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# Oxygen-Isotope-Based Modeling of the Hydrothermal Fluid Processes of the Taochong Skarn Iron Deposit, Anhui Province, China

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Abstract: The Taochong iron deposit is one of the important skarn deposits in the Middle–Lower Yangtze River metallogenic belt, Eastern China. There are two types of ores in the deposit: skarnand quartz-calcite-type ores. The skarn-type ore, which is composed of hematite (Hm-1), garnet, pyroxene, actinolite, chlorite, quartz (Q-1), and calcite (Cal-1), is crosscut locally by a quartz-calcitetype ore vein. The quartz-calcite-type ore consists mainly of hematite (Hm-2), magnetite, quartz (Q-2 and 3), and calcite (Cal-2). The  $\delta^{18}O_{water}$  value (~2.67‰) of the fluids in equilibrium with Hm-1 is similar to the values of the mixtures of magmatic and meteoric fluids. However, the  $\delta^{18}$ O values of the fluids in equilibrium with Hm-2 are in the range of 7.64–8.54‰, similar to those of magmatic fluids. The  $\delta^{18}$ O values decrease systematically from the fluids in equilibrium with Hm-2 (7.64‰ to 8.54%) to the fluids in equilibrium with magnetite, Q-3, and Cal-2 (-0.12% to 4.17%) and the fluids in equilibrium with Cal-3 (-2.17% to 0.36%). These features of oxygen isotopes indicate that two episodes of hydrothermal activity took place in the Taochong deposit, and both episodes began with a magmatic origin and then progressively evolved by mixing with meteoric water. The results of quantitative simulations suggest that the deposition of the skarn-type ores was most likely caused by the mixing of magmatic and meteoric fluids, whilst the deposition of the quartz-calcite-type ores was most likely caused by the boiling of magmatic fluids and the mixtures of magmatic brine and meteoric water.

Keywords: iron-rich skarn deposit; oxygen isotope; quantitative simulation; Middle–Lower Yangtze Valley

# 1. Introduction

Fluid processes are critical for understanding the transport and concentration of metals in hydrothermal systems. Experimental studies and chemical modelling [1–3] have demonstrated that most base and precious metals (e.g., Cu, Fe, Au, Pb, and Zn) are transported mainly in the form of chloride and bisulfide complexes in natural hydrothermal fluids. The metal precipitation that follows the breakdown of chloride or bisulfide complexes during fluid transport is probably induced by changes in pH and  $fO_2$ , as well as decreases in temperature and ligand (chloride and bisulfide) ion activity [1,3-6]. The following mechanisms that can cause changes in these physico-chemical parameters have been proposed: cooling, wall-rock alteration, boiling, mixing, or a combination of some of the above [4,7–11]. Among these, boiling and the mixing of magmatic and meteoric waters are considered to be the two most effective ways to form high-grade ores in skarn deposits (e.g., the Chengchao high-grade skarn iron deposit [8], the Huanggang skarn iron-tin deposit [12], and the Xishimen high-grade skarn iron deposit [13] in China, and the Big Gossan Cu-Au skarn deposit in Irian Jaya [14]). Interestingly, the evidence from geologic and textural observations, fluid inclusions, and stable isotopes indicates that both fluid boiling and mixing of magmatic brine with meteoric water occurred during



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the main mineralization stage in many high-grade deposits, especially in many large- to super-large-scale skarn deposits [8,13–16]. Experimental and simulation studies also suggest that the boiling of mixtures of magmatic brine and meteoric water is a very effective mechanism for metal participation [17]. However, the relative importance of boiling and mixing, and the contribution of meteoric water to the skarn system depositing metals, remains poorly understood.

The Middle–Lower Yangtze River metallogenic belt (MLYRB) is one of the most important world-class economic mineral districts in China [18] and contains more than 200 polymetallic Cu–Fe–Au, Mo, Zn, Pb, and Ag deposits (Figure 1A) [19–21]. Most of these deposits are of skarn, porphyry, or strata-bound type [20–23]. The Taochong deposit is one of the important skarn iron deposits in the MLYRB. The deposit has defined reserves of about 28.84 Mt of Fe at a grade of 35.9–58.6%, with 68.7% of the total reserves at a grade higher than 50% Fe [24]. The skarn and orebodies mainly developed in the detachment faults between the Middle Carboniferous and Lower Permian limestones [24-26]. The skarn consists mainly of garnet and pyroxene with minor actinolite and chlorite [7]. The  $\delta^{18}O_{\text{water}}$  values (-2.2‰ to 7.29‰ [7]) and  $\delta D$  values (-40‰ to -94‰ [7]) of hydrothermal fluids from the Taochong deposit show a mixing trend between magmatic water and meteoric water [7], indicating that the ore-forming fluid is a mixture of the two water types. The coexisting solid-bearing inclusions (32-36 wt.% NaCl equiv.) and vapor-rich inclusions (0.4-0.9 wt.% NaCl equiv.) within quartz in equilibrium with hematite in the Taochong deposit share similar homogenization temperatures [7,26], suggesting that fluid boiling took place during the main mineralization stage. Therefore, the Taochong skarn iron deposit is an ideal natural laboratory in which to evaluate fluid mixing and boiling scenarios and their relative importance for the formation of iron-rich ores.

