiation in a Siemens D-500 automated diffractometer. Minerals were identified on the basis of peak position and peak intensity. On each plot the individual peaks are labeled in angstroms (Å) indicating the actual interatomic distance represented by that reflection. Major-element contents for the K-bentonites were determined using X-ray fluorescence spectrometry (XRF). Data quality was evaluated by parallel samples and standard reference material during the process of determination, and the analytical precision is better than 3%. Trace-element concentrations of the K-bentonites were analyzed with an ELAN6000 ICP-MS. The detailed sample-preparation and analytical procedures, along with the analytical precision and accuracy, are given by Qi et al. (2000). Concentrations of platinum-group elements (PGE) were also analyzed by ICP-MS. The detailed analytical procedures are given by Qi et al. (2011). X-ray powder diffraction analyses were performed at the XRD laboratory in the Department of Geology, University of Cincinnati, the other analyses were accomplished at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

RESULTS AND DISCUSSION

Mineralogy

Liu (1993) analyzed the clay-mineral composition of the K-bentonite in the middle Zhujiaqing Formation in eastern Yunnan Province. The results showed that the clay fraction of the K-bentonite consists dominantly of illite and irregularly mixed-layer illite–smectite (I-S) with

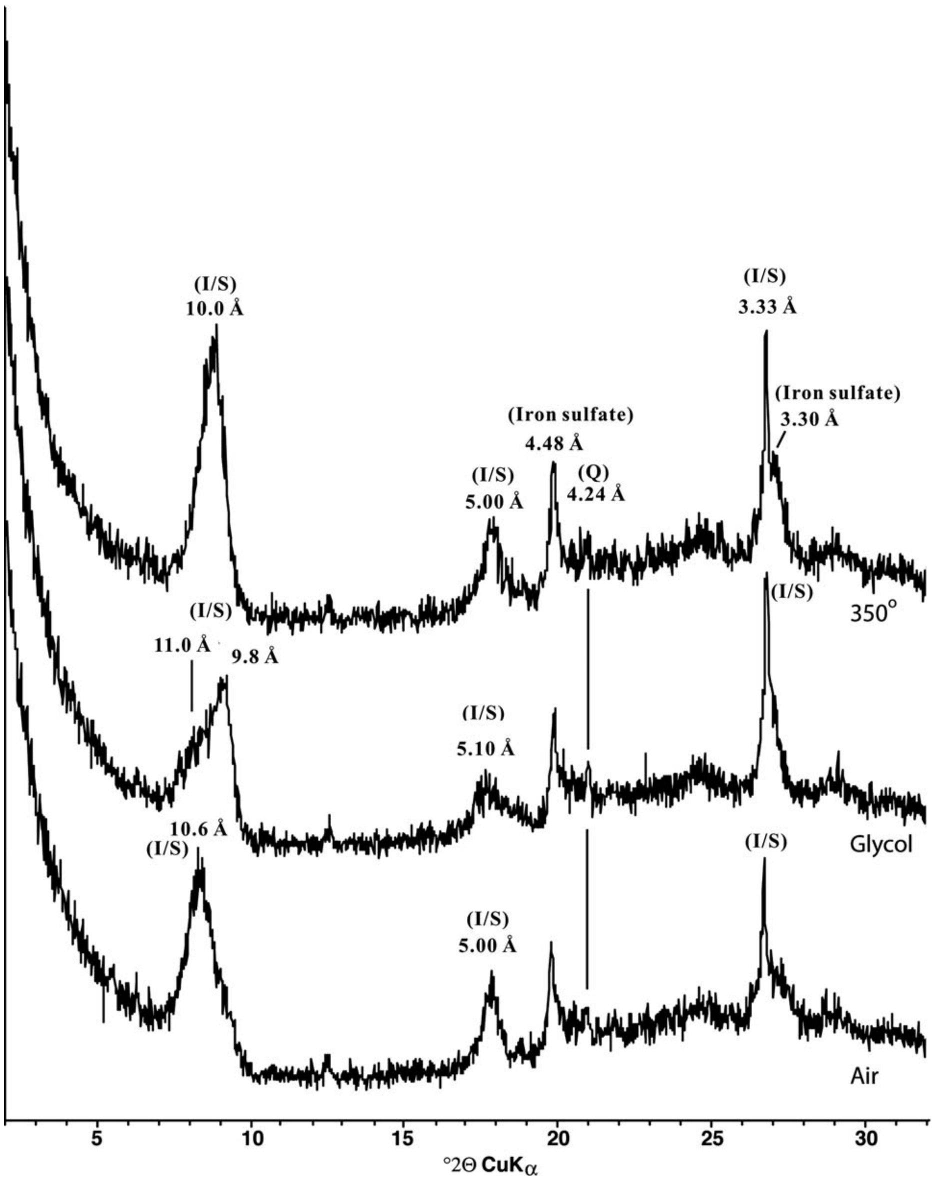

FIG. 5.—Powder X-ray diffraction patterns of the clay fraction from the K-bentonite in the base of the Niutitang Formation at the Songlin section in Guizhou Province. I/S, mixed-layer illite–smectite; Q, quartz.

