

Carbon–oxygen isotopic covariations of calcite from Langdu skarn copper deposit, China: implications for sulfide precipitation

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Abstract The Langdu skarn copper deposit in the Zhongdian area, Yunnan Province, China, has an average Cu grade of 6.49 %. The deposit is related to a porphyry intrusion (~216 Ma), which was emplaced in the Upper Triassic sedimentary rocks of the Tumugou and Qugasi Formations. At the Langdu skarn copper deposit, carbon and oxygen isotope ratios of fresh limestones ($\delta^{18}\text{O} = 3.0\text{--}5.6\text{ ‰}$ relative to V-SMOW; $\delta^{13}\text{C} = 24.5\text{--}25.7\text{ ‰}$ relative to PDB) and partly altered limestones ($\delta^{18}\text{O} = 27\text{--}7.2$ to -1.9 ‰ ; $\delta^{13}\text{C} = 11.8\text{--}15.2\text{ ‰}$) indicated that the deposit was a typical marine carbonate source. Oxygen and carbon isotope values for calcites formed at different hydrothermal stages are -9.1 to 0.2 and $10.1\text{--}16.3\text{ ‰}$, respectively. Moreover, the carbon–oxygen isotopic composition of an ore-forming fluid ($\delta^{18}\text{O} = 5.0\text{--}9.5\text{ ‰}$, $\delta^{13}\text{C} = -7.3$ to -5.3 ‰) suggested the presence of magmatic water, which most likely came from the differentiation or melting of a homologous magma chamber. The deposition of Calcite I may arise from metasomatism in an open system with a progressively decreasing temperature. Later, the minerals chalcopyrite, pyrrhotite, quartz and Calcite II were precipitated due to immiscibility. Water–rock interaction could potentially be responsible for Calcite III precipitation in the post-ore stage.

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1 Introduction

For decades, stable isotopes have been successfully used in geochemical studies as powerful petrogenetic tracers and paleothermometers. Quantitative stable isotope models and their applications have become the mainstay of international stable isotope geochemistry. Using these models, researchers worldwide have elucidated the formation mechanisms of numerous deposits (e.g., Zheng 1990; Zheng and Hoefs 1993; Peng and Hu 2001; Choi et al. 2003; Zhou et al. 2013a, b, c). Carbon and oxygen isotopic covariation in carbonates associated with hydrothermal mineralization can supply useful mineralization information, such as temperature and isotopic composition of hydrothermal fluid, and the nature of dissolved carbon species (e.g., Rye and Williams 1981; Matsuhisa et al. 1985; Zheng 1990). In this paper, we present the first analysis of the isotopic compositions of carbon and oxygen in limestone, marble, silicate-bearing limestone, and calcite formed at different stages in the Langdu skarn copper deposit, Yunnan Province, China. Using the theoretical models of Zheng (1990) and Zheng and Hoefs (1993) with homogenized temperature data derived from fluid inclusions, this study investigates the nature and evolution of the hydrothermal fluid and the mechanism of calcite, sulfide, and quartz precipitation.

2 Geology of the Langdu skarn copper deposit

The Langdu skarn copper deposit is located about 50 km northeast of Xianggelila City, Yunnan Province, China.

The deposit was discovered in 1964 by Team No. 1 of the Regional Geological Survey, Bureau of Geology and Mineral Resources, Yunnan Province, China. Recently (particularly during 2006 and 2007), Yunnan Huaxi Mining Co., Ltd. has discovered several copper-rich ore bodies in the contact zone of porphyry bodies and marbleized limestone to the north and west of the original Langdu skarn deposit, containing 104,030 tons of copper reserves and over 50,000 tons of copper metal resources. With ongoing exploration, more copper metal resources may be discovered in the Langdu skarn copper deposit area.

The outcropped strata in the Langdu deposit mainly include the Upper Triassic Qugasi and Tumugou Formations. The valley, a small part of the deposit area, is covered with Quaternary alluvial sediments with a thickness varying from 0 to 30 m. The Tumugou Formation is mainly in the southwestern corner of the district, which consists of slate, sericitic slate, meta-sandstone and limestone with a thickness of 1433 m. The Qugasi Formation is mainly exposed in the deposit area. The Qugasi Formation forms the core part of the Langdu anticline and consists of layered limestone, sericitic slate, fine meta-sandstone, with a total thickness varying from 487 to 2,683 m. Under the influence of the porphyry intrusions, the clastic rock was hornfelsed to felsic hornfels and brecciated hornfels, and the limestone was metasomatized to skarn and marbleized in the contact zone.

