Original Article

Analysis of the data in Jingwen Mao's paper on the stable isotopes (δD_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{34}S$) of the gold deposits in Jiaodong Peninsula, China

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Abstract

In 2008, Jingwen Mao published a paper on the stable isotopes of gold deposits in the Jiaodong Peninsula. The paper has a series of problems in obtaining δD_{H2O} and $\delta^{18}O_{H2O}$ of ore-forming fluids and interpreting $\delta^{34}S$ data. ① In order to obtain δD_{H2O} and $\delta^{18}O_{H2O}$ data of ore-forming fluids, Jingwen Mao selected sericite (a total of 25 samples) as the target mineral. Sericite is not an independent mineral and has no fixed molecular formula. New research has shown that it is a fine-grained aggregate composed of muscovite, illite, and sodium mica (at least muscovite and sodium mica). The water content in sericite is very complicated, including structural water, interlayer water, fissure water, primary and secondary inclusion water. Jingwen Mao extracted water from sericite by crushing, and this mixed water cannot represent the ore-forming fluids. It is unreliable to determine the source of ore-forming fluids using δD_{H2O} measured by this kind of mixed water. ② So far, no oxygen isotope fractionation coefficient relationship between sericite and water has been obtained, whether through theoretical calculation or experimental research. In order to calculate the $\delta^{18}O_{H2O}$ of ore-forming fluids by measuring the $\delta^{18}O$ of sericite, Jingwen Mao used the oxygen isotope fractionation coefficient relationship between muscovite and water for calculation, which is completely wrong. ③ The data of $\delta^{18}O_{H2O}$ and δD_{H2O} of ore-forming fluids obtained by Jingwen Mao using sericite are very different from the relevant data obtained by previous researchers using quartz as the target mineral (131 samples). Based on those unreliable data, Jingwen Mao believed that the ore-forming fluids came from the mixed source of crust and mantle, while the relevant data of previous researchers proved that the ore-forming fluids came from the products of atmospheric precipitation exchanging with Jiaodong Group metamorphic rocks under different temperatures and different W/R ratios. ④ For the relationship between the high or low $\delta^{34}S$ value of sulfide minerals and the large or small $\log fO_2$ value, Jingwen Mao's explanation is completely opposite to the research results of Ohmoto and Wang. Ohmoto believed that the two were negatively correlated, while Jingwen Mao believed that they were positively correlated. This is a common sense mistake.

Key words: problem; the stable isotopes δD_{H2O}, $\delta^{18}O_{H2O}$ & $\delta^{34}S$; source of ore-forming fluid; sericite; genesis; Jiaodong gold deposits

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1 Introduction

The Jiaodong Peninsula gold deposit in China is a world-class super-large gold deposit. A lot of research has been done on the geology of the deposit, the source of ore-forming fluids and the genesis of the deposit. The research results of this deposit are of great significance to the genesis of gold deposits and the guidance of gold prospecting. In the paper titled "the relationship of mantle-derived fluids to gold metallogenesis in the Jiaodong Peninsula: Evidence from D–O–C–S isotope systematics" (hereinafter referred to as the 2008 paper) published in 2008 by Jingwen Mao[1], there are a series of problems in the determination of hydrogen and oxygen isotopes and the interpretation of sulfur isotope data of gold deposits in the region, which are described as follows.

2 Selection of target mineral samples

The best target mineral for studying the hydrogen and oxygen isotope composition of ore-forming fluids in hydrothermal endogenous metal deposits is quartz. The reasons are as follows:

- Quartz is widely distributed and is commonly found in metamorphic rocks, intermediate-acidic intrusive rocks, and various endogenous metal deposits.
- Quartz is stable, hard, and has no cleavage, and its primary fluid inclusions are easy to preserve.
- Quartz has good transparency, and its primary fluid inclusions are simple and reliable for temperature measurement.
- Quartz has a single chemical composition (SiO_2) and does not contain structural water. So, it is very reliable to use its primary fluid inclusion water to measure δD_{H2O}.

Although the oxygen in the water of the quartz's primary fluid inclusions will undergo isotopic exchange with the oxygen in the quartz lattice, the ratio of the two is very different, so the effect on the quartz $\delta^{18}O$ composition can be ignored.

The oxygen isotope fractionation coefficient of the quartz-water system and its difference in fractionation coefficients in different temperature ranges have the highest degree of research and are the most accurate.

Therefore, it has become a consensus in the academic community to use the oxygen isotope fractionation equation of the quartz-water system to calculate the $\delta^{18}O_{H2O}$ of ore-forming fluids.