As is well known, stable isotopes of fluids are important for monitoring the sources and evolution of ore-forming fluids [1,2], and oxygen stable isotope modeling places important constraints on the key factors and processes responsible for the transport and deposition of metals in hydrothermal systems [27–29]. Thus, in this paper, we report the results of an oxygen stable isotope study of the Taochong deposit, and then we quantitatively model the importance of fluid boiling and mixing in the evolution of the hydrothermal system at Taochong.

## 2. Geological Setting

The MLYRB is located on the northern margin of the Yangtze Craton of Eastern China, along the southeastern margins of the North China Craton and Qingling–Dabieshan orogenic belt (Figure 1A). This belt is composed of several deposit districts from west to east: Edong, Jiurui, Anqing-Guichi, Luzong, Tongling, Fanchang, Ningwu, and Ningzhen. The Taochong deposit is located in the northern part of the Fanchang district, at the middle segment of the MLYRB (Figure 1A). The regional strata in the Fanchang district are dominated by Paleozoic to Mesozoic sedimentary and volcanic rocks (Figure 1B). The strata were folded and faulted during the Indosinian and early Yanshan Orogeny [24] and intruded by late Mesozoic magmatic rocks. Magmatic rocks are mainly exposed in the northern, eastern, and central parts of the area. The main magmatic rocks are granodiorite and granite. Skarn alteration is widely developed in the contact zone between granite and Triassic limestone, and local hematite mineralization occurs in skarns.

The sedimentary rocks that crop out in the Taochong deposit are from Silurian to Triassic in age and consist mainly of carbonates, shales, and sandstones. Both skarn and iron mineralization are hosted within the Middle–Upper Carboniferous Huanglong and Chuanshan formations and the Lower Permian Qixia formation (Figure 2A,B). The Huanglong and Chuanshan formations are 45–100 m thick and are characterized by dolomitic limestone and limestone. The Qixia formation is ~220 m thick and consists of thick-bedded and stylolitic limestones, carbonaceous shale, and sandy shale. No igneous rocks other than lamprophyre and syenite dikes have been found in the Taochong deposit [7]. How-



ever, geophysical data indicate that igneous rocks are concealed below the Taochong orebody [30].

**Figure 1.** (**A**) Simplified structural map showing the locations of the Middle–Lower Yangtze River metallogenic belt (MLYRB) and Fanchang district (modified from [21,31]). (**B**) Geological map of the Fanchang district (modified from [32]).

Both the skarns and the iron orebodies of the Taochong iron deposit are remarkable for their tabular shapes, which were defined by interlayer-glide faulting between the Middle Carboniferous and Lower Permian limestones. The ore deposit strikes N75–80°E and is inclined 60–90° to the south from the surface down to 50 m, and is then inclined 20–30° to the north at depths between +50 and –200 m (Figure 2B). Drilling has demonstrated that the deposit extends a distance of 1150 m horizontally and 750 m vertically. The thicknesses of the orebodies vary from 2 to 110 m. The skarn consists mainly of garnet and pyroxene, with lesser amounts of actinolite and chlorite. The mineral composition of the ores is dominated by specular hematite, magnetite, calcite, and quartz. Except for carbonation and silicification, little other alteration has been found beyond the skarn within the marble that surrounds the Taochong deposit [24]. This may suggest that the circulation of fluids was restricted to the zone of the major fault, because beyond the major fault zone the rocks are less fractured.



**Figure 2.** (**A**) Geological map of the Taochong iron deposit (modified from [33]). (**B**) Cross section of the Taochong iron deposit showing the shape of orebodies and their relationship to host rocks (modified from [34]).

#### 3. Mineralization Styles and Paragenetic Sequence

We studied a suite of ore samples from the Taochong deposit that cover the principal mineralization stages of the hydrothermal system. The samples were investigated by microscopy and electron probe analysis. On the basis of the results of these studies, a subset of samples was selected for oxygen isotope analysis. In the following paragraphs, we provide a general description of the mineral composition, textures, and structures of the ores, and establish a detailed paragenesis in the Taochong deposit, which formed the basis of a texturally constrained oxygen isotope investigation.

