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ORIGINAL ARTICLE

Sm–Nd dating and rare earth element geochemistry of the hydrothermal calcites from Guling carbonate-hosted talc mineralization in the central Guangxi province, South China

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Abstract Many carbonate-hosted talc mineralization, which are widespread in South China, exclusively developed in Carboniferous dolomitic limestone with many siliceous bands and nodules, and cherts. One of those typical deposits is the Guling talc deposit in Mashan County, central Guangxi province, with a talc reserve of 1.51 million tons. Mineral associations in the deposit are sample, mainly including talc and calcite. In this paper, Sm–Nd isotopic system and rare earth elements and yttrium (REE + Y) for the hydrothermal calcite intergrown with talc are used to constrain the age and origin of the talc mineralization. The hydrothermal calcite samples from the deposit display Sm and Nd concentrations ranging from 0.18 to 0.85 and 0.85 to 4.56 ppm, respectively, and variable Sm/Nd ratios of 0.21–0.24. These calcites further yield an Sm–Nd isochron age of 232 ± 19 Ma (2σ) (MSWD = 0.47) with an concordant initial ^{143}Nd–^{144}Nd ratios of 0.511967 ± 0.000017, which should be interpreted as the mineralization age of the Guling talc deposit. In addition, the calcite samples are enriched in REE with the variable ΣREE contents ranging from 4.82 to 21.50 ppm and display relatively consistent chondrite-normalized REE + Y patterns with the LREE enrichment (LREE/HREE = 2.00–3.60) and the obvious negative Eu (δEu = 0.52–0.68) and Ce (δCe = 0.16–0.33) anomalies. The Y/Ho ratios of seven calcites varies from 43.30 to 59.34, with a mean value of 49.73. The available mineral associations and REE parameters (i.e., REE patterns and Y/Ho ratios) of those calcites indicate that the ore-forming fluids of the talc mineralization be probably derived from the meteoric waters, in particular evolved ones in the Karst areas and the ore-forming materials (e.g., Si and Mg) are likely to be originated from the ore-bearing dolostone in the Yanguan Formation (C_1y) and underlying siliceous rocks in the Liujiang Formation (D_3l). Furthermore, the talc mineralization could take place within a hydrothermal system with relative oxidizing environment and middle temperature, due to the obvious negative Eu and Ce anomalies in the calcites in the Guling deposit.

Keywords Sm–Nd isotopic dating · Carbonate-hosted talc mineralization · Rare earth elements · Carboniferous

1 Introduction

Rare earth elements and yttrium (REE + Y) are easy to incorporate in calcite by substitution at Ca^{2+} structural sites, but the REE diffusion in calcite minerals is very slow (e.g. Cherniak 1998), enabling that the Sm–Nd isotopic systematics could keep closely, even weathering and/or alteration. Furthermore, if there are relatively discrete Sm/Nd ratios and homogeneous ^{143}Nd/^{144}Nd ratios in hydrothermal fluids from which minerals are precipitated, the Sm–Nd isotope is a powerful geochronometer for hydrothermal events (e.g. Chesley et al. 1991; Peng et al. 2003; Barker et al. 2009). Therefore, Sm–Nd isotope system of the hydrothermal calcites has been widely used to

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determine the age of a variety of hydrothermal systems (e.g. Hu et al. 1996; Peng et al. 2003; Li et al. 2007; Uysal et al. 2007; Barker et al. 2009; Su et al. 2009).

Many Carbonate-hosted talc deposits and prospects are widespread in South China, exclusively occurred in Carboniferous strata of dolostone and dolomitic limestone, mainly including Longhui, Dongkou, Huatan and Youxian in Hunan province, Yangguan in Guangdong province, and Huangjiang, Shanglin, Mashan and Wuxuan in Guangxi province (Gao 1983; Li 1985; Chen and Che 1989). Because hydrothermal minerals suitable for conventional isotopic dating are absent from these deposits. So far, there are a few reliable geochronological and geochemical data reported by previous study to constrain the age and origin of the mineralization, which strongly impedes our understanding for ore genesis of these deposits and prospects.

The Guling talc deposit located in the Mashan county, central Guangxi province is one of more economic importance with the talc reserve of 1.51 million tons, second only to the Zhenxu deposit (21.67 million tons). Therefore the deposit should be a typical representative of the carbonate-hosted talc mineralization in South China. In the current paper, Sm–Nd isotopic system is applied to date the timing of carbonate-hosted talc mineralization in the Guling talc deposit. Furthermore, the REE + Y data of the hydrothermal calcites are also used to constrain the origin of the ore-forming materials and physical and chemical environments of the deposit (Fig. 1).

2 Geology of the Guling deposit

The Guling talc deposit is located in the northwest part of the Damingshan tungsten-copper polymetallic metallogenic belt (DMB), central Guangxi province, South China (Fig. 2). Silurian unconformity between Cambrian to Ordovician and Devonian to Triassic structural layers are recognized in this area. The Cambrian to Ordovician stratigraphic unite below this unconformity are a set of weakly metamorphosed arkositic quartzose sandstone with minor intercalations of shale whereas the upper covering strata of the Silurian unconformity is composed predominately of Devonian sandstone, siliceous rock and black shale, Carboniferous to Middle-Late Triassic dolostone, dolomitic limestone and shale (Guangxi, BGMR 1985). Besides, Cretaceous and Quaternary strata are distributed around the anticlinorium and dominated by conglomerate, sandstone as well as tuff. The Guling deposit is hosted within Lower Carboniferous Yanguan Formation (C_1y) that contains dark grey and black, thin-layered, fine grain dolomite with a lot of siliceous band and nodule, chert and manganese-bearing nodule (Fig. 3).