In fact, it is common sense for ore deposit geologists to use quartz as a target mineral to determine the source of ore-forming fluids. For example, the earliest study on determining the source of ore-forming fluids in volcanic massive sulfide deposits was completed by Japanese scholars using quartz in black ore deposits. The results showed that the ore-forming fluid of this type of deposit is a mixture of seawater and magmatic water[2].

3 Analysis and problem

In his 2008 paper, Jingwen Mao measured hydrogen and oxygen isotopes on 37 single mineral samples from 9 deposits in the study area. Unlike other researchers, Mao measured 7 samples of potassium feldspar and 25 samples of sericite for the altered broken rock type and quartz vein type deposits (Tables 1 and 2), but he did not use quartz as the target mineral.

During the analytical process, the method of obtaining elemental hydrogen is as follows: first, the water in the fluid inclusions in the mineral is extracted by crushing, and then the water reacts with zinc to produce hydrogen[1].

There are the following problems here:

Table 1. Comparison of $\delta^{18}O_{H2O}$ (‰) of ore-forming fluids and δD_{H2O} (‰) of water in quartz inclusions in different gold deposits of Jiaojia type at different mineralization stages with the corresponding data of sericite and potassium feldspar

Mine	**Metallogenic stage**	**Mineralizition type**	**Analyzed mineral**	**$\delta^{18}O$**	**$\delta^{18}O_{H2O}$ ①**	**δD_{H2O}**	**Source**
Taishang	Ⅰ	Massive quartz vein	quartz	12.1(2)	4.7	-78(1)	[11]
Hobu			quartz	11.9（2）	4.5		
Cangshang			quartz	12.7（3）	5.3	−77（1）	
Sanshandao			quartz	14.2（2）	6.9	-62（2）	
Dayigezhuang			quartz	10.9（1）	3.5	-78（1）	
			average	12.4±1.2	4.7±1.2	-73±7.8	
Taishang	Ⅱ	Sulfide quartz vein	quartz	12.2（4）	2.8	−85（2）	[11]
Jiaojia			quartz	11.4（2）	2		
Hobu			quartz	13.1（1）	3.7		
Cangshang			quartz	14.1（1）	4.7	-82 （1）	
Sanshandao			quartz	14.7（2）	5.3	−71（1）	
Dayigezhuang			quartz	11.3（4）	1.9	-78（2）	
Xincheng			quartz	13.9（4）	4.5	−87（3）	[12]
			average	13.2±1.3	3.5±1.3	-80±6.3	
Taishang	Ⅲ	Quartz-calcite vein	quartz	15.4（3）	4.5	-91（1）	[11]
Xincheng			quartz	15.0（2）	4.1		[12]
Sanshandao			quartz	13.4（2）	2.5	-92（1）	[11]
Jiaojia			quartz	13.7（1）	2.8	-107（1）	
			average	14.4±1.0	3.5±1.0	-92±0.6	
Sanshandao	Ⅱ②③	Quartz sulfide vein	Sericite	11.7（6）	7.85	-53.6（6）	[1]
Cangshang			Sericite	11.12（5）	7.97	-51.8 （5）	
Jiaojia			Sericite	9.9（3）	6.75	-60.0 （3）	
Wangershan			Sericite	9.58（4）	6.44	-57.3 （4）	
Dayigezhuang ②			Sericite	9.22（5）	6.01	-58.4（5）	
			average	10.3±0.95	7.0±0.78	- 56.2±3	
Jiaojia	Ⅱ②③	Quartz sulfide vein	K-spar	10.1（2）	4.27	-85.5±0.5（2）	
Dayigezhuang ②			K-spar	8.87（3）	3.03	-78±11.3（3）	
			average	9.5 ±0.62	3.65±0.62	-81.8±3.8	

Note: ① According to the best estimate of homogenization temperature: 300°C in the first mineralization stage, 250°C in the second mineralization stage, and 220°C in the third mineralization stage. ② Jingwen Mao classified the Dayigezhuang gold deposit as a quartz vein-type gold deposit, but Li[10] and Zhang[11] believed that the deposit belonged to the altered broken rock type (Jiaojia type) gold deposit. ③ When Jingwen Mao used sericite and potassium feldspar to determine the hydrogen and oxygen isotope composition of the ore-forming fluid, he did not divide the mineralization stage. According to the inference of its mineralization type, the target minerals he selected may belong to the mineralization stage II. （）is the number of samples

Jingwen Mao did not conduct a microscopic study on potassium feldspar or sericite, and did not describe the size of its mineral grains, the relationship of paragenesis, the freshness of the minerals, and the state of preservation (i.e., whether there are microscopic cracks).

There is no description of whether there are fluid inclusions in the minerals, whether there are secondary inclusions, and their number and size. In particular, the grain size of sericite is generally very small, and the cleavage is well developed, so it is doubtful whether there are primary fluid inclusions in it.