In the Taochong deposit, there are two mineralization styles: skarn-type ores and quartz–calcite-type ores [35]. The skarn-type ores only account for a small amount of the reserve of the Taochong deposit. The ores normally occur with a metasomatic relict texture and disseminated structure (Figure 3A,B). The dominant minerals in the skarn-type ores are garnet, pyroxene, hematite (Hm-1), chlorite, actinolite, quartz, and calcite (Figure 3A–E). Most hematites (Hm-1) occur as anhedral–subhedral crystals and are associated with actinolite, chlorite, quartz (Q-1), and calcite (Cal-1), which replaced the garnet and pyroxene (Figure 3B,C). Locally, the skarn-type ores (containing Hm-1) are crosscut by the quartz–calcite-type ore vein (containing Hm-2) (Figure 3F). The quartz–calcite-type ores are more

common and are widely distributed in the deposit. They normally show massive and vein-type structures (Figure 3F) and a euhedral platy texture (Figure 3E). The ore minerals include hematite (Hm-2) and magnetite. The gangue minerals only include quartz and calcite. Hematite (Hm-2) was the first mineral to be precipitated in the quartz-calcite-type ores, and it normally occurs as bladed crystals (Figure 3E). The replacement of hematite (Hm-2) by magnetite is common throughout the deposit, where the hematite crystals are rimmed by magnetite (Figure 3D). Some large and locally euhedral quartz crystals (Q-2) (Figure 3G) are associated with the hematite (Hm-2). Most of the quartz (Q-3), which is typically fine-grained (Figure 3G), is associated with magnetite. Some of the calcite (Cal-2) is intergrown with magnetite and quartz (Q-3) (Figure 3F), indicating that the precipitation of calcite coincided with or was slightly later than the precipitation of magnetite and quartz (Q-3) [7]. The late-stage calcite (Cal-3) occurs as fillings in fractures crosscutting the skarn and the orebody, locally producing a dense stockwork (Figure 3H); this indicates that ore-forming fluid activities are weakening and ending. Based on the mineralogical assemblages, crosscutting, and replacement relationship mentioned above, mineralization in the Taochong deposit can be divided into three stages: the skarn stage (garnet + pyroxene), oxide stage (further divided into early (Hm1 + Q-1 + Cal-1  $\pm$  actinolite  $\pm$  chlorite), middle (Hm2 + Q-2  $\pm$  chlorite), and late (magnetite + Q-3 + Cal-2) stages), and carbonate stage (Cal-3). The paragenetic sequence of the minerals in the Taochong deposit is illustrated in Figure 3I.



**Figure 3.** Photographs of representative samples from the Taochong iron deposit. **(A)** Skarn-type ore with metasomatic relict texture and disseminated structure. **(B)** Garnet (Grt) replaced by hematite (Hm-1), quartz (Q-1), and calcite (Cal-1) (plane polarized light). **(C)** Pyroxene (Px) replaced by chlorite (Chl), quartz (Q-1), calcite (Cal-1), and hematite (Hm-1) (crossed polars). **(D)** The quartz–calcite-type ore occurs as a vein and cuts the skarn-type ore. **(E)** Elongate euhedral crystals of hematite (Hm-2) intergrown with quartz (Q-2) (reflected light). **(F)** Replacement of hematite by magnetite (Mag) along the rims (reflected light). **(G)** Fine-grained quartz (Q-3), which is associated with magnetite, filled in inter-granule spaces among the relatively large and euhedral quartz crystals (Q-2) that are associated with hematite (Hm-2) (crossed polars). **(H)** Calcite veins cut across the orebody. **(I)** Paragenetic sequence of the Taochong deposit. R-Sk: retrograde skarn minerals.

## 4. Samples and Analytical Techniques

Separate samples of the main ore and gangue minerals for isotope analyses were crushed into grains with size of 40–60 mesh. After panning and filtration, more than 10 g of clear mineral grains were carefully picked out for each sample under a binocular microscope. These mineral grains were cleaned in doubly distilled water, and then dried in an oven at 120 °C before analysis. The purity of the grains for oxygen isotope analysis was better than 99%.