The major structure of the deposit area includes the NW-trending Langdu anticline and some NW-trending and NE-trending faults. The NW-trending fractures are mainly inter-layer fractures along the striking of the Langdu anticline. A part of the NE-trending Bidu fault cuts through the core part of the Langdu anticline. The copper mineralization mainly occurs in the conjunction between the NW and NE trending faults, in the southwest limb of the Langdu anticline.

The known copper ore bodies occur mainly in the contact zone between the porphyry bodies and limestone of the Upper Triassic Qugasi Formation. Using Ar–Ar dating of biotite which had been separated from the intrusive rock, Zeng et al. (2004) obtained the age of 216.93 Ma. The only ore body that occurs within the monzonite porphyry is orebody III₃. Currently, 6 ore blocks and 21 ore bodies have been identified in the deposits (Fig. 1). Ore blocks I, III, and IV, which collectively contain 13 ore bodies, are under mining operation.

The Langdu deposit is characterized by multistage skarn formation and complex mineralization which result in a diversity of minerals. Dominant Ca–Fe anhydrous silicate minerals (andradite and hedenbergite) were formed during the prograde skarn stage (Ia). Electron microprobe analyses show that the composition of andradite varies from Ad₅₇ to Ad₉₄, while that of pyroxene is Hd_{78–92}Di_{3–11}Jo_{5–11}.

Hydrous silicate minerals, including actinolite and grunerite, form during the retrograde stage (I), with later a deposition of minor Cu–Fe sulfide, quartz, and calcite. Chalcopyrite and pyrrhotite dominate the main ore-forming stage (II). These minerals occur as veins, veinlets or patches in the coarse veins of quartz or calcite, which contain an average copper grade of 6.49 wt% (exceeding 10 wt% in some localities). During the later ore-forming stage, chalcopyrite occurs as veins or veinlets that fill the fissures of marble, or as patches in Fe–dolomite coarse veins. Post-ore hydrothermal minerals (III) are prominent and occur with calcite, quartz, and chlorite.

3 Sampling and analytical methods

Based on its petrochemical characteristics, limestone is divided into two distinct groups: fresh limestone and silicate-bearing limestone. The fresh limestone is light gray and fine-grained, whereas silicate-bearing limestone is brown and coarse-grained and characterized by its high SiO₂ content and low CaO content. For analysis, 21 grains of calcites were collected from the Langdu deposit. These calcites were classified into Calcite I, Calcite II, and Calcite III, according to their geological characteristics and mineral assemblages. Calcite I is usually white, and fills the fractures of altered pyroxene or garnet in patches or veins (Fig. 2a, b). Calcite II is generally milky and associated with quartz, pyrrhotite, and chalcopyrite (Fig. 2c). Calcite III occurs as coarse veins (Fig. 2d). Carbonate samples were crushed and reacted with phosphoric acid at 25 °C, and the carbon and oxygen isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively) in the liberated CO₂ gas were measured using a mass spectrometer with a precision of $\pm 0.2\text{ ‰}$ (Finnigan MAT252) at the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences.

4 Results and discussion

4.1 Results

The fresh limestones were more enriched in carbon and oxygen isotopic compositions (Table 1; $\delta^{13}\text{C} = 3.0\text{–}5.6\text{ ‰}$, $\delta^{18}\text{O} = 24.5\text{–}25.7\text{ ‰}$) in comparison to the marbles ($\delta^{13}\text{C} = 2.0\text{–}2.8\text{ ‰}$, $\delta^{18}\text{O} = 24.9\text{–}25.4\text{ ‰}$). Similarly, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the marbles were higher than those of silicate-bearing carbonate rocks ($\delta^{13}\text{C} = -7.2\text{ to }-1.9\text{ ‰}$, $\delta^{18}\text{O} = 11.8\text{–}15.2\text{ ‰}$). This decreasing trend of carbon and oxygen isotope ratios from limestones to silicate-bearing limestones indicates that the fresh limestones were modified due to repeatedly interacting with a hydrothermal fluid with a lower carbon and oxygen