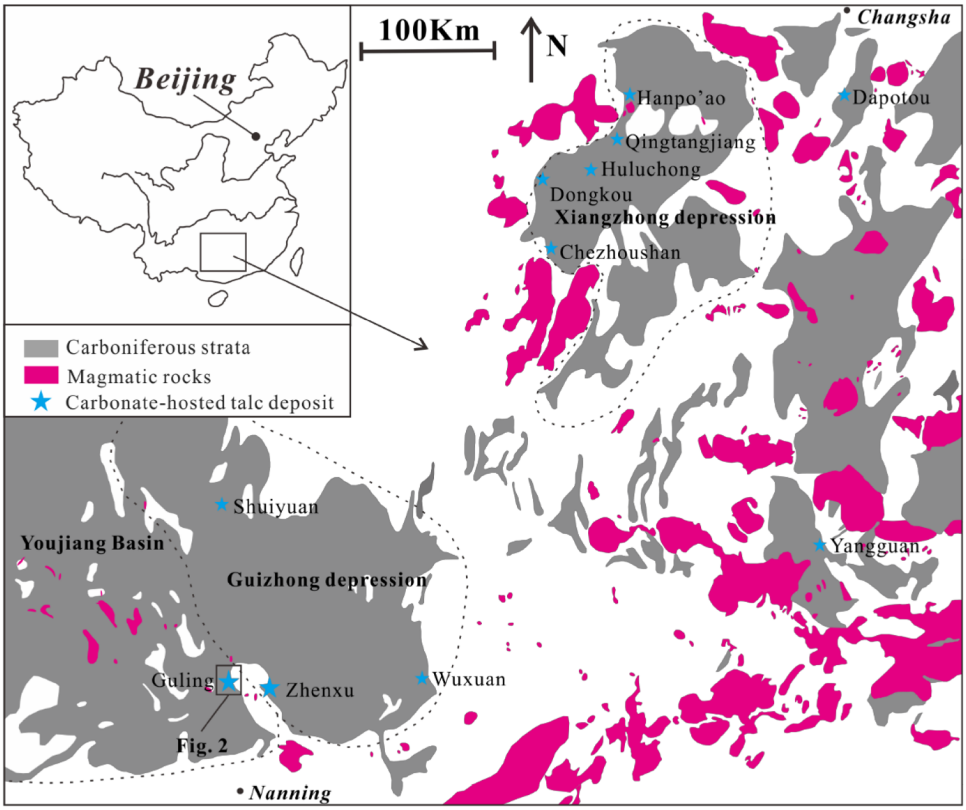

Fig. 1 Distribution of the Carboniferous strata, magmatic rocks and predominate carbonate-hosted talc deposits and prospects in South China

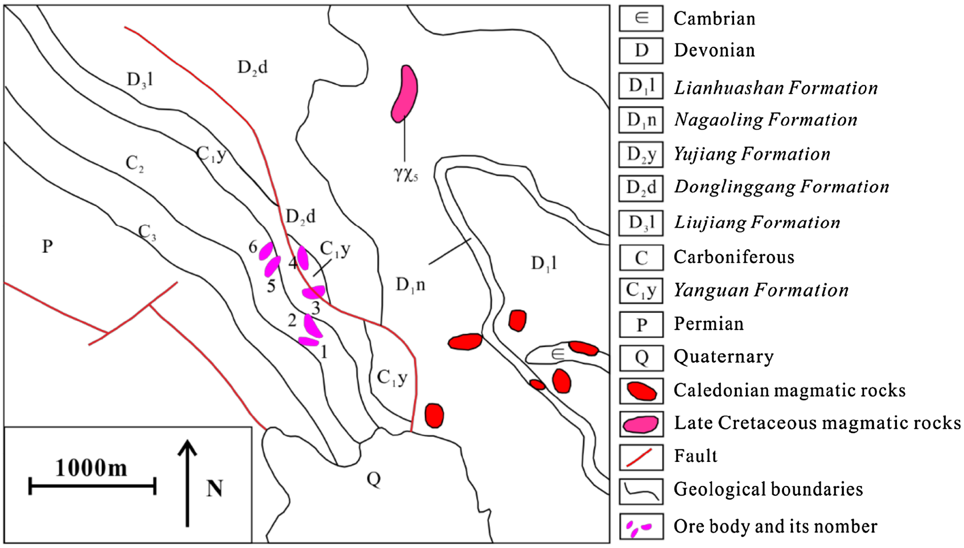

Fig. 2 Geological map of the carbonate-hosted talc mineralization in the Guling deposit

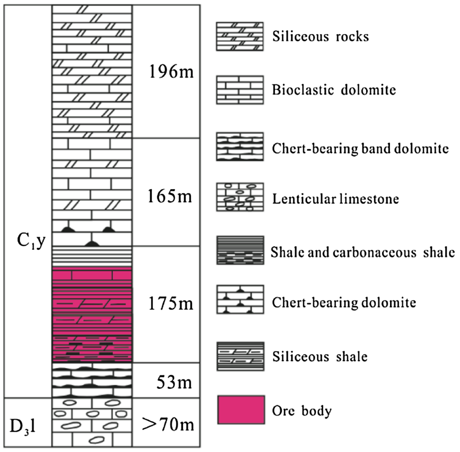

Fig. 3 Stratigraphic column of the Liujiang Formation (D_3l) and ore-bearing Yanguan Formation (C_1y) in the Guling talc ore district