In this study, the oxygen isotope compositions of hematite (Hm-1, Hm-2) and magnetite were measured, and the oxygen isotope compositions of quartz (Q-3) and calcite (Cal-2, Cal-3) were obtained from Cao et al. [7,35] and Xu and Lin [24,25]. These analyses were made using the MAT-252 mass spectrometer at the Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geophysics, Beijing, China. For analyses the oxygen isotopes were measured using the conventional bromine pentafluoride (BrF<sub>5</sub>) method of Clayton and Mayeda [36]. Oxygen gas was generated from the minerals (e.g., hematite and magnetite) by quantitatively reaction with BrF<sub>5</sub> in externally heated nickel vessels, and subsequently converted to carbon dioxide through a carbon reduction procedure on a platinum-coated carbon rod. Oxygen isotope analyses were made on carbon dioxide with the MAT-252 mass spectrometer. The analytical reproducibility of laboratory standards during this study was about  $\pm 0.1\%(1\sigma)$ .

The oxygen isotope data are presented in the standard notation of  $\delta^{18}$ O relative to Vienna standard mean ocean water (V-SMOW) in per mil. The oxygen isotope ratios of water in equilibrium with the minerals are calculated using the fractionation formula reported by Clayton et al. [37] and Zheng and Chen [38].

### 5. Results

The oxygen isotopic characteristics of the host minerals and the calculated oxygen isotopic characteristics of the fluid inclusions are described below, and the main oxygen isotope data are summarized in Table 1. The  $\delta^{18}$ O values for minerals and fluids in this paper are reported in per mil relative to V-SMOW. The  $\delta^{18}$ O value of Hm-1 was -6.86%(n = 1). The  $\delta^{18}$ O values were in the range of -2.50% to -1.60% for Hm-2 (n = 3), -8.20% to -3.91% for magnetite (*n* = 4), 7.89\% to 8.80% for Q-3 (*n* = 4), 8.96\% to 9.15% for Cal-2 (n = 2), and 5.30% to 7.81% for Cal-3 (n = 5). The transition from the early, skarntype ores to the quartz-calcite-type ores is characterized by a marked increase in the  $\delta^{18}$ O values of hematite. Using these  $\delta^{18}$ O values and fluid inclusion homogenization temperatures [7,35], together with the fractionation equations of Clayton et al. [37] for quartz (10<sup>3</sup> ln  $\alpha_{\text{Quartz-waters}} = 3.38 \times 10^6 \text{ T}^{-2} - 3.40$ ) and of Zheng and Chen [38] for hematite ( $10^3 \ln \alpha_{\text{Hematite-waters}} = 2.52 \times 10^6 \text{ T}^{-2} - 12.03 \times 10^3 \text{ T}^{-1} + 2.98$ ), magnetite  $(10^3 \ln \alpha_{Magnetite-waters} = 2.88 \times 10^6 \text{ T}^{-2} - 11.36 \times 10^3 \text{ T}^{-1} + 2.89)$ , and calcite (10<sup>3</sup> ln  $\alpha_{\text{Magnetite-waters}} = 4.01 \times 10^{6} \text{ T}^{-2} - 4.66 \times 10^{3} \text{ T}^{-1} + 1.71$ ), the  $\delta^{18}O_{\text{water}}$  values were calculated to be 2.67%, 7.64% to 8.54%, -0.12% to 4.17%, 1.73% to 2.59%, 1.88% to 2.07%, and -2.17% to 0.36% for the fluids in equilibrium with Hm-1, Hm-2, magnetite, Q-3, Cal-2, and Cal-3, respectively.

Sample	Mineral	Temperature (°C) <sup>a</sup>	$\delta^{18} \mathrm{O}\%$	$\delta^{18} \mathrm{O}_{\mathrm{water}}$ (‰) <sup>b</sup>
TCYQ101	Hematite (Hm-1)	380	-6.86	2.67
TCYQ102	Hematite (Hm-2)	320	-1.60	8.54
TCYQ103	Hematite (Hm-2)	320	-2.50	7.64
TCYQ104	Hematite (Hm-2)	320	-2.10	8.04
TCYQ129	Magnetite	320	-5.00	3.08
TCYQ139	Magnetite	320	-3.91	4.17
TCYQ183	Magnetite	320	-8.20	-0.12
TCYQ100 <sup>c</sup>	Magnetite	320	-4.70	3.38
TCYQ106-1 <sup>d</sup>	Quartz (Q-3)	300	8.74	1.85
TCYQ128 <sup>d</sup>	Quartz (Q-3)	320	7.89	1.68
TCYQ132 <sup>d</sup>	Quartz (Q-3)	320	8.80	2.59
TCYQ143 d	Quartz (Q-3)	320	7.94	1.73
TCYQ101 d	Calcite (Cal-2)	260	8.96	1.88
TCYO132 <sup>d</sup>	Calcite (Cal-2)	260	9.15	2.07
TCYO139 <sup>d</sup>	Calcite (Cal-3)	250	7.81	0.36
TCYQ003 <sup>c</sup>	Calcite (Cal-3)	250	5.80	-1.65
TCYQ004 <sup>c</sup>	Calcite (Cal-3)	250	5.50	-1.95
TCYQ005 <sup>c</sup>	Calcite (Cal-3)	250	5.30	-2.15
TCYQ006 c	Calcite (Cal-3)	250	5.28	-2.17

Table 1. Oxygen isotope values of fluid inclusions and host minerals in the Taochong deposit.