Table 2. Comparison of $\delta^{18}O_{H2O}$ (‰) of ore-forming fluids and δD_{H2O} (‰) of water in quartz inclusions, sericite and feldspar at different mineralization stages in different Linglong-type (quartz vein-type) gold deposits

Mine	Metallogenic stage	Mineralizition type	Minerals	$\delta^{18}O$	$\delta^{18}O_{H2O}$	δD_{H2O}	Source
Qixia	I	Beresitization	Quartz（4）	12.7±0.66	3.78±0.67	-62.5±7.8	[14]
Lingllon		Pyrite-quartz vein	Quartz（2）		3.25±1.79	-62.7±4.8	[13]
Rushan		Pyrite-quartz vein	Quartz（4）	10.9±1.45	2.06±1.51		[9]①
Qixia		Pyrite-quartz vein	Quartz（1）	12.53	5.3	-66.4	[8]
Denggezhuang		Pyrite-quartz vein	Quartz（2）	14.1±0.52	5.29±1.17	-78.9±4.4	[10]
			average	12.6±1.13	3.94±1.24	-67.6±6.6	
Qixia	Ⅱ	Pyrite-quartz vein	Quartz（5）	12.24±0.8	1.16±0.89	-78.2±9.3	[14]
Qixiaq		Sulfide-quartz vein	Quartz（1）	12.56	2.67	58.5	[8]
Denggezhuang		Au-bearing quartz vein	Quartz（3）	13.53±1.9	4.57±1.97	-77±5.7	[10]
Tangjiagou		Sulfide-quartz vein	Quartz（2）	10.47±1.7	3.05±0.82	-72±1.5	
			average	12.20±1.1	2.86±1.21	-71.4±7.8	
Qixia	Ⅲ	Quartz-carbonate vein	Quartz（4）	12.25±1.1	-2.4±1.03	-91.3±2.6	[14]
Rushan		Siderite-quartz vein	Quartz（1）	11.6	0.06		[9]
Lingnan		Au-bearing pyrite	Quartz（3）		-4.7±0.1	-86±0.8	[16]
Jiuqu		Pyrite-quartz vein	Quartz（2）		-8.4±1.8	-100±10.0	
Shilipu		Carbonate-quartz vein	Quartz（21）	9.7	-3.6（15）	-84（7）	[17]
			average	11.18±1.1	-4.77±2.3	-90.3±6.2	
Denggezhuang	Ⅱ	Sulfide-quartz vein	Sericite（2）	9.6±0.9	6.45±0.9	-66.5±9.5	[1]
Denggezhuang	Ⅱ	Sulfide-quartz vein	K-spar（2）	8.85±0.3	3.02±0.25	-86±1.0	

Note: ① The $\delta^{18}O_{H2O}$ here is calculated by the original author Li[9] based on the ore-forming temperature of 295°C, while Li[13] calculated it based on the ore-forming temperature of 265°C. This paper uses the latter. The number of samples is in parentheses

When the above crushing method is used to extract water from fluid inclusions in minerals, water in secondary inclusions, cleavage cracks, and microscopic cracks is also extracted at the same time. In addition, there is interlayer water in sericite, which obviously cannot represent the water of the ore-forming fluid.

Sericite also contains structural water, and it is inevitable that the hydrogen in its structural water will undergo isotope exchange with the hydrogen in the inclusion water. Therefore, its δD_{H2O} result is unreliable.

Regarding the oxygen isotope problem, there is no experimental research result on the oxygen isotope fractionation coefficient of the sericite-water system. Jingwen Mao used the oxygen isotope fractionation coefficient of the muscovite-water system instead to calculate the oxygen isotope comparison of the fluid water in equilibrium with sericite.

Is this feasible?

To answer this, it is necessary to explain what sericite is. The old traditional view is that sericite is a fine-grained aggregate (variant) of muscovite. It is not an independent mineral and has no fixed molecular formula. Therefore, Wang (1965) believed that compared with muscovite, sericite may contain slightly less potassium and slightly more water[3]. However, new research in the Western mineralogy community believes that very fine-grained and irregular aggregates of white mica minerals are named sericite, and white mica minerals are typically composed of muscovite, illite and sodium mica[4]. Of course, it is not ruled out that in a few cases, sericite is just a fine-grained variant of muscovite or sodium mica[5]. Dietrich believes that a variant composed of fine transparent crystals of muscovite or sodium mica (or both) is usually called sericite[6]. This variant of fine transparent crystals has a silky luster.

Because of this, sericite is not included in the theoretically calculated oxygen isotope fractionation coefficients of the 72 minerals and water so far. Sericite is also not included in the experimentally measured oxygen isotope fractionation coefficients of the 46 minerals and water[7].

