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# Evidence for metasomatic mantle carbonatitic magma extrusion in Mesoproterozoic ore-hosting dolomite rocks in the middle Kunyang rift, central Yunnan, China

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#### Abstract

The Kunyang rift lying on the western margin of the Yangtze platform is a rare Precambrian Fe-Cu mineralization zone. Wuding– Lufeng basin that is an important part of the zone is located on the west edge in the middle of the rift. The most important ore-hosting rocks are Mesoproterozoic dolomite rocks in the basin controlled by a ring fracture system, which is a fundamental structure of the basin. Plenty of silicate minerals and acicular apatite, feldspar phenocrysts and small vesicular, flown line and flown plane structures, melt inclusion and high temperature fluid inclusion found in most ore-hosting dolomites suggest that this kind of rocks could not be sedimentary dolomite, marble or hydrothermal carbonate rocks. The Zr/Hf and Nb/Ta values of the rocks are identical with those of associated mantle-derived rocks, and vary widely. For the monomineral dolomite,  $\delta^{18}O_{\text{SMOW}}\% = +5.99$  to +18.4 and  $\delta^{13}C_{\text{PDB}}\% = -3.01$  to +0.94, which fall within the range for all carbonatitic volcanic rocks of the world. As for the accessory minerals, the values of  $\delta^{18}O_{\text{SMOW}}\%$  of magnetite (=+3.47 to +5.99‰) are close to that of the mantle (<5.7%), and the  $\delta^{34}S\%$  values of sulfides (-5.09 to +5.78, averaging +1.50) are close to that of meteorite. For all the ore-bearing dolomite rocks,  $\varepsilon_{\text{Nd}} = +0.19$  to +2.27, and the calculated  $I_{\text{Sr}} = 0.699143$ , while for the associated mantle-derived rocks,  $\varepsilon_{\text{Nd}} = +3.18$  to +3.72. All the data suggest that the mineral assemblage is not only igneous but also of metasomatic mantle origin. And the presence of acicular apatite indicates that the rocks were formed by magma rapidly cooling. And the phenocryst texture and vesicular, flown and ropy and pyroclastic structures suggest that the igneous rocks were extrusive. Therefore, the ore-bearing dolomite rocks are carbonatitic volcanic rocks. This conclusion implies that most iron and copper ore deposits hosted in the dolomite rocks are carbonatitic volcanic rocks. This conclusion implies that most iron

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## 1. Introduction

The Kunyang rift, famous for its Precambrian ore deposits, is a polymetallic mineralization zone found in

China. There are large copper ore deposits in Dongchuang to its north and Yimen to its south. A few years ago, another large deposit called as the Xikuangshan-type chalcopyrite-bearing magnetite ore deposit was also discovered at Xikuangshan near Dongchuang. So there are many localities of iron and copper mineralization in the rift.

For many decades, the geology of the mineralization zone has been studied, with many geological discoveries

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of this area achieved [1,2], and the understanding of the area improved. In the 1990s, geologists found that most of the ores and mineralization spots occurred in a series of rocks consisting of carbonate minerals known as the ore-bearing dolomite of the Luoxue Formation of the Kunyang Group. However, the petrogenesis of this dolomite and the metallogenesis of those ores are still unknown. In the early 1990s, most geologists thought that the rocks were carbonate sedimentary rocks because their rock-forming minerals were carbonates [1], and in the late 1990s, some thought that they were hydrothermal sedimentary rocks [2], but they lack isotopic and geochemical evidence.

This work studied the ore-bearing dolomite. In order to avoid the petrogenesis argument, the rocks are named orebearing dolomite rocks by rock classification on the basis of mineral content. In 1997, a carbonatitic volcanic genesis was suggested for the Wuding ore-bearing dolomite in the Yinmin and Luoxue formations of the Kunyang Group on the western side of the Proterozoic Wuding–Lufeng basin in the middle Kunyang rift [3–6]. The Wuding–Lufeng basin is rich in iron and copper ore deposits, for instance, there are the Yinachang and Etouchang copper-bearing iron ore deposits, and the Guangtian, Daqing and Zhongchun copper ore deposits. Therefore, it is an important part of the mineralization zone. If the carbonatitic volcanic rocks can be confirmed, it will be of great scientific significance in understanding the metallogenesis [6].

Recently, new lines of evidence have also been found in ore-bearing dolomites in the Yinachang mine [7] and Shaojiapo mine of the Wuding basin. The present paper will further present the carbonatitic magma extrusive evidence by providing HFSEs and Sm-Nd and Rb-Sr isotope data of the whole rocks and stable isotope data of rock-forming and accessory minerals as well as some new petrographical evidence.

## 2. Geological setting

The Kunyang rift is located on the western margin of the Yangtze platform in the southern Kangding axis. The Wuding–Lufeng basin lies on its west side in the middle of the rift and was formed during the continent rifting, and assumes the shape of an ellipse (Fig. 1(a) and (b)) [1,8].

The fundamental structure of Wuding–Lufeng basin is a series of ring fractures partly covered with Sinian–Cenozoic strata identified from the TM image (Fig. 1(b) and (c)). Therefore, the distribution of the Mesoproterozoic strata is controlled by this fracture system: the older (the Yinmin and Luoxue formations) are distributed around the margin of the basin while the newer (the Luzhijiang Formation) is at the center (Fig. 1(b)).