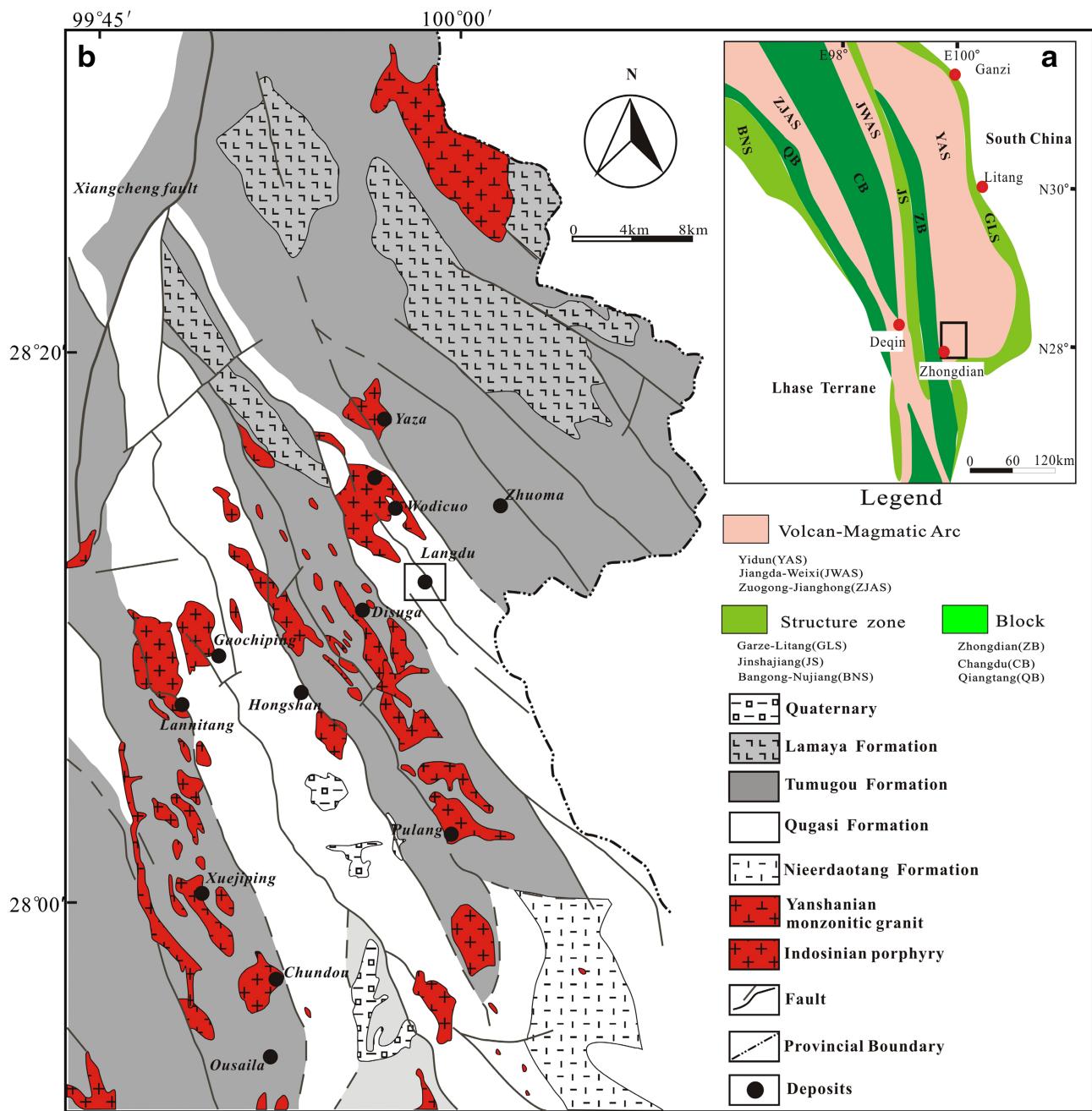


Fig. 1 a Simplified geological map of the tectonic framework of the Sanjiang Tethys. b Simplified geological map of the Langdu deposit, adapted from the detailed geological report of the Langdu skarn deposit