Obviously, it is wrong for Jingwen Mao to use the oxygen isotope fractionation coefficient of the muscovite-water system to replace the oxygen isotope fractionation coefficient of the sericite-water system. There are uncertainties in the interpretation of the $\delta^{18}O_{H2O}$ values of his 25 sericite single minerals.

As for the Jiaodong gold deposits, preliminary research found that 14 predecessors[8-17] used quartz as the target mineral to study the hydrogen and oxygen isotopes of the deposits, and measured as many as 131 samples. As far as we know, only Wang had one sample and Li had five samples that used sericite as the target mineral[8-9]. But, both of them did not explain how they determined the $\delta D_{sericite}$.

In particular, it is wrong that Li used $1000\ln\alpha$ muscovite–water = $-22.1 \times 10^6/T^2 + 19.1$ to replace the hydrogen isotope fractionation coefficient of the sericite-water system for calculating the hydrogen isotope comparison of the ore-forming fluid. But what is worse, Li openly wrote the above hydrogen isotope fractionation relationship as δDsericite - δDwater = $-22.1 \times 10^6/T^2 + 19.1$ in his article[9]. These blatantly fake data are of course not usable. For this reason, Li (1993) did not cite the δD_{H2O} and $\delta^{18}O_{H2O}$ data obtained by a few researchers using sericite in his monograph on the Jiaodong gold mine[10]. On this basis, the relevant test results are listed in Tables 1 and 2 according to the two mineralization types; namely, the Jiaojia type and Linglong type.

It must be pointed out that the test results in Tables 1 and 2 are classified and arranged according to the mineralization stages. Those test results that cannot determine the mineralization stage are not included in the tables.

4 Discussion

The data and corresponding figures of hydrogen and oxygen isotopes by previous researchers using quartz as the target minerals and by Jingwen Mao using sericite and potassium feldspar as the target minerals are listed in Table 1, in the hope that through comparison, it will be clear which is right and which is wrong.

Figure 1 below is a diagram of δD_{H2O} - $\delta^{18}O_{H2O}$ of the altered broken rock type and quartz vein type gold deposits in Jiaodong. As can be seen from Figure 1, the projection points of potassium feldspar and sericite are obviously located in two intervals. The projection point of potassium feldspar is located in the C and D evolution curve range of the water/rock exchange process, while the projection points of sericite, with a few exceptions, are all located in the range of magmatic water or metamorphic water. Why is there such a big difference between the two? This will be discussed later.

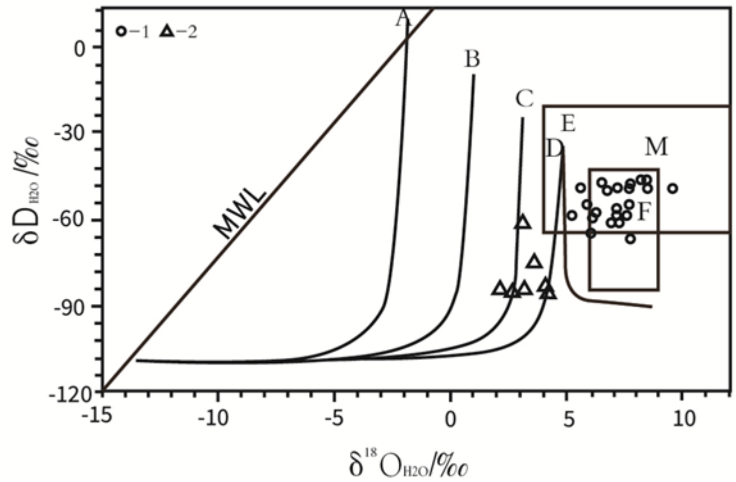

Figure 1. δD_{H2O} - $\delta^{18}O_{H2O}$ diagram of altered broken rock type and quartz vein type gold deposits in Jiaodong (data quoted from Mao in the reference 1 of this paper)

1 – Sericite, 2 - Potassium feldspar

The curves A, B, C, and D in the figure are the evolution curves of atmospheric precipitation at 150℃, 200℃, 250℃ and 300℃ in the process of water/rock exchange, and E is the evolution curve of magmatic water at 300℃[14]; MWL is the atmospheric precipitation line; F and M are the isotopic compositions of magmatic water and metamorphic water.