The igneous activity in the basin is also controlled by the ring fracture system, and forming three volcanoes concentration rings, which are called the outer ring, the middle ring and the inner ring from the margin to center of the basin. The age of the volcanic rocks increases gradually from the inner ring outwards. The occurrence of the volcanic rocks changes from pyroclastic rocks with a few lavas and sub-volcanic rocks of alkaline series in the outer ring to sub-volcanic rocks of tholeiite basaltic series (lacking extrusive rocks) in the inner ring. The volcanic rocks identified from outer ring include nephelinite, basanite, alkaline basalts, basalt, porphyrite, trachy-basaltic porphyrite, high-potassium rhyolite and trachy-andesite, and most of them had been chloritized and cericitized. Ones found in middle ring include alkaline basaltic porphyrite, albitite and alkaline lamprophyre. Ones from inner ring are basaltic porphyrite and picrite–basaltic porphyrite. The orebearing dolomite rocks are closely associated with alkaline silicate rocks of the outer and middle rings, which consist of nephelinite, basanite, alkaline basalts, albitite, etc.

## 3. Petrological characteristics

Most of the dolomite rocks known as ore-bearing dolomites are found at Pingdichang, Guangtianchang, Daqing, Hetaoqing, Yinachang, Zhoumadi and Shaojiapo, along the outer and middle rings in the western part of the basin. They occur in the upper part of the Yinmin Formation and the lower part of the Luoxue Formation, and are also controlled by faults of the ring fracture system. They can be differentiated into two occurrences. The first one is bedding terranes in outer ring, coexisting with pyroclastic rocks and a few lava of nephelinitic, basanitic and alkaline basaltic, as well as high-potasium rhyolitic to trachy-andesitic. The second one is veinlets and breccia dikes in middle ring, coexisting with massive alkaline basaltic and basanitic porphyrite, and alkaline lamprophyre dikes.

The dolomite rocks of the first occurrence have the petrographical characteristics of lava flow (such as the flown line and plane, vesicular, ropy and encrusting structures) and pyroclastic rocks of extrusive facies. Some appear as epiclastites, which are of transitional facies between the extrusive and sedimentary facies and are graded gradually upward into submarine hydrothermal carbonate rocks (such as siliceous stripe dolomite and pseudostromatolitic dolomite). Those volcanic-sedimentary rocks mainly occur in the top part of the Yinmin Formation and the lower part of the Luoxue Formation formed in early depression of the basin and covered by the overlying Luoxue–Etouchang and Luzhijiang formations.

The dolomites are light yellow, pale red, milky white, brown and grayish in color, with anhedral fine-grained textures, and showing banded, streaky and flown structures. The most common mineral assemblage of the ore-bearing dolomite rocks is ankerite and dolomite plus biotite, phlogopite, albite-oligoclase, hornblende, arfvedsonite (e.g. in Guantian and Hetaoqing), microcline and accessory apatite, rutile, zircon, magnetite, pyrite, perovskite and parisite (rare). Samples from the first occurrence have round vesicular and feldspar phenocrysts; those from both the first and the second occurrences (especially the margin of the dolomite vents) contain acicular apatite. Most major rock-

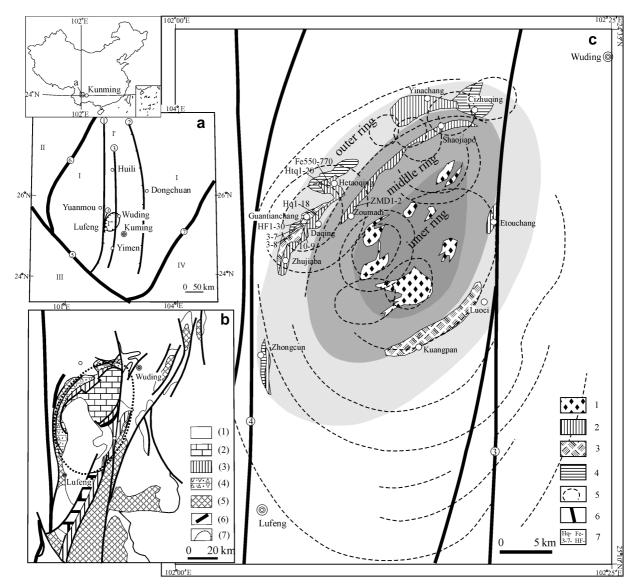


Fig. 1. Structural setting of Proterozoic Wuding–Lufeng basin and its carbonatite volcanic rocks. (a) I, west margin of Yangtze platform; I', Kunyang rift; I'', Wuding–Lufeng basin; II, Songpan-Ganzi Indo-sinian fold bundle; III, Three rivers fold bundle; IV, Southern China fold bundle; ①, Yuanmou-Luzhijiang fault; ②, Xiaojiang fault; ③, Tandan-Yimen fault; ④, Degulao fault; ⑤, Jinshajiang-Honghe fault; ⑥, Longmenshan fault; ⑦, Zhaotong-Luliang-Shizong-Mine fault. (b) 1, Paleozoic-Cenozoic cover; 2, Luzhijiang formation; 3, Luoxue-Etouchang formation; 4, Yinmin formation; 5, Meidang formation; 6, large scale faults; 7, Wuding-Lufeng ellipse basin. (c) 1, tholeiite basalt subvolcanic breccia; legend of 2 to 4, show volcanic and pyroclastic sedimentary rocks; 2, alkaline-volcanic with ore-bearing dolomite rocks; 3, trachyte-andesite volcanic; 4, rhyolite; 5, ring structures deciphered from remote sensing; 6, fracture; 7, position of the samples.

forming minerals such as dolomite can find melt inclusion and high temperature fluid inclusion frequently [9].