<sup>a</sup> The temperatures are the homogenization temperatures of fluid inclusion within the minerals [7,35]; <sup>b</sup>  $\delta^{18}O_{water}$  values were calculated using  $\delta^{18}O$  values, fluid inclusion homogenization temperatures, and the fractionation equations (Clayton et al. [37] for quartz, and Zheng and Chen [38] for hematite, magnetite, and calcite); <sup>c</sup> Data from [24,25]; <sup>d</sup> Data from [7,35].

#### 6. Discussion

## 6.1. Sources of Hydrothermal Fluids

We calculated the oxygen isotope composition of the ore fluids (Figure 4) during different mineralization stages to constrain the most likely fluid sources for the Taochong deposit. Cao et al. [7] reported the hydrogen and oxygen isotopic composition (-60.7%to -71.3%and 7.09%to 7.29%, respectively) of the early fluids in equilibrium with garnet. These values are very close to those of magmatic water [2,39,40]. Fluid inclusion studies [7] indicated that these early fluids were hot ( $\sim$ 500 °C) and hypersaline brines ( $\sim$ 47 wt.% NaCl equiv.), providing further support for the idea that the fluids were probably of magmatic origin. In contrast, the late fluids in equilibrium with Cal-3 were cold and low-salinity ( $\sim$ 220 °C and  $\sim$ 2 wt.% NaCl equiv.) [7] fluids. This, together with the hydrogen and oxygen isotopic composition ( $\delta D = -40\%$ to -81%,  $\delta^{18}$ Owater = -2.2%to 0.4%) [7] of these late fluids and the carbon and oxygen isotope compositions (-1.3%to -1.7%and 5.2%to 5.8%, respectively) [24] of Cal-3, indicates that the late fluids in equilibrium with Cal-3 were probably mixtures of meteoric water and small amounts of magmatic water.



**Figure 4.** Oxygen isotope compositions ( $\delta^{18}O_{water}$ ) of the fluids in equilibrium with major minerals in the Taochong deposit. The magmatic field is according to Barnes [1,2]. The meteoric water field of the study area is according to Zhang [41] and Zhou and Yue [42]. The Y axis is the paragenetic sequence of the minerals as shown in Figure 3I.

Compared with the fluids in equilibrium with garnet, the fluids in equilibrium with Hm-1 had isotopically lighter oxygen and plotted between the magmatic and meteoric water in Figure 4, indicating that the fluids were mixtures of magmatic and meteoric water. The  $\delta^{18}O_{water}$  values of the water in equilibrium with Hm-2 are in the range of 7.64‰-8.54‰, similar to those of magmatic fluids. Interestingly, compared to the Hm-1 data, the  $\delta^{18}O_{water}$  values of the water in equilibrium with Hm-2 are significantly increased (Figure 4). This feature suggests that a re-influx of magmatic water followed Hm-1 precipitation, or the fluids were in equilibrium with time is clearly indicated by the calculated oxygen isotope compositions of fluids in equilibrium with Hm-2, magnetite, Q-2, Cal-2, and Cal-3 (Figure 4). This decreasing trend is paralleled by marked corresponding decreases in fluid salinity and temperature, as indicated by the fluid inclusion data [7], representing an initially magmatic origin progressively evolving by mixing with meteoric water.

## 6.2. Modeling of Hydrothermal Fluid Processes

The evidence from geologic and textural observations, fluid inclusions, and stable isotopes supports the idea that fluid boiling and mixing of magmatic brine with meteoric water took place during the main mineralization stage [7,35]. It is known that both fluid boiling and mixing would have destabilized iron chloride complexes and triggered hematite and magnetite precipitation [4,7,27]. Thus, an ore deposition mechanism that involves fluid boiling and the mixing of magmatic and meteoric water was proposed by Cao et al. [7,35] to explain the formation of the Taochong iron-rich skarn deposit. However, the relative importance of boiling and mixing and the contribution of meteoric water to the hydrothermal system that deposited the iron remain poorly understood.