lesser amounts of kaolinite. Determination by the irregularly mixed-layer triangular diagram (Jonas and Brown 1959) indicated that the I-S in three samples contains 76% to 85% illite. Wang and Dai (1995) carried out a mineralogical study on the same K-bentonite bed as Liu (1993) and obtained a similar clay-mineral assemblage. Calculation of two samples by Wang and Dai (1995) showed that the illite content in the mixed-layer I/S is 76.2% and 80.9%, respectively. In addition, Wang and Dai (1995) found that the non-clay-mineral composition of the K-bentonite consists largely of quartz accompanied by minor dolomite. Mineralogical studies on the Lower Cambrian K-bentonites in eastern Yunnan Province by Zhang et al. (1997) showed that the < 2 μm clay fraction of the K-bentonites consists of illite, mixed-layer I/S, and kaolinite and that the non-clay-mineral composition of the coarse fraction consists of sanidine, pyrite, collophanite, glauconite, and beta-form quartz. A similar mineralogical result was acquired by Pasava et al. (2010) from the study of the K-bentonite in the Lower Cambrian Zhujiaqing Formation at the Meishucun section in Yunnan Province. During U-Pb zircon dating of the Lower Cambrian K-bentonites from the two stratigraphic levels at various sections in South China, the cathodoluminescence (CL) images indicated that the euhedral to sub-euhedral zircons in the K-bentonites have obvious oscillatory zoning, suggesting their volcanic origin (Jiang et al. 2009; Zhu et al. 2009; Chen et al. 2009; Wang et al. 2012; Zhou et al. 2013). In the present study, we analyzed the clay fraction of the K-bentonite in the base of the Niutitang Formation at the Songlin section in Guizhou Province using X-ray diffraction (see Fig. 5). In the air-dried sample prominent peaks at 10.6 Å, 5.0 Å and 3.33 Å indicate a predominantly illite phase but with a small amount of mixed-layer smectite. Saturation with ethylene glycol broadens the first-order reflection further to reveal two components at 11.0 Å and 9.8 Å. The second-order peak is shifted slightly to 5.10 Å indicating a ratio of 10% smectite and 90% illite (Moore and Reynolds 1997). Upon heating to 350 degrees C the expanded phase collapses to 10.0 Å. Peaks at 4.48 Å and 3.30 Å reflect the presence of a small amount of iron sulfate, and peaks at 3.33 Å overlapping the illite peak and at 4.24 Å belong to trace amounts of clay-size quartz. Meanwhile, primary volcanogenic phenocrysts such as euhedral quartz, euhedral to sub-euhedral prismatic zircon, and euhedral sanidine were discovered in the coarse fraction of the K-bentonites from various sections in this study (Fig. 6). Therefore, the above mineralogical