There are no magmatism and metamorphism in the Guling ore mining area, although abundant magmatic rocks and low metamorphic clastic rocks are widespread in the DMB. Many petrology researches and zircon U–Pb datings show that the magmatism could further subdivide into Silurian and Late Cretaceous magmatic activities (Cai et al., unpublished data). The former is mainly composed of granodiorite (443.1 ± 1.6 Ma), diorite porhpyrite (432.9 ± 4.3 Ma), quartz porphyrite (424.9 ± 2.2 Ma), muscovite granite (419.7 ± 2.7 Ma) and biotite granite (405.2 ± 1.4 Ma) while the latter consists predominately of biotite granite (93.1 ± 1.0 Ma), quartz porphyrite (94.2 ± 1.2 Ma), aplite (93.5 ± 2.1 Ma) and minette (Cai et al., unpublished data). However, it is likely that all those magmatism and metamorphism are genetically unrelated to the talc mineralization because there are no magmatism, metamorphism and polymetallic mineralization in the Guling talc ore district.

NW-, NE- and NS-trending faults occur in the DMB. NW-trending fault system of Kunlunguan dominates over the whole Damingshan area. Besides, other important geological structure is a huge Damingshan anticlinorium with a variable northwest strike. The huge fault and anticline extend from northwest to southeast with the length of more than 100 km and essentially control magmatism, metamorphism, sedimentation and mineralization. The ore bodies of Guling deposit are developed at the core of a secondary syncline of the Damingshan anticlinorium (Fig. 2).

Field investigations indicated that morphology of all ore bodies are stratiform, lenticular and irregular. Six ore bodies extend more than several kilometers and individual ore body in length and width range from 200 to 300 and 50 to 100 m, respectively (Table 1). Three type talc ores has been recognized including the black, white and red ones (Fig. 4). All of three type ores have many uniform features,

Table 1 Scale and reserves of talc ore bodies from the Guling deposit

Ore body no	Scale (m)			Reserves (million tons)
	Length	Width	Depth	
1	220	29	55	0.93
2	50	5	13	0.24
3	145	21.5	36	0.30
4	70	18	18	0.02
5	70	4	18	0.01
6	30	5	9	0.01
Total				1.51

Fig. 4 Photographs of ores from the Guling deposit in central Guangxi, South China. **a** *White* talc and colorless euhedral calcite; **b** *Red* talc; **c** *Black* calcite; **d** *Black* talc and *milky* calcite

e.g., the mineral association of talc and calcite, the massive and partly taxitic, brecciated and banded ore structures and blastic textures. There are some researches indicated that the black talc ores with talc content of 70 %–80 % are enriched in organic materials up to 1.64 %, originated from that of the Yanguan Formation (C_1y) (e.g., Tong 1994). The white and red talc ores with the minor organic materials have relatively higher talc contents of 85 % and 95 %, respectively. In general, most calcites are colorless, black and milk white and intergrown with talc. They are characteristic of euhedral megacryst surrounded by massive talc in the orebody (Fig. 4), thus indicating the hydrothermal calcites were deposited before the massive talc.

3 Analytical methods

3.1 Sm and Nd contents and isotopic ratio

All calcite samples were collected from the Guling ore district. And pure calcite separates were hand-picked under a binocular microscope and crushed to 200 mesh using an agate mortar. Sm and Nd content and Nd isotopic ratio analysis for calcite separates were determined using an IsoProbe T thermal ionization mass spectrometer (IT-TIMS) at Tianjin Institute of Geology and Mineral Resources, CAGS. Two separated sample aliquots for every calcite separates, each weighing 150 mg, were dissolved with a mixture of HF and $HClO_4$ in a ratio of 10:1 at 150 °C for more than 12 h, one for spiking and determination of Sm and Nd concentrations and the other for the determination of present-day $^{143}Nd/^{144}Nd$ ratios, respectively. Separation of Sm and Nd was conducted by a reverse-phase extraction technique with HDEHP coated on Teflon powder. Sm and Nd concentrations were determined by isotope dilution using ^{149}Sm–^{146}Nd spike solution. Nd ratios were normalized to $^{146}Nd/^{144}Nd$ ratio of 0.7219. The reproducibility of the isotopic ratios is better than 0.005 % (2σ) and the precision for Sm and Nd concentrations is less than 0.5 % of the quoted values (2σ). Concentrations for BCR-1 determined during this study were 6.57 ppm for Sm, 28.75 ppm for Nd and 0.512644 ± 5 (2σ, $n = 6$) for $^{143}Nd/^{144}Nd$, consistent with the 6.58 ppm for Sm, 28.8 ppm for Nd reported by Bell et al. (1989). Blanks during this study are 0.03 ng for Sm and 0.05 ng for Nd. The Sm–Nd isochron ages were calculated with the ISOPLOT 4.0 computer program recommended by Ludwig (2003) with a decay constant ($\lambda^{147}Sm$) of 6.54×10^{-12}/year.

3.2 Rare earth elements and yttrium (REE + Y)

The contents of rare earth elements and yttrium (REE + Y) of the separated calcites were also carried out by an ELAN 6000 inductively coupled plasma quadrupole mass spectrometer (ICP–MS) at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Detailed analytical methods were adopted from Qi and Gregoire (2000). Precision and accuracy for the GSR-3 and JG-2, as determined by ICP–MS, are within 5 %–10 %.