The average bulk composition of the ore-bearing dolomite rocks is as follows: SiO<sub>2</sub> 5.01%, TiO<sub>2</sub> 2.00%, Al<sub>2</sub>O<sub>3</sub> 3.14%, Fe<sub>2</sub>O<sub>3</sub> 2.45%, FeO 8.34%, MnO 1.55%, MgO 12.30%, CaO 29.31%, Na<sub>2</sub>O 0.35%, K<sub>2</sub>O 0.44%, P<sub>2</sub>O<sub>5</sub> 1.03%, and CO<sub>2</sub> 35.55%. LREE/HREE = 10–19.  $\Sigma$ REE varies in a wide range from 27.03 (µg/g) to 141.10 (µg/g). This content is similar to that (20–200 µg/g) of the carbonatites in an ultramafic complex in Kola Peninsula, northwestern Russia [10] and the carbonatitic complexes of Michanshan in Sichuan, China [11].

In summary, the ore-bearing dolomites, in view of their mineral assemblage and petrographical and petrochemical characteristics, cannot be sedimentary or hydrothermal dolomites. Some features, such as acicular apatite, vesicular, flow structures and melt-high temperature fluid inclusion, are commonly seen in magma rapidly cooling igneous rocks. Minerals such as arfvedsonite, perovskite and parisite are indicators of carbonatites.

# 4. Analysis methods

The paper discusses the carbonatitic magma evidences of the ore-bearing dolomites using isotopic data and the data from high-field-strength elements (HFSE) of Zr, Hf, Nb and Ta of the rocks. Samples for those purposes are collected from the mines of Yinachang, Hetaoqing, Guantian and Daqing. They were selected from both the ores and their wall rocks or the ore-bearing dolomites.

The ICPMS analysis of the HFSEs and isotopic analysis of O, C, S and Sr, Nd were carried out on the Finningan MAT element system, GIMS/EA system (Delta S/ EA1108), Finingan MAT 252 and Finingan MAT 262 with five Faraday cups separately.

The samples for the ICPMS analysis were prepared by the following steps. (1) Take 40 mg of sample in a pot, and dissolve it by adding the liquid of 1 ml HF with 0.3 ml HNO<sub>3</sub> (1:1). And then dry the sample at 150 °C. (2) Dissolve the sample again by adding the liquid of 1 ml HF with 0.3 ml (1:1) HNO<sub>3</sub> in 3 days in a tight obturation tin at 200 °C, then open the tin, and dry the sample again. (3) Dissolve the sample again in 12 h into the liquid of 2 ml HNO<sub>3</sub> (1:1) in the tight obturation tin at 150 °C, open the tin and dry the solution. (4) Dissolve the sample in 2–3 h into the liquid of 2 ml HNO<sub>3</sub> (1:1), and then, after making sure that the sample is fully dissolved, add 1 ml of 500 ppb standard solution into it and dilute the sample using 50 ml of 1% HNO<sub>3</sub>. After all the steps, the sample is ready for the ICPMS measurement.

The data of oxygen and carbon isotopes were obtained from separated carbonate minerals of the ore-bearing dolomite rocks.  $CO_2$  was distilled from a mixture of 15 mg of sample and 100% HPO<sub>3</sub> under a vacuum condition and at pressure 1/10 Pa and constant at the temperature of 25 °C.

The normalizing factors used to correct the isotopic fractionation of Sr and Nd are  ${}^{86}\text{Sr}/{}^{88}\text{Sr} = 0.1194$  and  ${}^{146}\text{Nd}/{}^{144}\text{Nd} = 0.7219$ , respectively. The procedure of sample preparation for the measurement is as follows. (1) Weigh 50 mg of the sample with 50 mg of  ${}^{87}\text{Rb}-{}^{84}\text{Sr}$  and 100 mg of  ${}^{150}\text{Nd}-{}^{149}\text{Sm}$  spike solutions into a cup. (2) Dissolve the sample completely in hot concentrated HF and HClO<sub>4</sub> solutions at atmospheric pressure. (3) Dry the sample and dissolve it with 6 N HCl. (4) Dry the sample and dissolve it with 2.5 HCl. And then transfer the sample into a centrifugal tube, collect the solution and discard the precipitate after turning on the centrifugal tube for 6 min.

For the chemical separation of Rb–Sr and Sm–Nd the following steps are followed: move the clear solution from the centrifugal tube to the Dowex  $AG50W \times 12$  (mesh) cation exchange column, elute the column with dilute HCl, collect the solution when Rb, Sr and REEs are released from the column one after another. After the above steps, pour the REE solution into the P507 cation exchange column and collect the Sm–Nd solution during eluting the column with dilute HCl. By this way, Rb–Sr and Sm–Nd are separated from the sample.

# 5. Zr/Hf and Nb/Ta ratios

The average abundance and ratios of zirconium and hafnium, and niobium and tantalum from the ore-bearing dolomite rocks, mantle-source silicate rocks and sedimentary rocks are listed in Table 1. And Fig. 2 is a Zr/HfNb/Ta diagram of the ore-bearing dolomites, nephelitires, basanitic and picritic basaltic porphyrites and sedimentary dolomites of different origins.

The trace elements Zr–Hf and Nb–Ta are similar in terms of ionic radius and valence state, and usually cannot be detached from each other during the magma evolution process [12,13]. Single-source magmas can evolve into different products by crystal fractionation, but no matter how the abundances of those elements change, their ratios will remain basically the same if there is no addition of other source materials. If the ratios are changed, it is most likely that other source materials have been mixed in or metasomatism has happened. Therefore, the ratios of those twin elements should be indicative of the source region [14].

The data in Table 1 and the datum spot distribution feature in Fig. 2 from different rocks show that the ore-bearing dolomite rocks and their co-existing mantle-derived rocks are overlapping in the same region. This phenomenon reveals that the sources of two kinds of the rocks are similar to each other, but different from those of the adjacent sedimentary dolomite and hydrothermal metasomatic rocks. Data spots of both dolomite rocks and mantlederived rocks do not concentrate in the mantle area in Fig. 2, but disperse in a wide region around the mantle area, suggesting that the material source must be from a metasomatic mantle.