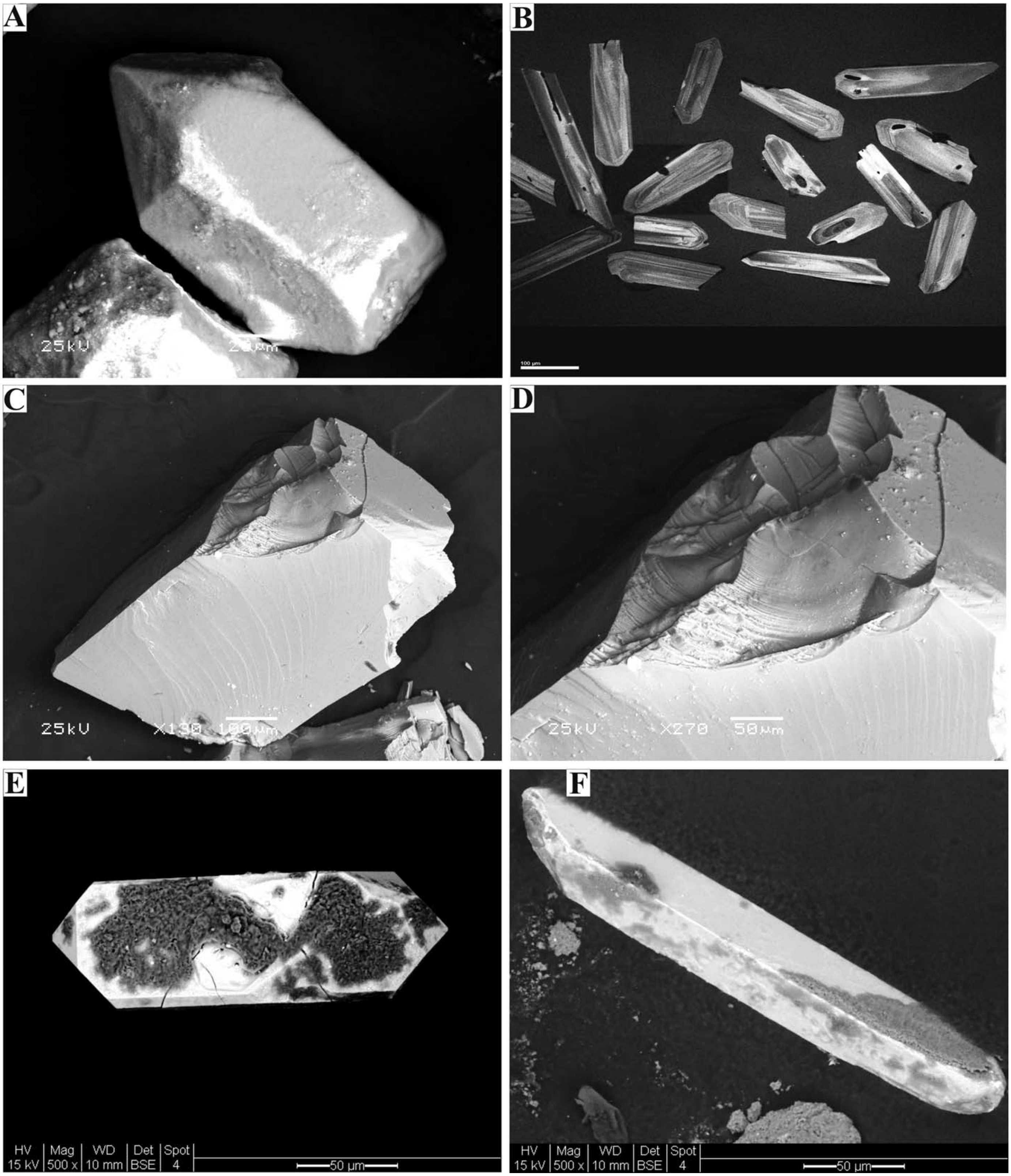

FIG. 6.—SEM and CL images of primary volcanogenic phenocrysts from the Lower Cambrian K-bentonites in South China. **A)** Euhedral quartz (SEM) in the K-bentonite in the basal Shiyantou Formation at the Meishucun section in Yunnan Province. **B)** Euhedral to sub-euhedral prismatic zircon (CL) with oscillatory zoning from the K-bentonite in the top of the Laobao Formation (or Liuchapo Formation) at the Pingyin section in Guizhou Province. **C)** Euhedral sanidine (SEM) in the K-bentonite in the basal Niutitang Formation at the Songlin section in Guizhou Province. **D)** Close-up photo of the uneven step-like fracture of the sanidine (SEM) shown in Part C. **E)** Euhedral zircon (SEM) from the K-bentonite in the basal Niutitang Formation at the Songlin section. **F)** Sub-euhedral prismatic zircon (SEM) from the K-bentonite in the basal Niutitang Formation at the Songlin section.

TABLE 1.— *Major-element and trace-element compositions of the Lower Cambrian K-bentonites in South China.*