4 Results

4.1 Sm–Nd dating

The Sm and Nd concentrations and Nd isotopic ratios are listed in Table 2. The Sm contents of calcite samples from the Guling deposit vary from 0.18 to 0.95 ppm; the Nd contents range from 0.85 to 4.56 ppm; and the Sm/Nd ratios are 0.21 to 0.24. These data points display a relatively good linear relationship on the $^{147}Sm/^{144}Nd$ versus $^{143}Nd/^{144}Nd$ diagram (Fig. 5a) and yield a Sm–Nd isochron age of 232 ± 19 Ma (2σ) (MSWD = 0.47) with an initial $^{143}Nd–^{144}Nd$ ratios of 0.511967 ± 0.000017 ($\varepsilon Nd_{(t)} = -7.3$). Because there are, as revealed by Fig. 5b, no liner relationships on the 1/Nd versus $^{143}Nd/^{144}Nd$ diagram, which could preclude a possibility of mix line resulting from two different type fluids (e.g., Peng et al. 2003).

4.2 Rare earth elements and yttrium

The rare earth elements and yttrium (REE + Y) compositions of the calcite from the Guling deposit are listed in Table 3 and shown in Fig. 6, respectively. As shown in Tables 2 and 3, Sm and Nd contents measured by ICP are slightly lower than that of IT-TIMS determination, but the deviation is generally less than 10 %. Therefore the REE + Y data of this contribution are credible for any discussion as fellows. The REE contents of calcites are normalized to chondrite values recommended by Sun and McDonough (1989). It shows that seven calcites are enriched in REE with the variable ΣREE contents ranging from 4.82 to 21.50 ppm (Table 3) and display relatively consistent chondrite-normalized REE patterns with the LREE enrichment (LREE/HREE = 2.00–3.60) and the obvious negative Ce (δCe = 0.16–0.33) and Eu (δEu = 0.52–0.68) anomalies (Table 3; Fig. 6). The Y/Ho ratios of seven calcites vary from 43.30 to 59.34, with a mean value of 49.73.

5 Discussion

5.1 Timing of carbonate-hosted talc mineralization

Precise isotopic dating is crucial to understand the genesis and tectonic setting of the carbonate-hosted talc mineralization in the Guling deposit. Many calcite Sm–Nd dating studies were succeeded to interpret the timing of hydrothermal fluid activities in the mineralization and basin evolution processes (e.g. Hu et al. 1996; Peng et al. 2003; Li et al. 2007; Uysal et al. 2007; Su et al. 2009). There are some evidence shows that high Sm/Nd ratios and a large range of these ratios for calcite samples enable application of Sm–Nd geochronology to constrain the age of relatively young hydrothermal events (Peng et al. 2003).

In this study, a relatively reliable Sm–Nd isochron age of 232 ± 19 Ma (2σ) from the Guling deposit was reported, although there are relatively narrow Sm/Nd ratios (0.21–0.24) in hydrothermal calcites. It is likely to ascribe to relatively uniform $^{143}Nd/^{144}Nd$ ratios of ore-forming fluids ($^{143}Nd–^{144}Nd$ ratios: 0.511967 ± 0.000017) from which hydrothermal calcite minerals were precipitated. Therefore, such Sm–Nd isochron age of 232 ± 19 Ma should be interpreted as the timing of the Guling deposit, and thus probably representing the age of the carbonate-hosted talc mineralization in South China. As a result, the Guling deposit should be formed in the Middle Triassic, coeval with the Indosinian Orogeny in South China.

Furthermore, the above conclusion should be also supported by simple mineral association of talc and calcite. The Guling deposit is a typical epigenetic hydrothermal metasomatic deposit hosted within the Lower Carboniferous strata based largely on the blastic texture, and massive and partly taxitic brecciated and banded structures, suggesting a post-Lower Carboniferous ore-forming age. The talc and calcite dominate over the whole ore body in the mine, indicating that the talc mineralization would be formed by this reaction:

Table 2 Sm and Nd contents and Nd isotopic ratios in the calcites from the Guling deposit

Sample no	Analytical results						
	Sm (μg/g)	Nd (μg/g)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2σ (10^{-6})	εNd (*t*)	T_{2DM}
GL-1	0.298	1.362	0.1325	0.512165	6	−7.3	1,603
GL-11	0.183	0.846	0.1305	0.512164	3	−7.3	1,600
GL-b	0.596	2.622	0.1374	0.512178	7	−7.2	1,595
GL-d	0.954	4.557	0.1265	0.512159	2	−7.3	1,599
GL-7	0.842	3.823	0.1331	0.512168	3	−7.3	1,600
GL-3	0.346	1.678	0.1246	0.512155	3	−7.3	1,600
GL-a	0.490	2.047	0.1446	0.512186	2	−7.3	1,599