Fortunately, based on the evolution of the fluid's oxygen isotope compositions, it is possible to evaluate the boiling and fluid mixing and their relative importance [27,29]. Thus, to test the hypotheses of fluid mixing, boiling, and some combination of them, we calculated the oxygen isotope compositions of the hematite, magnetite, quartz, and calcite that were precipitated by each mechanism as a function of temperature, using the method suggested by Wagner et al. [27,29]. Since experimental research on liquid–vapor isotope partitioning in the H<sub>2</sub>O–NaCl system is limited to conditions below the critical point of

pure water [43,44], it is impossible to adequately model the boiling of the temperature– composition space relevant to Taochong. On the basis of boiling models for low-salinity fluids [29,45], it can be expected that boiling would generate a gradual increase in the  $\delta^{18}$ O values of the mineral deposited by residue liquids. This may be due to the preferential partitioning of the lighter  $\delta^{16}$ O isotope into the vapor phase [46], resulting in residual brine increasingly rich in  $\delta^{18}$ O. In addition, since the enthalpy is transferred from the liquid to the vapor required to maintain the enthalpy balance, the cooling of the residual brine enhances the effect of the precipitated minerals being rich in  $\delta^{18}$ O [27]. Therefore, the main effect of boiling on the  $\delta^{18}$ O values of the precipitated minerals is roughly similar to the effect of fluid cooling and can thus be simulated by the latter [27,29].

On the basis of the fluid inclusion data and the oxygen isotope data of skarn minerals [7], it was assumed that the temperature of the initial magmatic fluid was 500 °C, the salinity was 47 wt.% NaCl equiv., and the  $\delta^{18}$ O value was 8.6‰. Applying both closed- and opensystem conditions [47,48] for oxygen isotope exchange between water of meteoric origin  $(\delta^{18}\text{O} = -7.5\%\text{to} - 10\%)$  [41,42] and Huanglong marble ( $\delta^{18}\text{O} = 19.9\%\text{to} 23.4\%$ ) [35], the calculated  $\delta^{18}$ O values of hot groundwater at temperatures of 200 °C (assuming fluid/rock ratios between 0.7 and 3.0, calculated using the  $\delta^{18}$ O values of meteoric water and of unaltered and altered Huanglong marble) would be in the range of -5.4% to -0.8%. One model assumed that the magmatic fluid cooled to a temperature of 200 °C due to boiling, while the other assumed that the magam fluid gradually mixed with a colder dilute fluid (200 °C, zero salinity), assuming two possible  $\delta^{18}$ O compositions of -5.0% and -3.2%, representing the compositions of groundwater of meteoric origin that had equilibrated with Huanglong marble at a temperature of 200 °C. In each model, the temperature of the ore fluid gradually decreased, and in the model of mixing, the salinity and  $\delta^{18}$ O value of the fluid decreased in proportion to the aliquot of diluting fluid that was added. For simplicity, a linear relationship was assumed between the temperature and composition of the mixed fluid, although actually the enthalpy (rather than temperature) varies linearly with the composition during the mixing process [27,49,50]. Fluid salinity may have an effect on the oxygen concentration [51], but considering the absence of relevant experimental data, the mineral-water fractionation factors were assumed to be independent of fluid salinity. The latter were calculated for every temperature step in both models (by use of the equations of Clayton et al. [37] for quartz ( $10^3 \ln \alpha_{Quartz-waters} = 3.38 \times 10^6 T^{-2} - 3.40$ ) and of Zheng and Chen [38] for hematite ( $10^3 \ln \alpha_{\text{Hematite-waters}} = 2.52 \times 10^6 \text{ T}^{-2} - 12.03 \times 10^3 \text{ T}^{-1} + 2.98$ ), magnetite ( $10^3 \ln \alpha_{\text{Magnetite-waters}} = 2.88 \times 10^6 \text{ T}^{-2} - 11.36 \times 10^3 \text{ T}^{-1} + 2.89$ ), and calcite (10<sup>3</sup> ln  $\alpha_{Magnetite-waters} = 4.01 \times 10^{6} T^{-2} - 4.66 \times 10^{3} T^{-1} + 1.71$ ), enabling the  $\delta^{18}$ O compositions of quartz, calcite, hematite, and magnetite in equilibrium with the fluid to be determined.