Section	Meishucun				Wangjiawan				Songlin				Pingyin
Horizon (a)	MZF		BSF		MZF	BSF			BNF				TLF
Sample	M5-1	M5-2	M9-1	M9-2	W5-1	W9-1	W9-2	W9-3	SL-1	SL-2	SL-3	SL-4	PY-13
(wt%)													
SiO_2	63.87	65.90	53.97	51.49	48.78	55.15	52.72	51.48	43.96	52.21	50.18	49.86	52.39
Al_2O_3	13.50	13.87	21.85	20.60	24.78	19.31	22.49	23.21	18.64	15.50	25.08	24.27	27.86
CaO	3.16	2.12	0.49	1.59	0.87	2.34	0.91	0.51	5.12	4.04	0.09	1.20	0.19
MgO	3.85	3.06	3.79	3.48	2.79	2.98	3.79	3.93	1.74	1.56	2.45	3.10	3.32
Na_2O	0.03	0.03	0.02	0.05	0.04	0.05	0.03	0.03	0.10	0.13	0.11	0.18	0.24
K_2O	4.87	5.05	8.25	7.15	5.79	5.83	6.18	6.82	3.63	4.43	7.04	7.11	6.99
Fe_2O_3	0.81	1.19	1.97	4.44	3.89	2.68	1.41	3.31	3.18	4.28	2.33	5.59	0.54
TiO_2	0.09	0.10	0.38	1.05	0.45	0.43	0.25	0.22	0.60	0.70	0.39	0.26	0.11
P_2O_5	0.90	0.98	0.11	0.95	0.30	1.56	0.29	0.19	0.07	0.04	0.07	0.04	0.15
MnO	0.01	< 0.01	0.04	0.01	0.02	< 0.01	< 0.01	< 0.01	0.00	0.00	0.01	0.03	0.002
LOI	8.52	6.83	8.74	8.66	11.65	8.91	11.15	10.05	22.84	16.86	12.27	8.21	8.43
(ppm)													
Sc	9.83	3.90	3.50	13.7	7.96	8.59	5.18	4.01	7.63	5.44	4.63	3.79	6.39
Cr	14.2	14.5	17.3	30.0	50.4	43.4	32.7	51.0	721	889	166	11.3	15.0
Co	0.916	0.928	1.04	6.00	5.21	1.54	0.728	1.96	23.7	28.8	9.93	14.7	3.62
Ni	6.93	12.5	7.63	10.6	23.9	24.4	17.3	35.0	141	66.4	53.4	17.2	36.1
Cu	1.20	0.859	8.97	21.4	10.2	12.5	6.58	10.8	153	91.8	71.6	120	64.8
Zn	60.0	17.9	21.3	342	468	139	84.0	310	620	197.3	94.3	79.1	93.5
Ga	18.6	20.1	40.1	30.6	26.3	21.1	28.9	27.4	25.2	30.8	45.1	49.8	37.8
Rb	152	81.4	94.0	105	90.0	103	114	114	113	136	176	207	173
Sr	44.9	59.2	7.34	21.4	24.6	21.6	7.33	6.47	49.6	221	26.8	8.03	22.6
Y	128	50.5	46.4	42.1	17.6	54.6	50.3	41.6	82.4	90.4	83.2	128	27.4
Zr	144	160	328	400	304	231	298	274	209	255	370	392	178
Nb	11.4	10.0	115	38.7	15.8	21.9	22.2	21.6	54.9	66.3	110	95.0	11.9
Mo	3.18	0.646	21.3	6.79	1.83	0.907	0.904	4.10	115	138	70.8	106	5.40
Cs	14.3	23.8	14.9	14.1	23.2	12.1	20.7	17.7	60.9	37.9	19.3	22.8	23.7
Ba	90.2	832	215	159	109	182	52.2	48.1	2575	2943	4036	5641	5920
La	51.0	19.4	0.966	10.4	4.24	20.3	4.34	4.02	36.5	74.7	63.5	114	14.6
Ce	109	41.4	2.28	20.9	9.34	34.2	8.95	8.04	62.2	117	122.7	223	31.8
Pr	13.0	5.54	0.306	3.00	1.18	4.50	1.33	1.18	12.5	18.8	17.2	32.3	4.57
Nd	46.5	21.6	1.47	13.3	4.93	18.2	6.23	5.35	55.6	67.8	69.3	114	17.2
Sm	9.97	5.05	0.728	3.26	1.17	4.22	2.07	1.43	18.8	17.9	16.0	26.4	3.46
Eu	0.546	0.242	0.115	0.530	0.221	0.673	0.385	0.302	3.08	2.46	1.07	0.340	0.399
Gd	9.82	5.20	1.29	3.33	1.23	4.82	2.62	1.99	19.2	17.2	15.8	22.6	3.84
Tb	1.85	1.04	0.522	0.650	0.262	0.862	0.644	0.455	3.30	3.14	2.72	3.96	0.669
Dy	12.2	7.20	5.48	4.58	1.89	5.49	4.55	3.64	18.0	19.0	17.0	23.1	4.49
Ho	3.12	1.87	1.71	1.18	0.503	1.35	1.25	1.01	3.60	3.93	3.56	5.14	1.01
Er	9.62	5.98	6.30	4.21	1.82	4.21	4.02	3.35	9.14	10.6	10.5	14.1	2.99
Tm	1.46	0.938	1.16	0.770	0.346	0.658	0.628	0.565	1.52	1.77	1.56	2.42	0.511
Yb	10.1	6.29	8.92	5.58	2.56	4.40	4.51	3.79	8.30	9.35	10.4	13.4	3.35
Lu	1.47	0.904	1.29	0.890	0.376	0.638	0.654	0.585	1.58	1.52	1.48	2.19	0.492
Hf	5.94	5.94	16.5	11.8	11.0	7.89	10.6	10.5	6.29	9.32	17.9	19.2	8.24
Ta	1.35	1.14	11.2	2.80	2.06	1.78	3.17	3.15	2.42	4.14	10.1	11.7	3.89
Tl	1.23	0.534	0.366	0.390	0.614	1.03	0.807	0.718	4.36	4.91	8.58	6.37	14.0
Pb	12.6	14.8	14.1	47.3	81.9	85.8	14.9	28.7	44.3	44.7	12.2	47.8	20.7
Th	78.7	31.8	35.8	12.7	34.7	18.4	28.6	27.1	12.7	14.9	29.5	40.7	31.4
U	7.23	7.57	21.9	20.9	4.62	7.56	5.56	6.32	142	72.9	29.3	25.7	5.00

(a) Note: MZF denotes the middle Zhujiaqing Formation; BSF denotes the base of the Shiyantou Formation; BNF denotes the base of the Niutitang Formation; TLF denotes the top of the Laobao Formation.

findings confirmed the volcanic origin of the Lower Cambrian K-bentonites in the two distinctive horizons in South China.

Geochemistry

The whole-rock major-element content of thirteen selected samples of the Lower Cambrian K-bentonites in South China is listed in Table 1. The K_2O content of the samples ranges from 3.63% to 8.25%, and has an average of 6.09%. According to published data, K-bentonite has a distinctively higher K_2O content than the traditional bentonite, which is dominated by montmorillonite (reviewed by Zhou et al. 2007). Generally, the K_2O content of the former is higher than 3% while that of the latter is lower than 1% (Zhou et al. 2007). The K-bentonites in the present study are characterized by a higher K_2O content, which is consistent with their mineral composition (dominated by illite and illite–smectite). All of the K-bentonite samples have extremely low Na_2O content (between 0.02% and 0.24%), suggesting that the original sodium was removed during devitrification of the parent ashes.