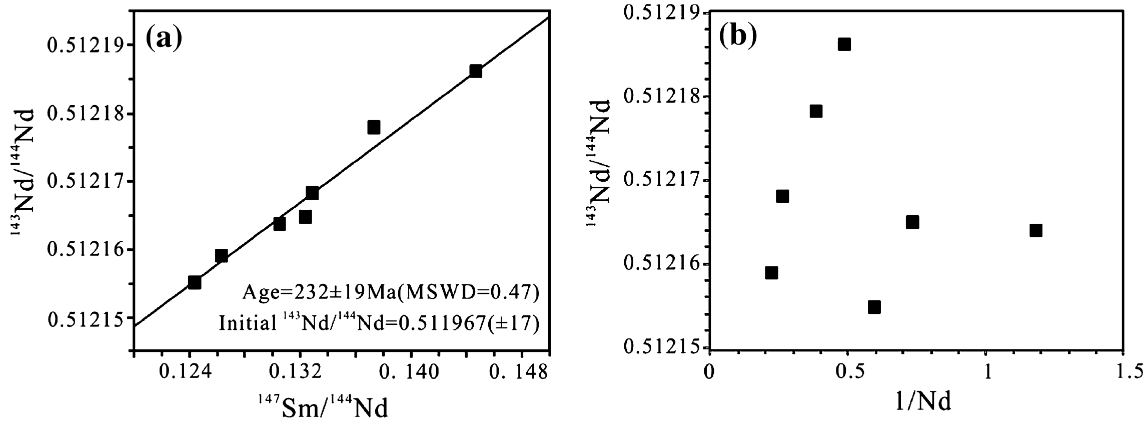

Fig. 5 Sm-Nd isochron age (**a**) and $^{143}Nd/^{144}Nd$ versus 1/Nd (**b**) for the calcites from the Guling talc deposit

Table 3 Rare earth element and yttrium composition in the calcites from the Guling deposit

Sample no	GL-1	GL-11	GL-b	GL-d	GL-7	GL-3	GL-a
La	1.92	1.60	3.59	6.71	5.35	2.64	2.46
Ce	0.72	0.43	1.64	3.03	2.22	1.28	1.52
Pr	0.29	0.19	0.58	1.06	0.84	0.42	0.44
Nd	1.26	0.78	2.49	4.34	3.61	1.69	1.92
Sm	0.27	0.17	0.51	0.83	0.75	0.35	0.46
Eu	0.07	0.04	0.14	0.21	0.18	0.06	0.11
Gd	0.44	0.29	0.81	1.22	0.97	0.40	0.63
Tb	0.07	0.05	0.14	0.21	0.17	0.07	0.11
Dy	0.52	0.42	1.01	1.45	1.30	0.50	0.75
Ho	0.13	0.11	0.23	0.32	0.30	0.11	0.16
Er	0.37	0.35	0.66	0.96	0.88	0.34	0.47
Tm	0.05	0.04	0.10	0.12	0.12	0.04	0.06
Yb	0.29	0.30	0.63	0.90	0.73	0.29	0.35
Lu	0.04	0.05	0.10	0.14	0.11	0.04	0.05
Y	7.43	6.46	11.36	14.87	14.43	4.95	6.83
ΣREE	6.45	4.82	12.65	21.50	17.55	8.24	9.48
LREE	4.54	3.21	8.97	16.18	12.96	6.45	6.91
HREE	1.91	1.61	3.68	5.33	4.59	1.79	2.57
LREE/HREE	2.37	2.00	2.44	3.04	2.82	3.60	2.69
δEu	0.62	0.52	0.68	0.62	0.66	0.52	0.61
δCe	0.21	0.16	0.25	0.25	0.23	0.27	0.33
La/Ho	15.38	14.42	15.68	20.73	17.71	23.48	15.59
Y/Ho	59.34	58.17	49.55	45.94	47.72	44.06	43.30

$$3CaMg(CO_3)_2(\text{dolomite}) + 4SiO_2(\text{fluids}) + 2H_2O \rightarrow Mg_3(Si_4O_{10})(OH)_2(\text{talc}) \downarrow + 3CaCO_3(\text{calcite}) \downarrow + 3CO_2 \uparrow$$

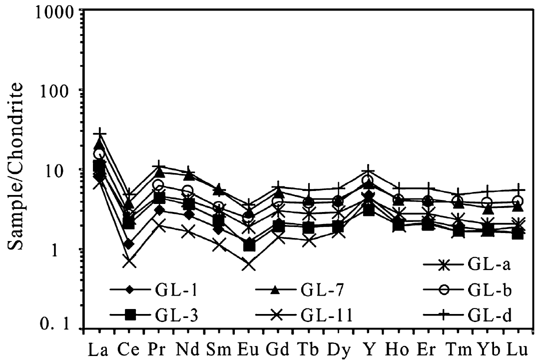

Fig. 6 The chondrite-normalized REE + Y patterns of the calcites from the Guling deposit. All data were normalized by the chrondrite REE + Y values from Sun and McDonough (1989)

This reaction precludes a possibility that sea water and submarine hydrothermal fluids are involved in the talc mineralization because the increasing CO_2 partial pressure due to the talc producing reaction and possibly a high NaCl component should favor the solubility of calcite as the following reaction:

$$3CaMg(CO_3)_2(\text{dolomite}) + 4SiO_2(\text{fluids}) + 6HCl \rightarrow Mg_3(Si_4O_{10})(OH)_2(\text{talc}) \downarrow + 3CaCaCl_2 + 2H_2CO_3 + 4CO_2 \uparrow$$

(Skippen and Trommsdorff 1986; Bowers and Helgeson 1983). If this was a case, then calcite should not had been pervasive in the Guling deposit. As a result, the talc mineralization in the Guling should take place in a continental environment. Previous studies have revealed that the shift from marine sedimentation to continental deposition in South China took place in the Middle-Late Triassic in Guangxi province (Guangxi, BGMR 1985). Therefore the geological evolution concord with the conclusion deduced from the mineral association of the talc deposit, which support that the talc mineralization took place in the middle-late Triassic.