Selected modeling results are listed in Tables 2 and 3, and the calculated changes in the  $\delta^{18}$ O values of minerals over time are shown in Figure 5, together with the measured ranges of  $\delta^{18}$ O values and fluid inclusion homogenization temperatures for hematite (Hm-1, Hm-2), magnetite, quartz (Q-3), and calcite (Cal-2, Cal-3). From the calculations, it is obvious that boiling and fluid mixing contrast in the ways in which they influence the oxygen isotope compositions of the precipitating minerals. Fluid mixing results in a gradual decrease in the  $\delta^{18}$ O value of the precipitating minerals (except for quartz and calcite—their  $\delta^{18}$ O values increased slightly below 250 °C), but fluid boiling leads to a systematic increase in the  $\delta^{18}$ O values of quartz and calcite over time and a slight decrease in the  $\delta^{18}$ O values of hematite and magnetite. Furthermore, the simulation results are in good agreement with mixing between magmatic brine and meteoric water for Hm-1 precipitation; the boiling of magmatic water for Hm-2 precipitation; the boiling of mixtures of magmatic brine and meteoric water for the precipitation of magnetite, Q-3, and Cal-2; and the mixing of meteoric water with small amounts of magmatic water for Cal-3 precipitation (Figure 5). The results of our calculations further indicate that the proportion of meteoric water in the fluids gradually increased from the precipitation of Hm-2 to magnetite and Q-3, and then to Cal-2 and Cal-3 (Figure 5), consistent with the fluid inclusion [7,35] and

stable isotopic data. The proportion of meteoric water during the precipitation of the Hm-2, magnetite, Q-3, and Cal-2 ranged from 0% to <5%, 37% to 71%, 46% to 71%, and 52% to 71%, respectively (Figure 5). The large range in the proportion of meteoric water during iron oxide precipitation may imply that the iron oxides were precipitated over a long period, consistent with the great accumulation of iron oxide and the formation of this iron-rich deposit.



**Figure 5.** Diagrams showing the effects of boiling (cooling), mixing of magmatic and meteoric water, and the cooling of boiling mixtures of fluids derived from magmatic and meteoric water on the oxygen isotope compositions of quartz (**A**), hematite (**B**), magnetite (**C**), and calcite (**D**). The starting conditions for the magmatic water were a temperature of 500 °C, a salinity of 47 wt.% NaCl equiv., and a  $\delta^{18}$ O value of 8.6%. Mixing lines were calculated assuming that the groundwater had a temperature of 200 °C, zero salinity, and  $\delta^{18}$ O values of –5.0‰ and –3.2‰ (labels on the mixing lines). The mixing proportions between magmatic and meteoric were derived based on the binary mixing model ( $R_M = R_A \times \omega_A + R_B \times \omega_B$ ,  $\omega_A + \omega_B = 1$ , where  $R_M$ ,  $R_A$ , and  $R_B$  represent the mixing value and end-number A and B values, respectively;  $\omega_A$  and  $\omega_B$  represent the mass fractions of A and B).