isotope ratio. Different carbon and oxygen isotope ratios in marbles and silicate-bearing limestones are attributed to different water/rock ratios. As shown in Fig. 3, the carbon and oxygen isotope values of fresh limestones are generally consistent with those of marine carbonates. Theoretical models indicate that marbles form at temperatures below 100 °C and have water/rock ratios less than 0.5 (Fig. 4). This suggests that limestone recrystallized at low temperatures and its heat energy was most likely derived from nearby magmatic fluid/rocks.

The carbon isotope values of the calcites (Calcite I and Calcite II) in the ore-forming stage were similar to those of calcites in porphyry copper deposits of the Zhongdian region, ranging from -9.1 to -7.6 ‰ (Table 1). These carbon isotopic compositions show that the carbon in the hydrothermal fluid may originate from deep regions of the earth (i.e., from the mantle or lower crust) or from the mixture of carbonate and organic matter. However, its narrow range of $\delta^{13}\text{C}$ values excludes the possibility of an organic origin. The oxygen isotopic compositions of the

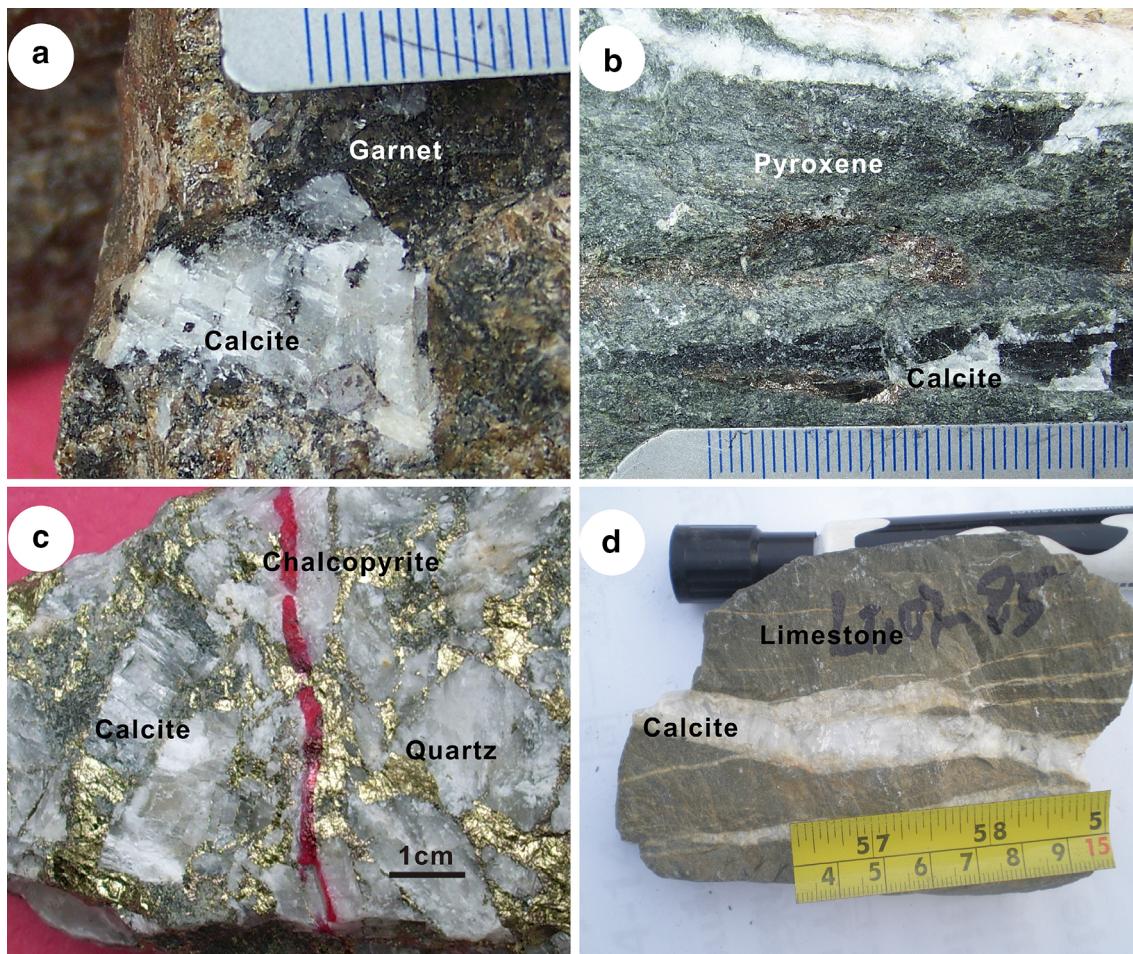


Fig. 2 Specimen photos: **a** cavity in the garnet filled by patch calcite; **b** calcite veins/veinlets occurring in pyroxene fractures; **c** coarse veins of calcite, quartz, and sulfide; **d** coarse veins of barren-sulfide calcite

ore-forming stage range from 10.1 to 12.6 ‰. Carbon and oxygen isotopic compositions of syn-ore and post-ore calcites (III) are significantly different from each other. In fact, the carbon and oxygen isotopic compositions of post-ore calcites (III) are similar to those of marine carbonates.