Figure 2 is a graph showing the δD_{H2O} - $\delta^{18}O_{H2O}$ variation of fluids in different mineralization stages of Jiaojia-type gold deposits in Jiaodong[11]. Zhang pointed out that the mineralization of Jiaojia-type large-scale gold deposits includes vein quartz in three different stages (but mainly in the second stage). As can be seen from Figure 2, the deposition temperature of Jiaojia-type large-scale gold deposits is between 300 ℃ and 200 ℃, the $\delta^{18}O_{H2O}$ value of the fluid is around +4‰, and the δD_{H2O} value changes from -70‰ to -90‰ from stage I to stage III. Combining the H and O isotopic compositions of Mesozoic atmospheric precipitation, the isotopic compositions of ore-forming hydrothermal water and temperature data, it is inferred that the ore-forming fluids of the Jiaojia-type gold deposits were formed by the exchange of Mesozoic atmospheric precipitation with intermediate-basic rocks at depths below 5 km at 350 – 400 ℃, with an effective W/R ratio ranging from 0.01 to 0.05, and were cooled and deposited at around 350 ℃ in a buffered open system[11].

Figure 3 is a diagram of the hydrogen and oxygen isotope evolution of hydrothermal fluids formed during the exchange of meteoric precipitation and magmatic water with the metamorphic rocks of the Jiaodong Group[14].

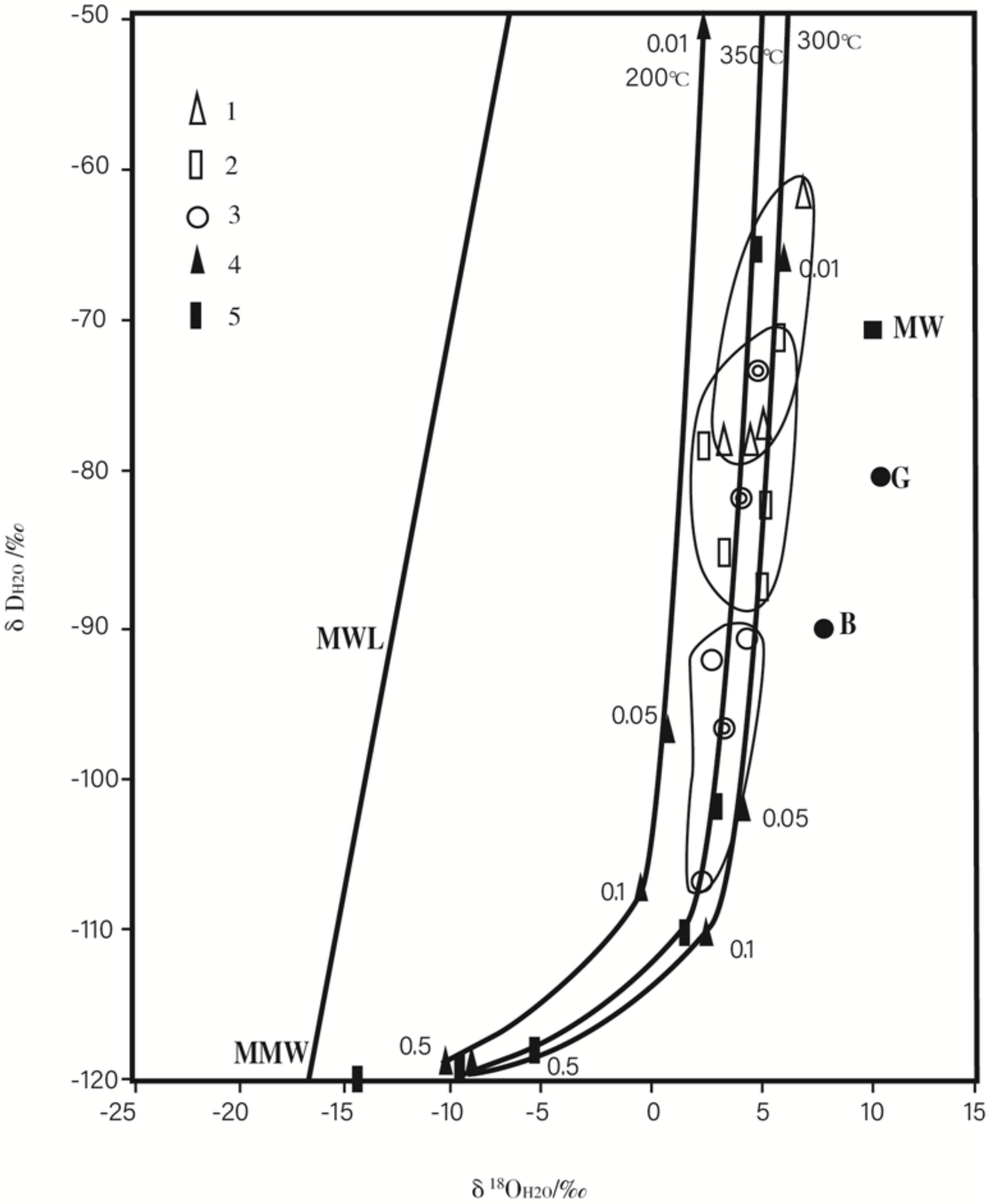

Figure 2. δD_{H2O} - $\delta^{18}O_{H2O}$ variation diagram of fluids in different mineralization stages of Jiaojia-type gold deposits in Jiaodong[11]