#### 6. Carbon, oxygen and sulfur isotopes

Dolomite (over 70% in content) is the rock-forming mineral of ore-bearing dolomite rocks in the Wuding–Lufeng basin, while magnetite, chalcopyrite and pyrite (their total contents ranging from 5% to 15%) are the important accessory minerals. The carbon, oxygen and sulfur isotope characteristics of these minerals are very important indicators for the petrogenesis of ore-bearing dolomite rocks.

#### 6.1. Carbon and oxygen isotopes in dolomite

Fig. 3 shows the typical isotope data of rocks of different origins: all carbonatites of the world [15,16]:  $\delta^{18}O_{\text{SMOW}}\% = +6 \text{ to } +25, \ \delta^{13}C_{\text{PDB}}\% = -8 \text{ to } +1; \text{ typical}$ carbonatites of the intrusive world [17]:  $\delta^{18}O_{SMOW} \ll +10, \ \delta^{13}C_{PDB} \ll = -8.0 \text{ to } -2.0; \text{ adjacent}$ metamorphose sedimentary dolomite [1]:  $\delta^{18}O_{SMOW}$ % = +19.08 to +23.99,  $\delta^{13}C_{PDB}$ % = +1.80 to +2.30.

The isotope data of the dolomite of the groundmass (Fig. 3, 2) of the ore-bearing dolomite rocks are distributed in high value field ( $\delta^{18}O_{SMOW}\% = +14.91$  to +18.75,  $\delta^{13}C_{PDB}\% = -1.99$  to +0.94); but those of dolomite crystal fragments (Fig. 3, 1) with color and size distinctly differing from the groundmass cluster have low values ( $\delta^{13}C_{PDB}\% = -3.01$  to -1.20,  $\delta^{18}O_{SMOW}\% = +5.99$  to +10.15).

Thus, it is easy to distinguish the ore-bearing dolomite rocks in the Wuding–Lufeng basin from the sedimentary Y.B. Zhang et al. | Progress in Natural Science 18 (2008) 965-974

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Table	1
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No.	Name of rocks (number of sample)	Source	Zr	Hf	Nb	Та	Zr/Hf	Nb/Ta
1	Ore-bearing dolomite rocks (7)	Hetaoqing iron mining	103	3.19	8.00	0.66	32.27	12.07
2	Nephelitire (2)	Coexisting mantle silicate	97	3.1	8.5	0.5	31.29	17.00
3	Picritic basalt porphyrite	-	42	1.5	7.5	0.6	28.00	12.50
4	Basanitic porphyrite (32)		301	7.9	31.3	2.2	37.94	14.41
5	Chondrite	Thompson (1982)	6.84	0.2	0.35	0.02	34.20	17.50
6	Primary mantle	McDonough (1985)	11.1	0.306	0.75	0.043	36.27	17.44
7	P-MORB	Wood (1979)	11.3	0.26	0.72	0.062	43.46	11.61
8	Continental crust	Bnhorpadob (1962)	200	3	24	2.1	66.67	11.43
9	Adjacent sedimentary dolomite (6)	Hetaoqing iron mining	7	0.08	1.50	0.35	87.50	4.35

Average abundance and ratios of Zr and Hf, Nb and Ta from ore-bearing dolomite rocks, mantle source silicate rocks and sedimentary rocks (µg/g)

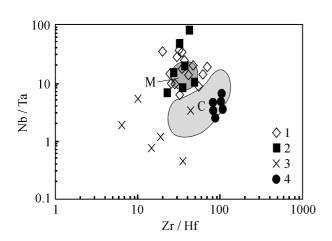


Fig. 2. Zr/Hf-Nb/Ta diagram of carbonatite, basite and sedimentary dolomite. 1, Mantle source silicate rocks; 2, ore-bearing dolomite rocks; 3, hydrothermal rocks; 4, sedimentary carbonate; M, mantle defined by 35 published data; C, crust defined by 250 published data.

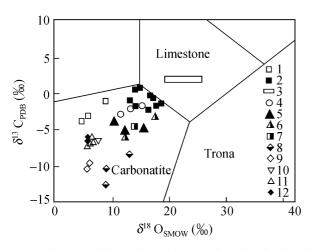


Fig. 3. Correlation graph for carbon and oxygen isotopics of carbonatite. 1, Dolomite crystal fragments; 2, dolomite in the groundmass of orebearing dolomite rocks; 3, adjacent sedimentary dolomite; 4, Bayan Obo ore-bearing carbonatite; 5, Bayan Obao carbonatite dykes; 6–12, carbonatite from Bell et al. [16].

dolomite, and also from the typical intrusive carbonatite, but they are still within the range of all the carbonatites of the world. Apparently, <sup>18</sup>O and <sup>13</sup>C are enriched mainly in the dolomite of bedded terranes, brieacia pipes and dikes, but not in dolomite crystal fragments. Dolomite crystal fragments should be considered as phenocrysts crystallized in magma chamber in the early stage; therefore, they have preserved more information of the original source of ore-bearing dolomite rocks, and their carbon and oxygen isotope data can be used to indicate the source of the rocks. However, the dolomite in the groundmass of the rocks was crystallized in the late stage; its carbon and oxygen isotopic system would be contaminated by country rocks or be fractionated, and thus it is rich in <sup>18</sup>O and <sup>13</sup>C.

## 6.2. Oxygen isotope of magnetite

There is plenty of magnetite in the ore-bearing dolomite rocks in the Wuding–Lufeng basin, which is abundant enough to form ore bodies in some areas. Most of magnetite occurs in its host rocks as mineral inclusions in dolomite, or as pyroclasts-like dolomite crystal fragments. Even in an ore body, magnetite intergrows with dolomite as idiomorphic granular crystals. Therefore, this magnetite, like the dolomite, was crystallized from the same material rather than a secondary mineral formed in the late mineralization period. The oxygen isotope data of this magnetite can be used to indicate the material source of the dolomite rocks.