From the plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ (Fig. 3), we observe that most of the samples originated from the igneous or surrounding fields. The isotopic composition progressively increased from the syn-ore stage (I and II) to the post-ore stage (III). According to theoretical models of water/rock interactions, calcites that form in the syn-ore stage at temperatures ranging from 300 to 400 °C (Fig. 4) are consistent with the principal microthermometric results of fluid inclusions in sulfide-bearing quartz. The water/rock ratios are greater than 20 (Fig. 4), indicating that the isotopic compositions of these samples were largely affected by that of the hydrothermal fluid. The formation temperatures of the post-ore calcites vary from 200 to 300 °C, and the water/rock ratios range from 2 to 10 (Fig. 4). These results suggest that both limestone and hydrothermal fluid contribute to the isotopic composition of Calcite III.

4.2 Origin of the hydrothermal fluid

The isotopic composition of the hydrothermal fluid, assuming that it existed in isotopic equilibrium with the hydrothermal minerals, can be calculated from the isotopic composition of the minerals, the fractionation equation at a given temperature, and the mineral precipitation temperature. The oxygen isotope fractionation equation between calcite and water occurs from 200 to 700 °C (O’Neil et al. 1969), whereas the carbon isotope fractionation equation between CO₂ and calcite occurs from 0 to 700 °C (Bottinga 1969). We assume that there is no fractionation between CO₂ and H₂CO₃ in the calculation.

The isotopic compositions were calculated from measured isotope values. The precipitation temperatures of Calcites I and II taken from fluid inclusions (which reflect the principal temperatures of fluid inclusions measured from quartz coexisting with calcite) range from 300 to 400 °C. While calculating the relevant isotopic value of the hydrothermal fluid, the formation temperature of Calcite III

Table 1 Oxygen and carbon isotope data and calculated compositions of equilibrium waters