5.2 The source of the ore-forming materials (water, Si and Mg)

The REE + Y characteristics of hydrothermal calcite could provide many valuable information on the source, and physical and chemical environment of the hydrothermal fluids from which the calcite precipitated (e.g. Sverjensky 1984; Michard 1989; Bau and Möller 1992). Importantly, these applications of REE + Y data had been amplified especially when several landmark studies had been carried out at the end of the last century (e.g., Bau and Möller 1992; Gammons et al. 1996; Cherniak 1998). For example, the distribution patterns of REE + Y may potentially trace origin of hydrothermal fluids because they generally migrate as an element group due to similar behavior in hydrothermal fluids. Hence, those geological bodies, which possess genetically kinships each other, would share an analogous REE + Y pattern in the normalized diagram. Besides, Y and Ho are twin elements in geochemical behavior and behave coherently in most geological environments (Bau and Dulski 1995; Uysal et al. 2007, 2009). Therefore, Y/Ho ratio is also a more better tracer in geological process than the normalized pattern of REE + Y, because Y/Ho ratio could keep constant in the most geological process, except for in the fluorine-rich hydrothermal fluids due to Y showing stronger complexion than Ho in this fluids, thus leading to the increase of the ratio (Wood 1990a, b; Bau and Dulski 1995). Abundant researches revealed that the carbonate-hosted talc mineralization was formed by hydrothermal alteration of carbonates, especially dolomite, by Si-bearing hydrothermal fluids, e.g., Göpfersgrün in Germany (Hecht et al. 1999), Lassing and Rebenwald in Austria (Boulvais et al. 2006). This research also suggested that the Si-bearing hydrothermal solutions are predominately derived from the basin brine (e.g., Puebla de Lillo in Spain; Tornos and Spiro 2000), sea water (e.g., Ruby area in the southwest Montana, USA; Brady et al. 1998) and magmatic water (e.g., Hwanggangri area in South Korea; Shin and Lee 2006), respectively. Importantly, the basin brine, sea water and magmatic fluids also provide the ore-forming fluids and materials (Si and Mg) for the carbonate-hosted talc mineralization whereas the ore-bearing carbonates also could afford abundant Mg. In the study, the Guling deposit is hosted with the dolostone and dolomitic limestone with many siliceous bands and nodules and cherts. Hence the ore-bearing strata could provide the talc mineralization with abundant Mg and Si. This is also supported by the REE + Y data. Seven calcite samples from the Guling deposit display relatively consistent chondrite-normalized REE + Y pattern with the LREE enrichment and the obvious negative Ce and Eu anomalies and positive Y anomaly (Fig. 6), consistent with that of the Paleozoic carbonates in South China (Fig. 7). In addition, the Y/Ho ratio of the seven calcites varies from 43.30 to 59.34, with a mean value of 49.73 (Table 4), concordant with that (Table 4; Fig. 8; Y/Ho ratio 35.06–74.86, mean 51.52) of the Paleozoic carbonates in South China. As a result, the ore-bearing strata provided the ore-forming materials (e.g., Si and Mg) for the talc mineralization. Here we further discussed the origin of the ore-forming materials of the carbonate talc mineralization in the Zhenxu deposit.

The basin brine are unlikely to provide ore-forming fluids (e.g., water) and materials (e.g., Si and Mg) for the talc mineralization. Because mica minerals are ubiquitous in the sandstone and shale of the sedimentary basin, the fluids that equilibrated with the sedimentary rocks would contain abundant K^+ and Al^{3+}, and further lead to formation of chlorite by the below reactions:

$$2KAl_2Si_3AlO_{10}(OH)_2(\text{mica}) + 3SiO_2(\text{fluid}) + 15Mg^{2+} + 24H_2O \rightarrow 3Mg_5AlSi_3AlO_{10}(OH)_8(\text{Chlorite}) + 2K^+ + 28H^+$$

(Moine et al.1989). For example, the mineral association of talc and chlorite were observed in many carbonate-hosted talc deposits in the world, e.g., Winterboro in the Alabama, USA (Blount and Vassiliou 1980), Trimouns in Pyrenees, French (e.g., Moine et al. 1989), Göpfersgrün in German (Hecht et al. 1999) and Lassing and Rebenwald in Austria (Boulvais et al. 2006). Hence, the ascended basin brine did not provide the talc mineralization with the ore-forming materials (e.g., water, Si and Mg), although a wealth of

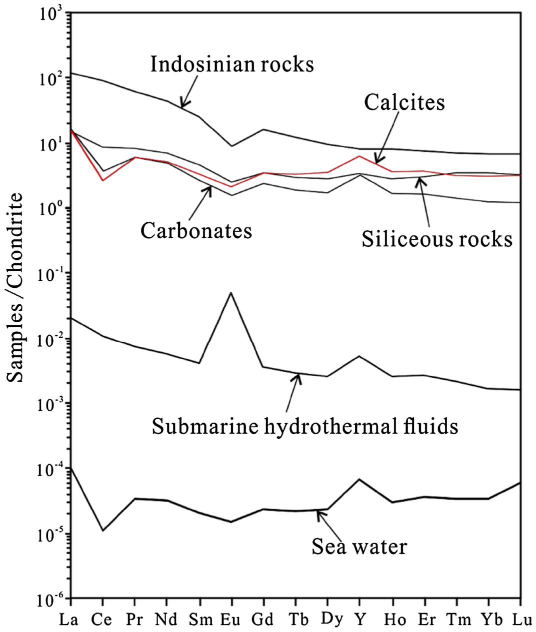

Fig. 7 The REE + Y patterns of the key possible sources for the talc mineralization in the Guling deposit. The data sources are the same as the Table 4