Platinum-group elements (PGEs) in the K-bentonite in the base of the Shiyantou Formation (bed 9) at the Meishucun section and its equivalents on the Yangtze Block were analyzed by several workers (Hsu et al. 1985). The results showed that the K-bentonite has an Ir

TABLE 2.—*Concentrations of PGEs in the Lower Cambrian K-bentonites in South China.*

Section	Meishucun	Songlin	Yankong		Gezhongwu	Taishanmiao
Horizon (a)	BSF	BNF	BNF		BNF	BShF
Sample	M9-1	SL-1	YK-1	YK-5	GZW-9	TSM-4
(ppb)						
Ru	0.015	0.088	0.109	0.199	0.410	0.384
Pd	0.264	2.336	1.429	8.935	4.355	76.206
Ir	0.002	0.011	0.019	0.019	0.027	0.136
Pt	0.062	1.006	0.213	2.522	1.006	22.849
Rh	0.005	0.042	0.009	0.112	0.092	1.118

(a) Note: BSF, BNF and BShF denote the base of the Shiyantou, Niutitang and Shuijingtuo Formations, respectively.

anomaly compared with its overlying and underlying sequences. Accordingly, the workers suggested that an extraterrestrial impact was responsible for the Ir anomaly (Hsu et al. 1985). However, the impact interpretation remains controversial (Zhang et al. 1997). We analyzed the PGEs in six samples of the K-bentonite in the same horizon. The results show that the Ir concentrations in the samples from five sections range from 0.002 to 0.136 ppb (Table 2). CI chondrite-normalized PGE patterns of the K-bentonite are highly fractionated, with the relative abundances increasing from left to right (Fig. 7). For most meteorites (> 96% in number), their PGE patterns are undifferentiated (namely chondrites) and hence have flat PGE patterns normalized to CI chondrite (McDonough and Sun 1995; Xu et al. 2007), obviously distinct from the strongly Ir-depleted patterns of the K-bentonite. Thus, the PGE distribution patterns of the K-bentonite argue against an extraterrestrial source for the PGEs in the K-bentonite. Furthermore, in the Ir/Pt vs. Pd/Pt plot (Fig. 8) the K-bentonite samples are plotted far from CI chondrites (McDonough and Sun 1995) and the Cretaceous–Paleogene (K/Pg) boundary clay rocks (Kyte et al. 1985; Lee et al. 2003) with acknowledged extraterrestrial origin. In contrast, the K-bentonite samples are near the K-bentonites from the Permian–Triassic (P/T) boundary at the Meishan section in Zhejiang Province, China (Xu et al. 2007). These data also argue against the extraterrestrial source for the PGEs in the K-bentonite. Therefore, we tend to believe the PGEs in the K-bentonite are from its parent magmas, which is similar to the conclusion drawn by Pasava et al. (2010) on the PGEs in the K-bentonite in the middle Zhujiaqing Formation at the Meishucun section in Yunnan Province.

Immobile trace elements have been used by numerous workers (Huff et al. 2000; Astini et al. 2007; Su et al. 2009) to provide information on the magmatic composition of K-bentonite ashes and tectonic setting of the source volcanoes. TiO_2 and the trace elements Zr, Nb, and Y are commonly considered to be immobile under processes of weathering, diagenesis, and low-grade metamorphism, and are thus useful indicators of past rock history. The Nb/Y ratio is widely used as an index of alkalinity and Zr/TiO_2 as a measure of differentiation. According to the Nb/Y and Zr/TiO_2 ratios of igneous rocks of known origin, Winchester and Floyd (1977) generated a plot of Nb/Y against Zr/TiO_2 that is organized around the petrology of the original rock type. The Lower Cambrian K-bentonite samples are plotted in the fields of trachyte, trachyandesite, rhyodacite (dacite), and rhyolite, suggesting that the K-bentonites are most probably derived from felsic magmas with sub-alkaline to alkaline composition (Fig. 9).

For K-bentonites whose source magmas are felsic in nature, previous studies (Huff et al. 2000; Astini et al. 2007; Su et al. 2009) have widely used the plot of Nb against Y defined by Pearce et al. (1984) to provide information on tectonic setting of the source volcanoes. In the Nb-Y plot (Fig. 10), ten K-bentonite samples from the base of the Shiyantou and Niutitang formations in the study area lie in the field of within-plate granites. Meanwhile, three of the four K-bentonite samples from the middle Zhujiaqing Formation and the top of the Laobao Formation lie within the volcanic arc (syn-collision) granite field. We consider that the K-bentonites in the base of the Shiyantou and Niutitang formations and their equivalents (e.g., the base of the Shuijingtuo and Jiulaodong formations) are records of a critical episode of volcanic activity. Likewise, we suggest that the K-bentonites in the middle Zhujiaqing Formation and the top of the Laobao Formation represent another large volcanic event (detailed correlation of the K-bentonites is discussed in the next section). If the correlation scheme of the K-bentonites is correct, the information on the tectonic settings from the K-bentonites suggests that the two episodes of volcanic eruptions might have taken place in different tectonic