Sample No	Mineral	Measure (‰)		Calculated $\delta^{18}\text{O}$ (SMOW) (‰) water composition at T (°C)			Calculated $\delta^{13}\text{C}$ (PDB) (‰) water composition at T (°C)		
		$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)	400 °C	300 °C	200 °C	400 °C	300 °C	200 °C
LD1001	Limestone	3.0	24.7						
LD1002		4.5	25.2						
LD1003		5.2	25.6						
LD1004		5.6	25.7						
LD1005		3.0	24.5						
LD1006		3.0	24.5						
LD078502	Silicate-bearing limestone	-1.9	15.2						
LD071802		-7.2	11.8						
LD0707	Marble	2.4	25.1						
LD0705		2.8	25.4						
LD0701		2.0	24.9						
LD0704		2.1	24.9						
LD0706	I calcite	-7.8	10.1	7.4	5.0		-5.5	-6.0	
LD0819		-8.3	10.2	7.5	5.2		-6.0	-6.5	
LD0815		-8.4	12.6	9.5	7.2		-6.1	-6.7	
LD0901	II calcite	-9.1	11.4	8.7	6.3		-6.8	-7.3	
LD0902		-8.4	11.4	8.7	6.4		-6.1	-6.6	
LD0903		-8.7	11.6	8.8	6.5		-6.4	-6.9	
LD0904		-7.7	11.5	8.8	6.4		-5.4	-6.0	
LD0905		-7.8	11.5	8.8	6.4		-5.5	-6.0	
LD0906		-8.7	11.3	8.6	6.3		-6.4	-6.9	
LD0907		-7.6	11.5	8.8	6.5		-5.3	-5.9	
LD0908		-8.0	11.5	8.8	6.5		-5.7	-6.2	
LD0754	III calcite	-6.2	12.2			3.2			-5.9
LD0749		-6.3	12.0			3.0			-6.0
LD0791		-6.1	13.0			3.9			-5.8
LD0790		-6.3	12.5			3.5			-5.9
LD0780		-1.8	13.2			4.2			-1.5
LD0788		0.2	16.3			7.2			0.6
LD0785		-1.1	15.2			6.2			-0.7
LD0718		-2.1	12.5			3.4			-1.7
LD0787		-5.6	12.5			3.4			-5.3
LD078802		-0.2	14.3			5.2			0.1

is assumed as 200 °C. Based on the aforementioned parameters, the stable isotopic compositions of Stage I, Stage II, and Stage III hydrothermal fluids that equilibrated with Calcite I, Calcite II, and Calcite III are $\delta^{18}\text{O} = 5.0\text{--}9.5\text{ ‰}$, $\delta^{13}\text{C} = -6.7\text{ to }-5.5\text{ ‰}$; $\delta^{18}\text{O} = 6.3\text{--}8.8\text{ ‰}$, $\delta^{13}\text{C} = -7.3\text{ to }-5.3\text{ ‰}$; and $\delta^{18}\text{O} = 3.0\text{--}7.2\text{ ‰}$, $\delta^{13}\text{C} = -6.0\text{ to }0.6\text{ ‰}$, respectively.

Three types of fluids of different origins magmatic water, meteoric water, and seawater contributed to the formation of the hydrothermal minerals. Each fluid has a distinctive stable

isotopic composition. The calculated stable isotopic compositions of ore-forming fluids in equilibrium with syn-ore calcite are consistent with the composition of magmatic water. High temperatures (300–400 °C) and high salinity (10–20 equiv. wt% NaCl) also typify fluid inclusions. This suggests that the ore-forming fluid was magmatic water supplied from the Langdu intrusives or the igneous chamber. This means that the post-ore fluid is in fact more complicated than previously suspected and that the input of seawater cannot be excluded.

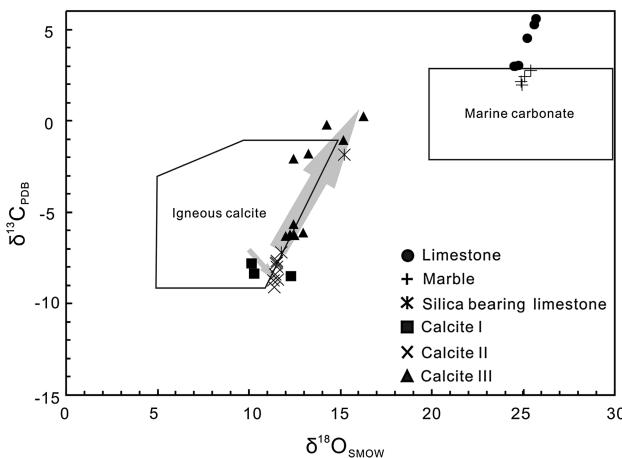


Fig. 3 Carbon and oxygen isotopic compositions of the Langdu deposit. Carbon and oxygen isotope data of igneous calcite and marine carbonates are from Ray et al. (2000) and Zheng (2001), respectively

4.3 Fluid evolution, calcite and sulfide precipitation

The observed positive correlation between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of all calcites shown in Fig. 3 can be explained by two processes: the mixing of two fluids with different isotopic compositions or the calcite precipitation, which is due to a temperature effect in the open system coupled with either CO_2 outgassing or fluid/rock interactions.