The oxygen isotopic data listed in Table 2 show that the  $\delta^{18}$ O (SMOW)‰ values vary in the range from +3.47 to +5.99, within the oxygen isotopic data (+2.40 to +6.9) [18] of the magnetite from Bayan Obo carbonatite magnetite deposit [19,20]. In addition, the magnetite crystals in the ore-bearing dolomite rocks frequently develop a corroded texture and occasionally contain melt inclusions. Therefore, the magnetite in the ore-bearing dolomite rocks was crystallized from magma, and the magnetite-bearing dolomite rocks were also solidified from the mantle source magma.

# 6.3. Sulfur isotope of sulfides

Chalcopyrite and pyrite are also abundant in the orebearing dolomite rocks of the basin. They are important mineral members of the rocks and usually concentrated to form sole copper ore deposits or intergrown with magne-

Table 2
Oxygen isotope value of magnetite mineral and ore from ore-bearing dolomite rocks

Location	Sample	Rocks/ Ores	Minerals	$\delta^{18}O(SMOW)\%$	
Hetaoqing iron mine, ore body I	Fe550	Fine granular chalcopyrite	Magnetite <sup>a</sup>	+4.05	
	551	massive magnetite ore	-	+4.87	
	552	Fine granular chalcopyrite		+5.41	
	553	Density dessemination magnetite ore		+5.99	
	554			+4.02	
	555	Fine granular banded magnetite ore		+5.54	
	556			+3.47	
Guangtianchang mine, line 0	HF1	Biotite dolomite rocks	Magnetite <sup>a</sup>	+3.45	
	HF4		U	+4.50	
Guangtianchang mine, line 8	HF13	Biotite trachy-andesite	Magnetite <sup>b</sup>	+5.30	
	HF21			+4.70	
Hetaoqing iron mine Ore body II	Htq9	Biotite dolomite rocks	Magnetite <sup>b</sup>	+4.55	
1 0 9	Htq12		C	+5.31	
Hetaoging iron mine Ore body I	Htq15			+4.76	
10	Htq19			+3.91	
	Htq5			+4.90	

<sup>a</sup> Data from Sun [1].

<sup>b</sup> Analyzed by the research center for the mineral sources and exploration.

tite to form magnetite-chalcopyrite ore deposits. They occur in ore-bearing dolomite rocks in the following forms: (1) Granular idiomorphic crystals in poikilitic growth with dolomite in veined, tubular and bedded rocks. They are usually concentrated in bedded rocks and form fine granular bandings, striations and irregular vesicles paralleling the flow structured of the host rock. (2) Pyrite and chalcopyrite crystal fragments (with deuterogenic chalcocite), coexisting with dolomite in epiclastic rocks, are usually concentrated at the bottom of graded beddings or in troughs of scour and ripple marks. (3) Sulfide crystal inclusions in dolomite or sulfide micro-crystals in melt inclusions or fluid inclusions in dolomite.

The mineral assemblage of those sulfides with the abovementioned growth features is shown in Table 3. The common assemblage is magnetite + pyrite + cobaltite + (arfvedsonite) + plogopite + (tschermakite) + rutitle + apatite, which indicates that the sulfides were crystallized in the primary stage of the ore-bearing dolomite rocks. Sulfide fragments coexisting with pyroclastics also grew as primary minerals in the dolomite rocks. Therefore, the sulfide aggregates in our dolomite rocks should be primary minerals. Their sulfur isotope gives information on the material source.

Some deuterogenic sulfides also exist in those dolomite rocks with the assemblage pyrite + quartz + malachite + azurite + chalcocite (Table 3). They appear in crannies in the rocks as veins or intergrown with other deuterogenic minerals filling in quartz, calcite and dolomite veins. This kind of sulfides resulted from late-stage hydrothermal fluids, and their sulfur isotopes do not indicate the source of the ore-bearing dolomite.

The  $\delta^{34}$ S values of the primary sulfides from the dolomite rocks in the Wuding–Lufeng basin are listed in Table 3. Those of all other dolomite rocks are in the range of -5.09 to  $+5.78\%_0$ , averaging  $+1.50\%_0$ .

It is shown that the  $\delta^{34}$ S values of primary sulfides fall into a narrow range, which are similar to those of the ultramafic rocks ( $\delta^{34}$ S‰ = -1 to +5) [21] and mafic rocks ( $\delta^{34}$ S‰ = -2.5 to +10.5), with the median close to that of meteorite. They are not only distinctly different from those of chalcopyrite in the adjacent sedimentary dolomite ( $\delta^{34}$ S‰ = -3.2 to +17.9, median = +5.52), but also different from those of sedimentary rocks ( $\delta^{34}$ S‰ = -64 to +100), evaporites ( $\delta^{34}$ S‰ = +10 to +20) and metamorphic rocks ( $\delta^{34}$ S‰ = -20 to +20) of the world.

# 7. Samarium and neodymium isotopes

Table 4 shows the Sm and Nd isotope data of 5 samples from the bedded ore-bearing dolomite rocks and 5 samples from the trachy-basaltic porphyrite of a radial dike swarm in the outer ring.