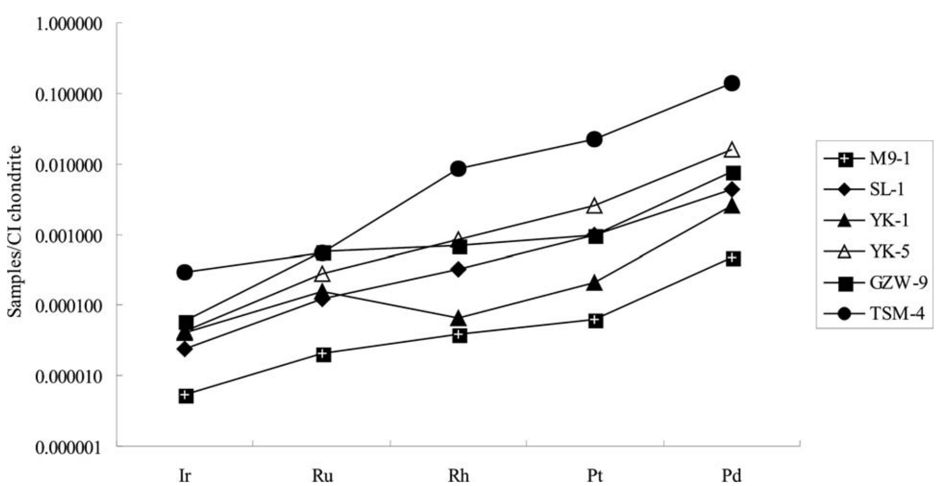

FIG. 7.—CI chondrite-normalized PGE patterns of the K-bentonite in the base of the Shiyantou Formation and its equivalents in South China.

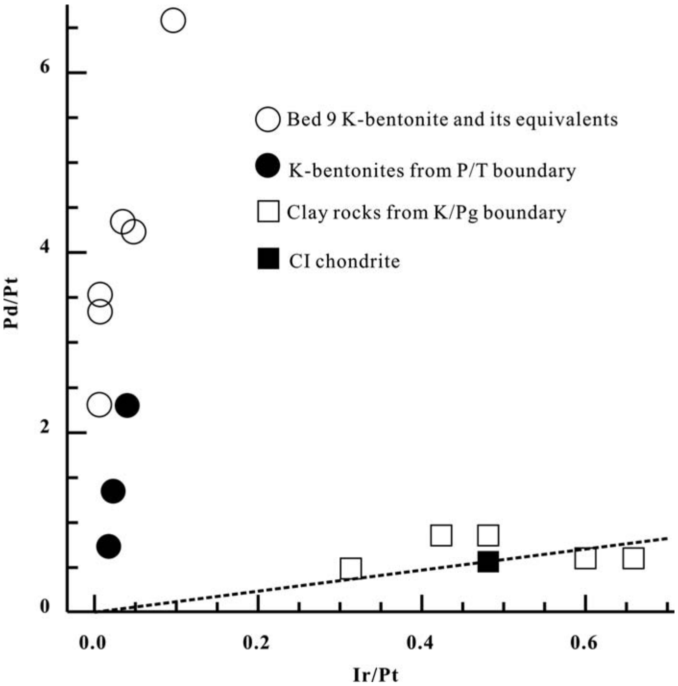

FIG. 8.—Ir/Pt vs. Pd/Pt plot of the K-bentonite in the base of the Shiyantou Formation and its equivalents in South China.

positions or that the two volcanic events erupted possibly during an interval of tectonic transformation.

Previous studies (Wan 2012) have been carried out on the tectonic setting of China during the Precambrian–Cambrian transition. The results have shown that the Cathaysia block lay to the southeast of the

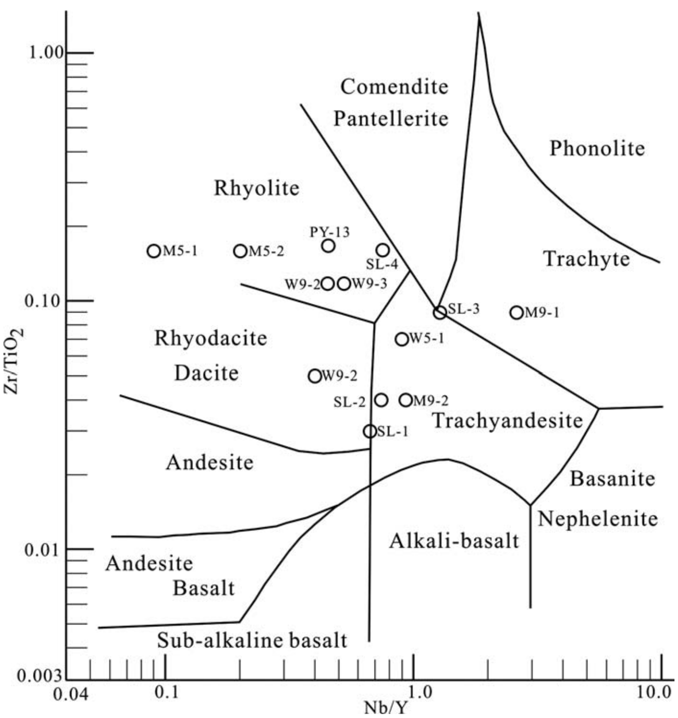

FIG. 9.—Nb/Y vs. Zr/TiO_2 plot of the Lower Cambrian K-bentonites in South China.