Table 4 The Y/Ho ratio composition of the main possible sources for Guling talc mineralization

Possible sources of ore-forming fluids (n)	Y/Ho ratios			References
	Minimum	Maximum	Average	
Indosinian granite (34)	24.63	32.82	28.09	Wang et al. (2007c)
Carbonates (31)	35.06	74.86	51.52	Zhou et al. (2012), Qiu et al. (2013)
Siliceous rocks (32)	25.43	52.00	35.82	Huang et al. (2012) and Wang et al. (2007a, b)
Submarine hydrothermal fluids (16)	25.74	76.58	48.17	Hongo et al. (2007)
Sea water (183)	43.22	110.19	62.51	Zhang and Nozaki (1996, 1998), Alibo and Nozaki (1999) and Hongo et al. (2007)
Calcite (7)	43.30	59.34	49.73	This study

n number of Y/Ho ratio data

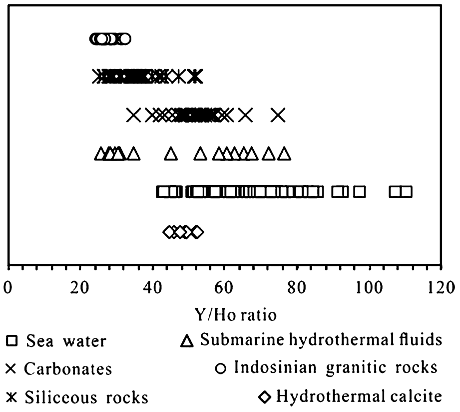

Fig. 8 The Y/Ho ratio distribution of the key possible sources for the Guling deposit. Data sources are the same as Table 4

MVT type Pb–Zn deposits and prospects are observed in the Guizhong depressions in the Guangxi province (Lei et al. 2002, 2006) and Xiangzhong depressions in the Hunan province (Liu and Zheng 1999; Liu et al. 1999).

The sea water and submarine hydrothermal fluids would not be the origin of ore-forming fluids. First, because a lot of calcites are observed in the Guling deposit, the ore-forming system should contain relatively less content of Cl^-, in contrast with the compositions of the sea water and submarine hydrothermal fluids with relatively high content of Cl^-. Second, as suggested by Fig. 7, the sea water and submarine hydrothermal fluids from today's ocean are depleted in REE + Y with a flat REE + Y pattern with a positive Y anomaly (Zhang and Nozaki 1996, 1998; Alibo and Nozaki 1999; Hongo et al. 2007). However, the former has a relatively negative Ce anomaly whereas the latter displays an extremely obvious Eu positive anomalies, different from that (Fig. 7: the LREE enrichment and obvious negative Ce and Eu anomalies) of the calcites from the Guling deposit. Third, the sea water display relatively higher Y/Ho ratio (Table 4; Y/Ho ratio: 43.22–110.19, mean value 62.51) than the ratio (Y/Ho ratio 43.30–39.34, mean value 49.73) of the calcites whereas the submarine hydrothermal fluids show the Y/Ho ratio variation (Table 4; Y/Ho ratio 25.74–76.58, mean value 48.17), similar to that (Y/Ho ratio 43.30–39.34, mean value 49.73) of the calcites. It seems that the ore-forming fluids should be derived from the submarine thermal fluids coeval with the talc mineralization. However, sixteen Y/Ho ratios of submarine hydrothermal fluids are easily subdivided into two groups in the Fig. 8, i.e., 25.74–34.83 (n = 8) and 45.16–76.58 (n = 11). It should be ascribed to the mixing of two fluids with the two different Y/Ho ratios, namely, the felsic rocks (ca. 28; Bau and Dulski 1995) and sea water (mean 62.51; Table 4). Therefore, the ore-forming fluids were not derived from the sea water and submarine hydrothermal fluids.

The magmatic water that derived from the Indosinian magmatism are also ruled out. For example, many talc deposits with an origin of the typical magmatic hydrothermal fluids are developed at the contact with the igneous intrusion of the Muamsa granite, South Korea. These talc deposits display a typical altered zone of amphibolite, talc and chlorite and dolomitic marble from intrusions to ore-hosting marble and a mineral association of high temperature including tremolite, diopside and phlogopite (Shin and Lee 2002). However, no similar alteration zones and mineral associations are observed in Guling deposit. Besides, there are no Indosinian magmatism recognized in the DMB by abundant zircon U–Pb datings (Cai et al., unpublished data). Therefore, the ore-forming fluids and materials were not sourced from the magmatic water. In addition, it is also supported by the REE + Y data. The Indosinian magmatic rocks in South China are enriched in LREE with an obvious Eu negative anomaly (Fig. 7; Wang et al. 2007c), considerably different from that (a negative cerium anomaly and a positive Y anomaly) of the calcites from the Guling deposit. These rocks have the Y/Ho ratio of 0.24.63–32.82 with an average of 28.09 (Table 4; Fig. 8; Wang et al. 2007c), in contrast with that (Y/Ho ratio 43.30–39.34, mean value 49.73) of the calcites. Hence, it is obvious that the magmatic hydrothermal fluids are not the origin of the ore-forming materials (water, Si and Mg) for the talc mineralization.