The whole-rock Sm–Nd isochron ages calculated from the ore-bearing dolomite rocks and basaltic porphyrite in Table 4 are as  $1685 \pm 250$  Myr and  $1645 \pm 133$  Myr, respectively. On the basis of Ludwing's process (2.90 edition), the values of  $I_{\rm Nd}$ ,  $\varepsilon_{\rm Nd}(t)$  and  $T_{\rm DM}$  (model age of the depleted mantle) are obtained and also listed in Table 4. For the ore-bearing dolomite rocks,  $I_{\rm Nd} = 0.507078-$ 0.509280,  $\varepsilon_{\rm Nd}(t) = 0.19-2.27$ ,  $T_{\rm DM} = 2.68-3.66$  (Ga); for the basaltic porphyrite,  $I_{\rm Nd} = 0.509996-0.510383$ ,  $\varepsilon_{\rm Nd}(t) = 3.18-3.72$ ,  $T_{\rm DM} = 1.89-2.16$  (Ga).

## 8. Rubidium and strontium isotopes

The Rb–Sr isotope data of the ore-bearing dolomite rocks are given in Table 5. Altogether 10 samples were used

 Table 3

 Sulphur isotopic values of sulfides in ore-bearing dolomite rocks and sedimentary dolomite

Sample	Location	Ores/host rocks	Minerals	Association minerals	$\delta^{34}$ S‰	Central value
Hfdq-1	Daqing mine ore body 1	Pyroclastic rocks	Chalcopyrite	Pyrite	+3.01	
Daing16	Daqing mine Stope I <sup>a</sup>	Blocky dolomite rocks	Chalcopyrite	Cobaltite	+1.36	
19-1	Daqing mine Stope I <sup>a</sup>	Blocky dolomite rocks	Chalcopyrite	Magnetite	-2.63	
19-2	Daqing mine Stope I <sup>a</sup>	Blocky dolomite rocks	Chalcopyrite	Rutile	-2.93	
20	Daqing mine Stope II <sup>a</sup>	Pyroclastic rocks	Chalcopyrite	plogopite	-2.85	
24	Daqing mine Stope III <sup>a</sup>	Pyroclastic rocks	Chalcopyrite	Apatite	-1.28	
Guang 1	Guantianchang mine	Banded rock	Pyrite, Chalcopyrite	Magnetite, Cobaltite	+5.78	
HFgtc	Guantianchang mine	Vesicular rock	Pyrite, Chalcopyrite	Arfvedsonite	+3.71	
Zou 1	Zoumadi mine	Dolomite dyke	Pyrite, Chalcopyrite	Plogopite	-5.09	
Fe750	Hetaoqing mine ore body I	Disseminated bornite	Chalcopyrite	Magnetite	+3.30	1.50
751	Hetaoqing mine ore body I	and chalcopyrite ores	Chalcopyrite	Magnetite	+5.70	
752	Hetaoqing mine ore body I	Speckle bornite and	Chalcopyrite	Pyrite	+4.70	
753	Hetaoqing mine ore body I	chalcopyrite ores	Chalcopyrite	Cobaltite	+0.10	
754	Hetaoqing mine ore body I	Bornite and chalcopyrite	Chalcopyrite	Plogopite	+3.87	
755	Hetaoqing mine ore body I	Disseminated alcopyrite	Chalcopyrite	Tschermakite	-3.50	
856	Hetaoqing mine ore body I	and bornite ore	Chalcopyrite	Rutile	+4.20	
757	Hetaoqing mine ore body I		Chalcopyrite	Apatite	+2.60	
K10	Pingdichang vents	Dolomite dyke	Chalcopyrite	Cobaltite	+3.72	
K9	Pingdichang braccia pipe	Volcanic neck breccia	Chalcopyrite	Pyrite, Magnetite	+3.36	
Hetao-6	Hetaoqing mine ore body I	Vein chalcopyrite ores	Chalcopyrite	Pyrite, Quartz	+10.50	
Above mine		Sedimentary dolomite <sup>a</sup>	Pyrite, Chalcopyrite	Dolomite, Quartz Malachite, Azurite Chalcocite	-3.2 ~ +17.9	+5.52

<sup>a</sup> Data from Sun [1].

in the analysis, among which 8 were collected from bedded rocks in a continuous section in the outer ring, and the other two from a dolomite dike (ZMD-1, 2) in the middle ring.

The whole-rock isochron age of the 8 samples (Hq3– Hq18) of the bedded ore-bearing dolomite rocks is  $892 \pm 12.9$  Myr, and  $I_{\rm Sr} = 0.71963 \pm 0.00037$ . This age is corresponding to the low-grade metamorphic event in the Jinningian movement [22,23]. The average model age calculated from the average data of the 8 samples is 1.782 Ga, and the average  $I_{\rm Sr}$  (1.782 Ga) is 0.702014, and the corresponding  $\varepsilon_{\rm Sr}$  (t = 1782 Ma) is -0.14.

The other two samples (ZMD-1, 2) were picked up from a dolomite dike consisting of dolomite and feldspar. Sample ZMD-1 of the dike is feldspar (including albite and potash feldspar) and ZMD-2 is dolomite. Therefore, the isochron of samples ZMD-1 and ZMD-2 should be considered as an internal isochron; its isochron age is 1048 Myr, and  $I_{\rm Sr} = 0.699143$ . This age agrees with the whole-rocks Rb–Sr isochron age (1024 Myr) of adjacent albite analyzed by others [4].

In addition, the model ages of these samples calculated on the basis of Ludwing's process (2.90 edition) are also listed in Table 5.

The Rb–Sr isotopic system was easily reformed by later thermal events. The Jinningian movement occurred in central Yunnan at the end of the Mesoproterozoic (861 Myr) [22], in which possibly induced a regional thermal event of low-temperature metamorphism. All of the above model ages are close to or older than that of the Jinningian movement, therefore, their isotopic systems would be affected by the Jinningian movement if alteration was too intensive, and the corresponding initial value of  $I_{\rm Sr}$  could not be used to indicate the material source.