Note: Initial conditions of evolution line: MW is magmatic water ($\delta^{18}O_{H2O}$ = 9.1‰, δD_{H2O} = -71‰); MMW is Mesozoic atmospheric precipitation ($\delta^{18}O_{H2O}$ = -16‰, δD_{H2O} = -120‰); G is granite ($\delta^{18}O_{H2O}$ = 11‰, δD_{H2O} = -80‰); B is basic rock ($\delta^{18}O_{H2O}$ = 7.5‰, δD_{H2O} = -90‰). 1-stage I ore-forming fluid; 2-stage II ore-forming fluid; 3-stage III ore-forming fluid; 4-The Mesozoic precipitation evolution curve of atmospheric precipitation (MMW) and granite (G) at 200 ℃ and 300 ℃ and under different W/R ratios; 5-The Mesozoic precipitation evolution curve of atmospheric precipitation (MMW) and basic rock (B) at 350 ℃ and under different W/R ratios

As can be seen from Figure 3, the hydrogen and oxygen isotope values of the ore-forming solutions of the Qixia gold deposit at different mineralization stages are generally different from the magmatic water evolution curve at the projection points in Figure 3, but are consistent with the meteoric precipitation evolution curve of the corresponding temperature.

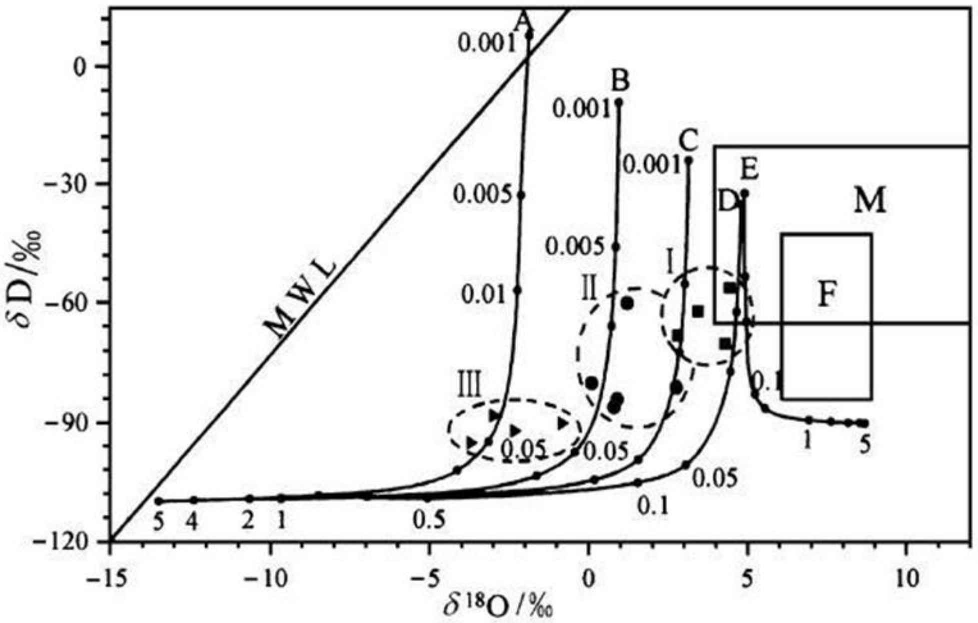

Figure 3. Hydrogen and oxygen isotope evolution during the exchange between atmospheric precipitation, magmatic water and metamorphic rocks[14]

Note: The curves A, B, C, and D in the figure are the evolution curves of atmospheric precipitation at 150 ℃, 200 ℃, 250 ℃ and 300 ℃ during the water/rock exchange process, and E is the evolution curve of magmatic water at 300 ℃; the number corresponding to each black dot on all curves represents the effective (W/R) mass value; MWL is the atmospheric precipitation line; F and M are the isotopic compositions of magmatic water and metamorphic water; Ⅰ, Ⅱ, and Ⅲ are the projection points of hydrothermal fluids in the early, main, and late stages of the Qixia gold deposit, respectively. The $\delta^{18}O_{H2O}$ values of the Jiaodong Group metamorphic rocks, magmatic water and atmospheric precipitation are 9.5‰, 9.0‰ and -15.0‰, respectively; and the δD_{H2O} values are -90‰, -90‰ and -110‰, respectively. The initial parameters used to calculate the evolution curve refer to the specific situation of the Qixia gold mine. The bottom layers of metamorphic rocks in the Jiaodong area mainly include the Jiaodong Group, Jingshan Group, Fenzishan Group, and Penglai Group, etc. Among them, the Jiaodong Group is the main component of the old metamorphic basement, and the lithology belongs to the Archean greenstone belt.