However, the results of Sm–Nd dating in this study documented that the carbonate-talc mineralization should take place in the Middle-Late Triassic. In those time, the South China had been a continental sedimentation (Guangxi, BGMR 1985). Hence the ore-forming fluids are likely to be sourced from the meteoric water. If this is a case, then the REE + Y features (e.g., REE + Y pattern and Y/Ho ratio) of the ore-forming system will not be obviously altered by the meteoric water and essentially controlled by the ore-bearing carbonates. This is supported by the facts that the calcites share an analogous Chondrite-normalized REE + Y pattern with the Paleozoic carbonates thus the ore-bearing strata (Fig. 7) and the Y/Ho ratio (Y/Ho ratio 43.30–59.34, mean 49.73) of the calcites also resemble that (Y/Ho ratio 35.06–74.86, mean 51.52) of the carbonates (Table 4; Fig. 8). Besides, the meteoric water are generally absent from a variety of ion including Cl^-, Al^{3+} and K^+, in contrast with that of the basin brine, sea water and submarine hydrothermal fluids. Namely, abundant calcites are observed in the Guling talc deposit and but no chlorite in the deposit. Hence the meteoric water should be the source of the ore-forming materials.

It is worth to note that the underlying siliceous rocks probably provide (partly) Si for the carbonate talc mineralization. The carbonate-hosted talc deposits in South China generally occur in the core of syncline. For example, the Guling deposit is developed at the secondary syncline of the huge Damingshan anticline (Fig. 2). The secondary syncline is formed by the Liujiang Formation (D_3l) and Yanguan Formation (C_1y). The former is the ore-bearing strata and comprised mainly of the dolostone and dolomitic limestone with many siliceous band and nodule while the latter consist predominately of siliceous rocks (Fig. 3). Therefore, it is likely that the siliceous rocks of the Liujiang Formation (D_3l) were involved in the talc mineralization and provided it with abundant Si. These siliceous rocks also share relatively analogous Chondrite-normalized REE + Y pattern with calcites apart from the absence from the strong Y positive anomaly (Fig. 7). The Y anomaly is easily reflected by Y/Ho ratio and the Y/Ho ratio of the siliceous rocks in central and north Guangxi varies from 25.43 to 52.00 with an average of 35.82. It is revealed by Table 4 and Fig. 8 that the Y/Ho ratio of the calcites ranges from 43.30 to 59.34 with a mean of 49.73, which is slightly lower than that (Y/Ho ratio 35.06–74.86, mean 51.52) of the Paleozoic carbonates in South China. It is likely that the REE + Y of the calcites could be a mixing of the ore-bearing dolostone of the Yanguan Formation (C_1y) and siliceous rocks of the underlying Liujiang Formation (D_3l). Hence, the siliceous rocks of the Liujiang Formation (D_3l) probably provided Si for the talc mineralization.

In summary, the meteoric water are advocate to be the source of the talc mineralization in the Guling deposit and the ore-forming materials (e.g., Si and Mg) were probably provided by the ore-bearing strata of the Yanguan Formation (C_1y) and underlying Liujiang Formation (D_3l).

5.2.1 *Physical and chemical conditions*

Europium is the most special REEs and the Eu^{3+}/Eu^{2+} redox potential in hydrothermal fluids are controlled predominately by the temperature, based on theoretical considerations and thermodynamic calculations (Sverjensky 1984 and Bau and Möller 1992). If the minerals absorbed in REE are deposited at temperatures exceeding 250 °C then Eu^{2+} dominates over Eu^{3+} and tend to substitute preferentially for Ca^{2+}, leading to a positive Eu anomaly. Elderfield and Sholkovitz (1987) documented that the Ce anomaly is a function of fO_2 and pH and the anomaly is more sensitive to pH than to fO_2. Bau (1991) further believed that the generation of Ce anomalies in high temperature environments seem unlikely, because the Ce^{4+}/Ce^{3+} redox equilibrium would shift towards higher fO_2 with increasing temperature.

In this study, the hydrothermal calcites with the negative Eu and Ce anomalies in the Guling deposit indicates that the talc mineralization never reaches such high temperature of 250 °C (Sverjensky 1984; Bau and Möller 1992). It should be also supported by field geological evidence because the Guling deposit consist of talc and calcite, a mineral association of middle temperature, without any high temperature minerals such as tremolite, diopside and phlogopite. In addition, the talc mineral should be deposited in a hydrothermal fluid with the temperature between 200 and 400 °C, as revealed by phase diagram provided by Delgado (1996). Therefore, it is most likely that the talc mineralization in Guling deposit formed at a temperature of 200–250 °C.

Besides, the consistent negative Ce anomaly of the calcite minerals indicates that the talc mineralization should take place in the hydrothermal fluid system with an oxidized environment (Elderfield and Sholkoviz 1987; Bau 1991).

6 Conclusion

In this paper, the Sm–Nd isotopic dating and rare earth elements of the hydrothermal calcite inter-grown with talc were carried out in the Guling deposit. Same valuable conclusions should be reached as follow.

(1) The calcite inter-grown with talc from Guling deposit yield a Sm–Nd isochron age of 232 ± 19 Ma, implying that the carbonate-hosted talc mineralization in central Guangxi province, south China took place at middle Triassic;
(2) Available rare earth elements and yttrium data of the calcites indicate that the ore-forming fluids are probably sourced from meteoric water and the ore-forming materials (i.e., Si and Mg) came mainly from the ore-bearing dolostone and dolomitic limestone of the Yanguan Formation (C_1y) and siliceous rocks of the Liujiang Formation (D_3l);
(3) Being obvious Eu and Ce negative anomalies of the calcites implies that the talc mineralization could take place in a hydrothermal system with the middle temperature and relatively oxidized environment.

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