If fluid mixing were responsible for calcite precipitation, then two different fluids with distinct isotopic compositions and temperatures would have been observed. However, the $\delta^{13}\text{C}$ values of the calcites (particularly those of Calcites I and II) do not support this mechanism. Although we found no evidence of CO_2 -bearing fluid inclusions, there is a possibility that the outgassing of CO_2 led to calcite precipitation. This mechanism is possible because CO_2 concentration in hydrothermal fluid is below 1.0 mol and therefore, the observed three-phase inclusions should not exist (Zheng 1990). Since the carbon isotopic fractionation factor between calcite and CO_2 is negative (temperature $>200\text{ }^\circ\text{C}$), CO_2 outgassing will inevitably deplete the quantity of carbon isotope in later-deposited calcites. On account of the high water/rock ratios of Calcite I and Calcite II, the observed isotopic signature of the various calcites cannot be reasonably explained by water/rock interactions.

The above analysis suggests that calcite precipitation in the Langdu deposit occurred in three stages under different precipitation formation mechanisms. Calcite I, which spatially coexists with skarn minerals, is depleted in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Theoretical models indicate that Calcite I was formed at high water/rock ratios (>50 ; see Fig. 4), which may represent the primitive isotopic composition of the

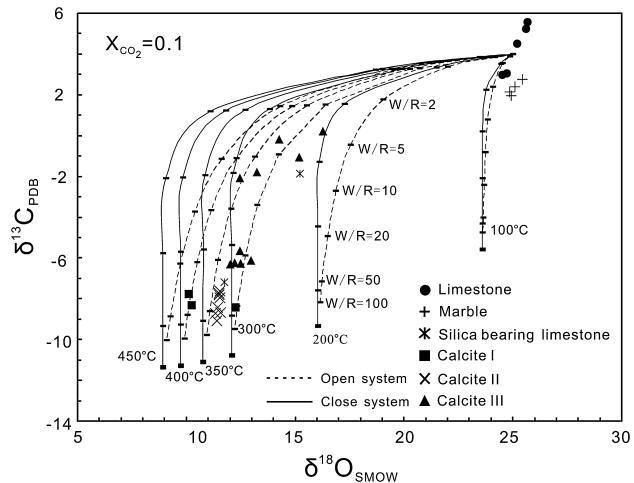


Fig. 4 Covariation of carbon vs oxygen isotopic compositions during water/rock interactions involving limestone with $\delta^{13}\text{C} = +4\text{ }^\circ\text{C}$ (PDB) and $\delta^{18}\text{O} = +26\text{ }^\circ\text{C}$ (V-SMOW), and a fluid with $\delta^{13}\text{C} = -9\text{ }^\circ\text{C}$ (PDB) and $\delta^{18}\text{O} = +7\text{ }^\circ\text{C}$ (V-SMOW). The dissolved carbon mainly exists as CO_2 at temperatures ranging from 100 to $450\text{ }^\circ\text{C}$. The solid and dashed curves denote the closed and open systems, respectively

magmatic fluid. For metasomatism, one must assume decreasing temperature (contact metasomatic processes related to hydrothermal fluid and cool sedimentary rocks), which can cause Calcite I precipitation in an open system. The slightly lower $\delta^{13}\text{C}$ values of Calcite II relative to Calcite I within the disseminated material or veinlets imply an identical isotope signature of carbon and oxygen in the fluid reservoir. The observed $\delta^{13}\text{C}$ values can be readily explained by CO_2 outgassing, as the boiling phenomenon has been identified in the coexisting quartz-hosted fluid inclusion. Since the oxygen in hydrothermal fluids generally exists as H_2O , CO_2 outgassing and calcite precipitation will affect the carbon isotope composition insignificantly. Theoretical models show that Calcite III was formed at lower temperatures and water/rock ratios than Calcites I and II were (Fig. 4). In the case of Calcite III, where the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were more enriched relative to Calcite I and Calcite II, water/rock interaction accompanied by a progressive decrease in temperature may have occurred at different water/rock ratios.