For example, the projection point in the early stage of mineralization is located near the 250 – 300 ℃ meteoric precipitation evolution curve C and D, the projection point in the main mineralization period is located between the 200 – 250 ℃ curves B and C, the projection point in the late stage of mineralization is located near the 150 – 200 ℃ curves A and B. Although the projection point in the early stage of mineralization seems to be close to the magmatic water evolution curve E, the temperature of the hydrothermal fluid in the early stage of mineralization is not that high. From the early to the late stage of mineralization, the effective W/R ratio of the interaction between meteoric precipitation and metamorphic rocks tends to increase. The W/R ratio in the early stage of mineralization is about 0.005 - 0.01, the W/R ratio in the main mineralization period is about 0.01 - 0.05, and the W/R ratio in the late stage of mineralization is close to 0.05.

That is, the distribution of hydrogen and oxygen isotope values of the ore-forming hydrothermal fluid of the Qixia gold deposit well reflects the characteristics of meteoric precipitation after exchange with the metamorphic rocks of the Jiaodong Group under different temperatures and different W/R ratios.

As can be seen from Figure 4 below, the hydrogen and oxygen isotopes of different mineralization stages (from early to late) of the quartz vein type (the Linglong type) gold deposit gradually drift towards the rainwater line from stage I to stage IV. This indicates that as the mineralization progresses, the proportion of atmospheric precipitation in the mineralizing fluid becomes larger and larger.

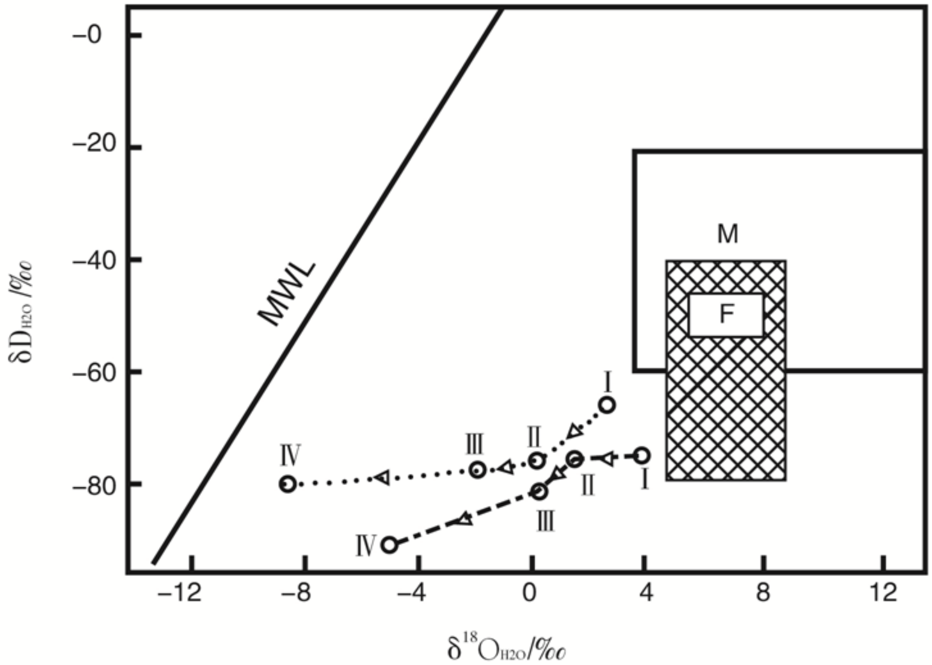

Figure 4. δD_{H2O} - $\delta^{18}O_{H2O}$ relationship of ore-forming fluids in each mineralization stage of Linglong Gold Mine[16]

Note: I - pyrite-quartz stage; Ⅱ - gold-polymetallic sulfide-quartz stage; Ⅲ - gold-silver-polymetallic sulfide stage; Ⅳ - pyrite-quartz-carbonate stage. MWL is the atmospheric precipitation line, F and M are the isotopic compositions of magmatic water and metamorphic water respectively. The dotted line is the fluid inclusion in quartz, and the dashed line is the fluid inclusion in pyrite