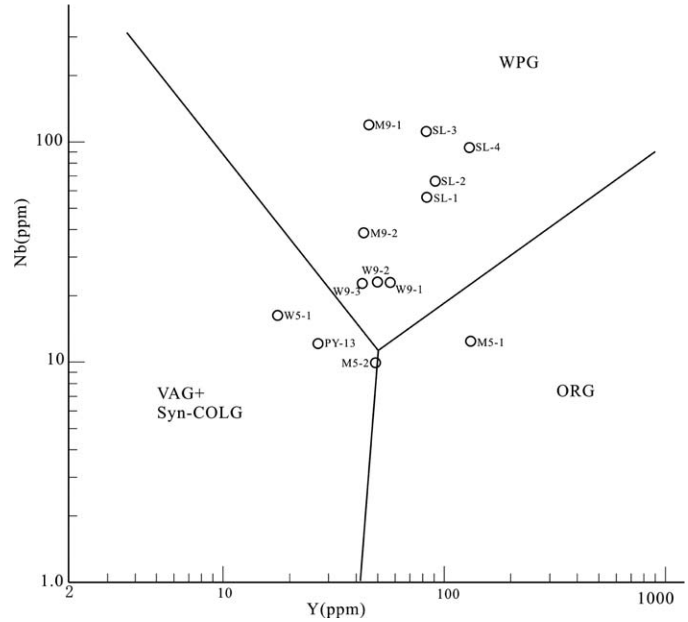

FIG. 10.—Nb-Y plot of the Lower Cambrian K-bentonites in South China. WPG, within-plate granite; VAG+Syn-COLG, volcanic arc granite plus syn-collision granite; ORG, ocean-ridge granite.

Yangtze Block, and an ocean was located between them. Meanwhile, the Sino-Korean block lay to the north of the Yangtze Block, and the two blocks were also separated by an ocean. To the west, the Yangtze Block was amalgamated by the Ganze–Songpan Block, and a continental rifting zone developed in the east margin of the Ganze–Songpan Block. The tectonic information provided by the Nb-Y plot indicates that the tectonic positions of the source volcanoes for the K-bentonites changed from volcanic arc (syn-collision setting) to within-plate extension setting. Therefore, combining the westward thickening trend of the K-bentonites in the two horizons, we suggest that the source volcanoes of the K-bentonites were probably located in the east margin of the Ganze–Songpan Block, which is west of the Yangtze Block (Fig. 1).

Chemical Fingerprinting and Implication for Stratigraphic Correlation

The Lower Cambrian K-bentonites of the Yangtze Block in South China were first discovered in the eastern Yunnan Province, and the Meishucun section in Jinning County of this area can be considered as their type section. The K-bentonites in the middle Zhujiaqing Formation (bed 5) and the base of the Shiyantou Formation (bed 9) have considerable thickness, which is significant for regionally lateral correlation. At the Meishucun section, compared with the K-bentonite in bed 5, the K-bentonite in the base of bed 9 is characterized by higher Zr and Nb concentrations. By comparison, it has been shown that the K-bentonites in the base of the Shiyantou Formation at the Wangjiawan section and in the basal Niutitang Formation at the Songlin section are characterized by higher Zr and Nb concentrations, which could be correlated with the bed 9 K-bentonite at the Meishucun section (Table 1, Fig. 11). Meanwhile, the K-bentonites in the middle Zhujiaqing Formation at the Wangjiawan section and in the topmost Laobao Formation at the Pingyin section are characterized by lower Zr and Nb contents, which could be correlated with the bed 5 K-bentonite at the Meishucun section (Table 1, Fig. 11). Such a regional correlation result is consistent with the conclusion made by Zhou et al. (2013) through studies on REE geochemistry and geochronology (Fig. 4). Thus, it is suggested that the Lower Cambrian on the Yangtze Block has recorded two

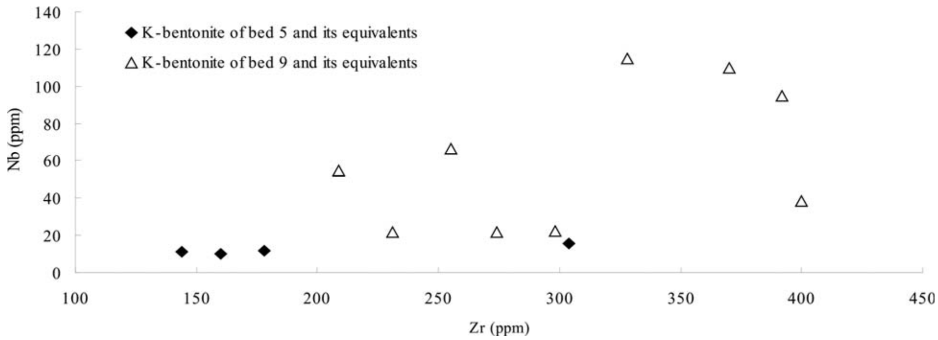

FIG. 11.—Zr-Nb diagram of the Lower Cambrian K-bentonites in South China.