The isochron age (892 Myr) of samples Hq3–18 is much younger than their model ages and also much younger than their Sm–Nd isochron ages, but close to the age of the Jinningian movement. This indicates that their Rb–Sr isochron age was the result of the metamorphic thermal event during the movement. Their initial value of  $I_{\rm Sr}$  should not be used as an indicator of the material source.

However, the average model age (1.782 Ga) calculated from the average data of all the 8 samples of the bedded dolomite rocks is completely close to the Sm–Nd isochron age (1865 Myr) of these samples. This fact suggests that no foreign material had been mixed in their Rb–Sr system during metamorphism of whole bedding dolomite rocks. Therefore, the initial <sup>87</sup>Sr/<sup>86</sup>Sr data calculated from the average data by using the rock-forming age (or model age) should be close to the character of primary magma [23]. The average  $I_{Sr}$  (0.7021) indicates that the bedded ore-bearing dolomite rocks in the outer ring are also from the mantle.

The isochron age (1048 Myr) of samples ZMD-1 and ZMD-2 is close to their model ages (1036–959 Myr), and higher than the age of the Jinningian movement (861 Myr). This means that the effect from the thermal metamorphic event was trivial. In this case, this age should be

Table 4
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Sm-Nd isotopic val	lue of ore-bearing	dolomite rocks an	d the basic ring	dyke group <sup>a</sup>

Rocks	Sample	Analysis results		Calculation results		
		143Nd/144Nd	147Sm/144Nd	INd	εNd(t)	TDM(Ga)
Carbonatite lavas and quenching smashing lavas	Hq13	$0.511836 \pm 06$	0.15629	0.509116	2.07	2.79
	Hq3	$0.511706 \pm 08$	0.14757	0.507911	0.19	3.66
	Hq5	$0.511900\pm15$	0.16178	0.508272	1.14	3.44
	Hq10	$0.511972 \pm 13$	0.16928	0.507078	0.24	3.27
	Hq18	$0.511495\pm10$	0.12538	0.509280	2.27	2.68
Trachy-basaltic	3-7-1	$0.511659\pm05$	0.10501	0.510327	3.64	1.93
	3-7-2	$0.512047\pm05$	0.13925	0.510194	3.46	2.02
Porphyrite	3-8-9	$0.512151 \pm 06$	0.15121	0.509996	3.18	2.16
	10-9-1	$0.512067\pm06$	0.14452	0.510035	3.24	2.12
	10-9-3	$0.511958\pm08$	0.12681	0.510383	3.72	1.89

Sample 3-8-9 was analyzed by Research Center for Mineral Resources Exploration Institute.

<sup>a</sup> Analyzed by the Mantle-Crust Opening Laboratory of China University of Geosciences.

approximate to the age of the rocks, and the corresponding initial value of  $I_{\rm Sr}$  indicates the age of the magma source.

The low initial value of 0.699143 obtained from the internal isochron of samples ZMD-1 and ZMD-2 shows a little higher than the <sup>87</sup>Sr/<sup>86</sup>Sr value of BABI (0.698990) and JUSI (0.698976). This proves that the dikes of ore-bearing dolomite rocks in the middle ring are not from the crust. However, this data seem to be too low compared to the value (0.702807) (calculated by using the data of <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70391, <sup>87</sup>Rb/<sup>86</sup>Sr = 0.0736) of the mantle at 1048 Myr. This case would be caused by hydrothermal metasomatism in late stage of magma evolution.

# 9. Discussion

Viewed from their unusual mineral assemblage and petrochemical and petrographical characteristics, the orebearing dolomite rocks in the Wuding–Lufeng basin could not occur in sedimentary or hydrothermal dolomites. The ratios of Zr/Hf and Nb/Ta show that the ore-bearing dolomite rocks are different from hydrothermal metasomatic rocks and sedimentary dolomites. Although the values of

to $+0.94\%$ ) of dolomite in the ore-bearing dolomite rocks
vary in wide ranges, they are still within the range of all
carbonatites of the world, and completely differ from those
of adjacent sedimentary dolomites ( $\delta^{18}O_{SMOW}$ % = +19.08
to +23.99, $\delta^{13}C_{PDB}$ % = +1.8 to +2.3). The $\delta^{34}S$ % values
of chalcopyrite from sedimentary dolomite vary between
-3.2 and $+17.9$ , but those of primary sulfides from carbon-
atite fall into a narrow range of $-5.09$ to $+5.95$ , corre-
sponding to those of ultramafic and mafic (i.e. basaltic)
rocks. All these prove that the major rock-forming materi-
als of the ore-bearing dolomite rocks are neither from sed-
imentary rocks nor from hydrothermal metasomatized
crustal rocks.
Melt inclusions and high temperature fluid inclusions

 $\delta^{18}O_{SMOW}$  (+14.91% to +18.48%) and  $\delta^{13}C_{PDB}$  (-1.99%)

Melt inclusions and high temperature fluid inclusions included in major rock-forming mineral dolomite means it is igneous minerals. Although the  $\delta^{18}$ O and  $\delta^{13}$ C values of dolomite of the whole rock vary in a wide range, those of dolomite porphyroclasts ( $\delta^{13}C_{PDB}\%_{c} = -3.01$  to -1.20,  $\delta^{18}O_{SMOW}\%_{c} = +5.99$  to +10.15) are in the range of typical carbonatites of the world. The  $\delta^{18}O_{SMOW}\%_{c}$  values of magnetite from ore-bearing dolomite rocks (+3.47 to +5.99)