During phase separation, most of the volatile compounds (CO_2 , SO_2 , HCl) partitioned into the vapor phase, and the high-saline residual liquid may have retained most of the metal elements, including Cu, Zn, Pb, and Fe. Consequently, the fluid became supersaturated with metal ions Ca^{2+} and Si^{4+} . The subsequent decrease of pressure and temperature and increase of pH of the fluid resulted in the precipitation of a large amount of ore materials, which formed coarse calcite-quartz-sulfide veins.

5 Conclusion

The deposit was devoid of CO₂-bearing fluid inclusions, and the modeled precipitation temperatures of various calcites in this study are consistent with microthermometry measurements of various fluid inclusions. Thus, the theoretically calculated CO₂ fraction of 0.1 mol percent is reasonable and the results obtained are credible.

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References

- Bottinga Y (1969) Calculated fractionation factors for carbon and hydrogen isotopic exchange in the system, calcite-carbon dioxide-graphite-methane-hydrogen-water-vapor [J]. *Geochim Cosmochim Acta* 33:9–64
- Choi SG, Kim ST, Lee JG (2003) Stable isotope systematics of Ulsan Fe-W skarn deposit, Korea [J]. *J Geochem Explor* 78–79:601–606
- Matsuhsia Y, Morishita Y, Sato T (1985) Oxygen and carbon isotope variations in gold-bearing hydrothermal veins in the Kushikino mining area, southern Kynshu, Japan [J]. *Econ Geol* 80:283–293
- O’Neil JR, Clayton RN, Mayeda TK (1969) Oxygen isotope fractionation in divalent metal carbonates [J]. *J Chem Phys* 51:5547–5558
- Peng J, Hu R (2001) Carbon and oxygen isotope systematics in Xikuangshan giant antimony deposit, central Hunan [J]. *Geol Rev* 47:34–41 (in Chinese with English abstract)
- Ray JS, Ramesha R, Pandea K, Trivedi JR, Shukla PN, Patel PP (2000) Isotope and rare earth element chemistry of carbonatite ± alkaline complexes of Deccan volcanic province: implications to magmatic and alteration processes [J]. *J Asian Earth Sci* 18:177–194
- Rye DM, Williams N (1981) Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: III. The stable isotope geochemistry of the H.Y.C. Ridge, and Cooley deposits [J]. *Econ Geol* 76:1–26
- Zeng P, Wang H, Mo X, Yu X, Li W, Li T, Li H, Yang C (2004) Tectonic setting and prospects of porphyry copper deposits in Zhongdian island arc belt [J]. *Acta Geosci Sin* 25:535–540 (in Chinese with English abstract)
- Zheng YF (1990) Carbon-oxygen isotopic covariation in hydrothermal calcite during degassing of CO₂: a quantitative evaluation and application to the Kushikino gold mining area in Japan. *Miner* [J]. *Miner Depos* 25:246–250
- Zheng YF (2001) Theoretical modeling of stable isotope systems and its applications to geochemistry of hydrothermal ore deposits [J]. *Miner Depos* 20:56–71 (in Chinese with English abstract)
- Zheng YF, Hoefs J (1993) Carbon and oxygen isotopic covariations in hydrothermal calcites: theoretical modeling on mixing processes and application to Pb-Zn deposits in the Harz Mountains, Germany [J]. *Miner Depos* 28:79–89
- Zhou JX, Huang ZL, Zhou MF, Li XB, Jin ZG (2013a) Constraints of C-O-S-Pb isotope compositions and Rb-Sr isotopic age on the origin of the Tianqiao carbonate-hosted Pb-Zn deposit, SW China [J]. *Ore Geol Rev* 53:77–92
- Zhou JX, Huang ZL, Yan ZF (2013b) The origin of the Maozu carbonate-hosted Pb-Zn deposit, southwest China: constrained by C-O-S-Pb isotopic compositions and Sm-Nd isotopic age [J]. *J Asian Earth Sci* 73:39–47
- Zhou JX, Gao JG, Chen D, Liu XK (2013c) Ore genesis of the Tianbaoshan carbonate-hosted Pb-Zn deposit, Southwest China: geologic and isotopic (C-H-O-S-Pb) evidence [J]. *Int Geol Rev* 55:1300–1310