significant episodes of volcanic activity marked by the two prominent K-bentonite beds. The primary magmas of the earlier volcanic eruption are characterized by relatively low Zr (range from 144 to 304 ppm, with an average of 197 ppm) and Nb (with a range of 10 to 15.8 ppm and an average of 12 ppm) concentrations, reflective of the sub-alkaline nature of the magmas. Those of the later volcanic event are typified by higher Zr (range from 209 to 400 ppm, with an average of 306 ppm) and Nb (with a range of 21.6 to 115 ppm and an average of 61 ppm) contents, indicative of the alkaline nature of the magmas and the within-plate setting of the source volcano.

The above regional correlation scheme of the K-bentonites is of valuable significance in studying the Lower Cambrian in South China. Firstly, the distribution area of the K-bentonites in the two horizons has been extended, and thus makes the K-bentonites distinguishable marker beds for lateral correlation across different facies of Lower Cambrian strata in South China. The K-bentonites in the middle Zhujiaqing Formation (bed 5) and the base of the Shiyantou Formation (bed 9) are widespread in eastern Yunnan Province. However, in regions other than eastern Yunnan, reports on their correlative equivalents are scarce. The correlation results in the present study have shown that the K-bentonites in the top of the Laobao Formation (or Liuchapo Formation) and the base of the Niutitang Formation in Guizhou Province may well be correlated with those in the middle Zhujiaqing Formation (bed 5) and the base of the Shiyantou Formation (bed 9) at the Meishucun section, respectively. Hence the distribution area of the K-bentonites in the two significant stratigraphic levels has expanded into the deep-water realms of the Yangtze Block. Furthermore, the correlation scheme of the K-bentonites in this study will facilitate placement of the Precambrian–Cambrian boundary in South China. Wille et al. (2008) considered the polymetallic Ni-Mo layer in the lowermost Niutitang Formation as the PC/C boundary in South China based on a Re-Os isochron age of 541 ± 16 Ma for this layer. Subsequently, Jiang et al. (2009) argued against the PC/C boundary scheme in South China by Wille et al. (2008) on the basis of a SHRIMP U-Pb zircon age (532.3 ± 0.7 Ma) for the K-bentonite in the basal Niutitang Formation at the Songlin section. The correlation results of the K-bentonites in the present study have shown that the K-bentonite in the basal Niutitang Formation at the Songlin section should represent the later one of the two gigantic volcanic events recorded in the Lower Cambrian of South China (Fig. 4). Thus, we believe that the viewpoint considering the polymetallic Ni-Mo layer as the PC/C boundary is inappropriate. Previous geochronology studies indicated that the age of the K-bentonite in the middle Zhujiaqing Formation (bed 5) in eastern Yunnan Province and its equivalent in deep-water realm has been constrained between 535.2 ± 1.7 Ma and 539.4 ± 2.9 Ma by U-Pb zircon ages (Compston et al. 2008; Sawaki et al. 2008; Zhu et al. 2009; Chen et al. 2009; Zhou et al. 2013). Therefore, either in the shallow-water platform or in the deep-water realm, the PC/C boundary in South China should be placed within the strata underlying the older one of the two significant Lower Cambrian K-bentonite beds.

CONCLUSIONS

The following conclusions have been drawn based on the field investigations and the mineralogical and geochemical studies on the Lower Cambrian K-bentonites in South China.

(1) The widespread Lower Cambrian K-bentonite beds in South China are preserved in two important stratigraphic levels: the middle Zhujiaqing Formation and the basal Shiyantou Formation and their lateral equivalents. They occur in both the shallow-water platform and deep-water deposits of the Yangtze Block. Biostratigraphically, the older K-bentonite bed is preserved in the *Anabarites trisulcatus–Protohertzina anabarica* Assemblage Zone, while the younger K-bentonite belongs to the poorly fossiliferous interzone.

(2) Mineralogical and geochemical characteristics of the K-bentonites in the two important Lower Cambrian horizons in South China have confirmed their volcanic origin rather than an extraterrestrial-impact genesis. The primary felsic magmas of the K-bentonites in the two horizons are sub-alkaline to alkaline in nature. Compared with the K-bentonite in the basal Shiyantou Formation and its equivalent sequence, the K-bentonite in the middle Zhujiaqing Formation and its correlative succession is characterized by lower Zr and Nb concentrations. The volcanic activities which produced the ashes of two K-bentonite beds occurred during an interval of tectonic transformation, and the source volcanoes of the K-bentonites were probably located in the east margin of the Ganze–Songpan Block.

(3) The correlation results of the two important Lower Cambrian K-bentonite beds indicate that placement of the PC/C boundary in South China at the polymetallic Ni-Mo layer in the lowermost Niutitang Formation (Wille et al. 2008) is inappropriate. Combined with published geochronological data, the boundary should be placed within the strata beneath the K-bentonite in the middle Zhujiaqing Formation and its correlative stratigraphic level.

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