F = Mass	<b>T</b> (2.2)	$\delta^{18} O_{water}$ —	$\delta^{18}O_{ m mineral}$					
Fraction Brine	raction Brine T <sub>mix</sub> (°C)		Quartz	Hematite	Magnetite	Calcite		
The Minerals in Equilibrium with A Magmatic Brine (T = 500 °C, $\delta^{18}$ O = 8.6‰) That Is Mixing with Meteoric Water								
$(T = 200 \ ^{\circ}\text{C}, \ \delta^{18}\text{O} = -3.2\%)$								
1.00	500	8.60	10.9	0.24	1.61	10.99		
0.95	485	8.01	10.5	-0.49	0.93	10.55		
0.90	470	7.42	10.1	-1.22	0.24	10.12		
0.85	455	6.83	9.8	-1.96	-0.45	9.70		
0.80	440	6.24	9.5	-2.69	-1.14	9.30		
0.75	425	5.65	9.2	-3.43	-1.82	8.91		
0.70	410	5.06	8.9	-4.17	-2.51	8.54		
0.65	395	4.47	8.6	-4.91	-3.50	8.19		
0.60	380	3.88	8.4	-5.65	-3.87	7.86		
0.55	365	3.29	8.2	-6.39	-4.55	7.54		
0.50	350	2.70	8.0	-7.14	-5.22	7.26		
0.45	335	2.11	7.8	-7.88	-5.89	7.00		
0.40	320	1.52	77	-8.62	-6.56	677		
0.35	305	0.93	7.6	_9.36	-7.21	6 58		
0.30	290	0.34	7.0	-10.10	-7.86	6.42		
0.30	275	-0.25	7.0	_10.83	-8 50	6 30		
0.20	260	-0.25	7.0	-10.05	-0.50	6.30		
0.20	200	-0.04	7.7	-11.50	-9.13	6.24		
0.15	245	-1.43	7.0	-12.28	-9.74	6.22		
0.10	230	-2.02	7.9	-13.00	-10.55	0.27		
0.05	215	-2.61	0.Z	-13.70	-10.91	6.38		
0.00	200	-3.20	8.5	-14.39	-11.45	6.37		
The Mineral	s in Equilibrium v	with A Magmatic B $(T = T)$	rine ( $T = 500 \circ C$ , 200 °C $\delta^{18} O = -$	$\delta$ 18O = 8.6‰) That 5.0‰)	Is Mixing with Me	teoric Water		
1.00	500	e 40	10.95	0.24	1 / 1	10.00		
1.00	500	8.60 7.00	10.85	0.24	1.61	10.99		
0.95	485	7.92	10.40	-0.58	0.84	10.46		
0.90	470	7.24	9.96	-1.40	0.06	9.94		
0.85	455	6.56	9.53	-2.23	-0.72	9.43		
0.80	440	5.88	9.13	-3.05	-1.50	8.94		
0.75	425	5.20	8.73	-3.88	-2.27	8.46		
0.70	410	4.52	8.36	-4.71	-3.05	8.00		
0.65	395	3.84	8.01	-5.54	-3.82	7.56		
0.60	380	3.16	7.68	-6.37	-5.05	7.14		
0.55	365	2.48	7.38	-7.20	-5.36	6.73		
0.50	350	1.80	7.10	-8.04	-6.12	6.36		
0.45	335	1.12	6.86	-8.87	-6.88	6.01		
0.40	320	0.44	6.65	-9.70	-7.64	5.69		
0.35	305	-0.24	6.47	-10.53	-8.38	5.41		
0.30	290	-0.92	6.34	-11.36	-9.12	5.16		
0.25	275	-1.60	6.25	-12.18	-9.85	4.95		
0.20	260	-2.28	6.21	-13.00	-10.57	4.80		
0.15	245	-2.96	6.23	-13.81	-11.27	4.69		
0.10	230	-3.64	6.31	-14.62	-11.95	4.65		
0.05	215	-4.32	6.46	-15.41	-12.62	4.67		
0.00	200	-5.00	6.70	-16.19	-13.25	4.77		

Table 2. Calculated oxygen isotope compositions of quartz, hematite, magnetite, and calcite in the mixing model.

T (°C)	$\delta^{18} O_{water}$ –			$\delta^{18} O_{mineral}$	
		Quartz	Hematite	Magnetite	Calcite
500	8.60	10.9	0.24	1.61	10.99
480	8.60	11.2	0.05	1.48	11.19
460	8.60	11.5	-0.14	1.35	11.41
440	8.60	11.8	-0.33	1.22	11.66
420	8.60	12.2	-0.53	1.10	11.93
400	8.60	12.7	-0.73	0.97	12.24
380	8.60	13.1	-0.93	0.85	12.58
360	8.60	13.6	-1.13	0.73	12.95
340	8.60	14.2	-1.34	0.62	13.38
320	8.60	14.8	-1.54	0.52	13.85
300	8.60	15.5	-1.74	0.44	14.39
280	8.60	16.2	-1.93	0.37	14.99
260	8.60	17.1	-2.12	0.31	15.68
240	8.60	18.0	-2.29	0.29	16.46
220	8.60	19.1	-2.45	0.30	17.35
200	8.60	20.3	-2.59	0.35	18.37

**Table 3.** Calculated oxygen isotope compositions of quartz, hematite, magnetite, and calcite in the boiling model, in equilibrium with a magmatic brine (T = 500 °C,  $\delta^{18}$ O = 8.6‰) that is progressively cooling.

## 7. Conclusions

The Taochong deposit is one of the most important iron-rich skarn deposits in the MLYRB. There are two types of ores in this deposit: skarn-type ores and quartz–calcite-type ores. The oxygen isotope data presented in this study are consistent with two episodes of hydrothermal activity, which are responsible for the formation of skarn and quartz–calcite-type ores, respectively. Both of the episodes' fluids were of magmatic origin and then progressively evolved by mixing with meteoric water.

The results of quantitative simulations suggest that the deposition of the skarn-type ores was most likely caused by the mixing of magmatic and meteoric fluids, whilst the deposition of the quartz–calcite-type ores was most likely caused by the boiling of magmatic fluids and the mixture of magmatic brine and meteoric water. We note that this has also been observed in other high-grade metal deposits worldwide. Additionally, a large range in the proportions of meteoric and magmatic water during iron oxide precipitation may also have contributed to the formation of the iron-rich deposit at Taochong.

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