Table 5	
Rb–Sr isotopic value of ore-bearing dolomite rocks <sup>a</sup>	

Rocks	Sample	Analysis results			Calculation results		
		$Rb(10^{-5})$	$Sr(10^{-5})$	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr	Tm(Ga)	
Dolomite dyke	ZMD-1	128.58	48.524	7.5544	$0.812381\pm19$	10.36	
	ZMD-2	96.156	106.09	2.4075	$0.735231\pm40$	09.59	
Bedform dolomite rocks	Hq6	61.149	78.693	2.2037	$0.756863 \pm 15$	17.67	
	Hq7	37.784	116.30	0.9191	$0.731491 \pm 18$	23.09	
	Hq8	36.613	99.991	1.0360	$0.737868\pm32$	24.95	
	Hq10	38.665	64.061	1.7102	$0.748176 \pm 32$	19.20	
	Hq3	144.854	109.757	3.4829	$0.764668 \pm 16$	12.71	
	Hq5	133.472	142.649	2.6497	$0.751457\pm23$	13.16	
	Hq13	169.262	2970.770	0.1610	$0.720518 \pm 31$	?	
	Hq18	130.532	1517.444	0.2431	$0.722995\pm15$	?	
Average of Bedform Dol. rock	ks	94.041	637.458	1.5507	0.741755	1.782	

<sup>a</sup> Analyzed by the mantle-crust opening laboratory of China University of Geosciences.

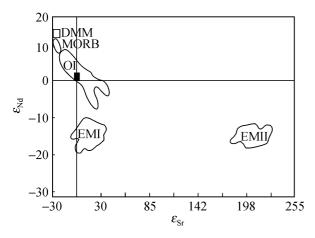


Fig. 4.  $\varepsilon_{Nd}$ – $\varepsilon_{Sr}$  graph of ore-bearing dolomite rocks in Wuding–Lufeng basin. Simplified from Qiu [11]. DMM, depleted mantle; MORB, mid oceanic ridge basalt; OI, oceanic island basalt; EMI, EM, type enrichment mantle; EMII, EM, type enrichment mantle; black pane shows the variation range of ore-bearing dolomite rocks.

correspond to those of the mantle ( $\delta^{18}O_{SMOW}$ % < 5.7). The median  $\delta^{34}S$ % of primary sulfides (+1.50) is close to that of meteorite. All these data indicate that the major rock-forming mineral (dolomite) and major accessory minerals of the ore-bearing dolomite rocks are igneous minerals.

Because the major rock-forming minerals and major accessory minerals are igneous, the rocks formed of those minerals should be igneous rocks. The igneous rock that consists of carbonate minerals (> 50%) is carbonatite [24]. On the other hand, although arfvedsonite, perovskite and parisite are rare in the rocks, they are indicators of carbonatite. The bulk composition is characterized by high TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and  $\Sigma$ REE, similar to carbonatites of the same type. Therefore, the ore-bearing dolomite rocks belong to carbonatite.

The sources for most carbonatites of the world are commonly known as the mantle [25-27], enriched mantle [28], metasomatized mantle [29] or crustal contamination [30]. In the Zr/Hf–Nb/Ta diagram, the ore-bearing dolomite rocks and coexisting mantle-source silicate rocks overlap each other. The value  $\varepsilon_{Nd}$  (t = 1865 Myr) = +0.19 to +2.27 of ore-bearing dolomite rocks is a little lower than that (+3.18 to +3.72) of basaltic porphyrite. The initial value of <sup>87</sup>Sr/<sup>86</sup>Sr of ore-bearing dolomite rocks in the middle ring and outer ring is as low as 0.699143-0.70214. These  $\varepsilon_{Nd}$  and  $\varepsilon_{Sr}$  values of the bedded rocks in outer ring show in the position of the ore-bearing dolomite in the  $\varepsilon_{Nd}$ - $\varepsilon_{Sr}$ graph (Fig. 4), and suggest that the source of ore-bearing dolomite rocks is also the mantle (like a mantle plume of oceanic island basalt). However, the wide dispersing region around mantle in Fig. 2 and low value of  $\varepsilon_{Nd}$  (+0.19 to +2.27) and wide variation of  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  (0.699143 to 0.70214) show that the mantle should not be normal, but metasomatic. The evidence of the mantle source strongly ensures that the ore-bearing dolomite rocks are metasomatic mantle derived carbonatites.

Meanwhile, the acicular apatite is usually crystallized in rapidly cooling facies. Those apatite crystals are commonly found in bedded ore-bearing dolomite rocks and on the margin of a dolomite vent. This suggests that the ore-bearing dolomite rocks were formed in rapidly cooling magma, and the dolomite vent has a quenching margin. Therefore, the presence of acicular apatite, melt inclusion and high temperature fluid inclusion implies that the ore-bearing dolomite rocks were formed in a condition of magma extrusion.

In addition, the bedded ore-bearing dolomite rocks in the Wuding–Lufeng basin have extrusive petrographical characteristics, such as vesicular, linear and planar flow, and ropy structures and phenocryst texture, and closely coexist with alkaline pyroclastic rocks. These features further ensure that the rocks are from carbonatitic magma extrusion. Therefore, the ore-bearing dolomite rocks belong to carbonatitic volcanic rocks.

# 10. Conclusion

The ore-bearing dolomite rocks from the outer and middle volcanic rings in the Wuding-Lufeng basin are derived neither from sedimentary dolomites nor from crustal (metasomatized) rocks, but from the same mantle source as the coexisting basalts and porphyrites. The dominating dolomite in the ore-bearing dolomite rocks as well as most of the accessory minerals are not only igneous minerals but also crystallized from rapidly cooling mantle magma. The rocks show the characteristics of carbonatitic volcanic petrography and metasomatic mantle petrochemistry, and are closely associated with mantle-derived alkaline volcanic rocks. Therefore, the ore-bearing dolomite rocks were forming in metasomatic mantle derived carbonatitic magma extrusion. This conclusion implies that most iron and copper ore deposits hosting in the dolomite rocks should be of the carbonatite type.

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