As can be seen from Figures 2 to 4 above, whether it is the Jiaojia-type gold deposit, or the Qixia type gold deposit or the Linglong type gold deposit, the δD_{H2O} and $\delta^{18}O_{H2O}$ values of the ore-forming fluid measured by quartz as the target mineral are generally quite different from the magmatic water area and the magmatic water evolution curve, but are consistent with the atmospheric precipitation evolution curve at the corresponding temperature. In addition, the hydrogen and oxygen isotope values of these deposits in different mineralization stages (from early to late) gradually drift toward the atmospheric precipitation line, indicating that with the progress of mineralization, the proportion of atmospheric precipitation in the ore-forming fluid is increasing. In short, these actual data well prove that the ore-forming fluid comes from the product of atmospheric precipitation exchanging with the metamorphic rocks of the Jiaodong Group under different temperatures and different W/R ratios. As Zhang pointed out, the ore-forming fluid is formed by the exchange of Mesozoic atmospheric precipitation with deep basic rocks at about 350 ℃ and W/R = 0.01, and then cooling in a buffered open system[11]. Of course, it is not ruled out that a small amount of magmatic hydrothermal fluid may be mixed in the early stage of mineralization. However, the metamorphic old basement in Jiaodong area is mainly composed of Archean Jiaodong Group and Early-Mesoproterozoic Jingshan Group. Among them, Jiaodong Group is the main component of the old metamorphic basement, and its lithology belongs to the Archean greenstone belt. The granite in this area is formed by the remelting of these old basement rock systems[10].

Finally, according to the data in Tables 1 and 2, the author made Figure 5. For the sake of eye-catching, we projected the average value of multiple groups of data in each mineralization stage on Figure 5 (see the figure caption for more detailed information).

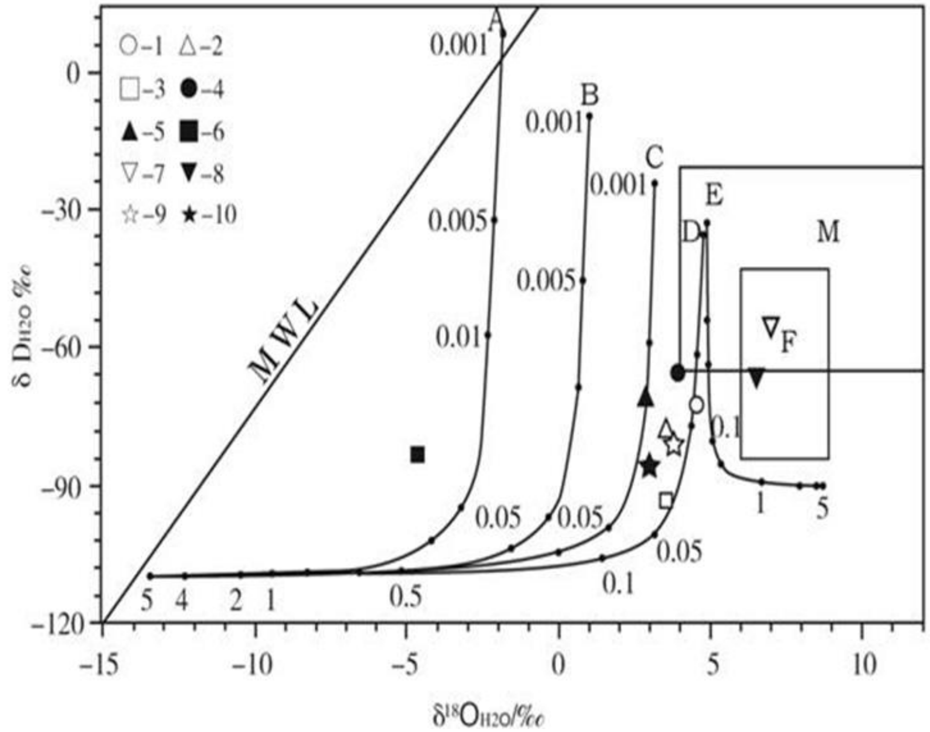

Figure 5. δD_{H2O} - $\delta^{18}O_{H2O}$ relationship diagram of ore-forming fluids in each mineralization stage of the Jiaojia-type and Linglong-type gold deposits

Note: The curves A, B, C, D, E, MW L, F, and M in the figure are the same as those in Figure 3. 1 - the Jiaojia-style mineralization stage I (average value of 10 samples from 5 deposits); 2 – the Jiaojia-style mineralization stage II (average value of 18 samples from 7 deposits); 3 – the Jiaojia-style mineralization stage III (average value of 6 samples from 4 deposits); 4 – the Linglong-style mineralization stage I (average value of 6 samples from 5 deposits); 5 – the Linglong-style mineralization stage II (average value of 10 samples from 4 deposits); 6 – the Linglong-style mineralization stage III (average value of 10 samples from 5 deposits); 7 – the Jiaojia-style mineralization stage II (average value of 23 sericite samples from 5 deposits); 8 – the Linglong-style mineralization stage II (average value of 2 sericite samples from 1 deposit); 9 – the Jiaojia-style mineralization stage II (average value of 5 potassium feldspar samples from 2 deposits); 10 – the Linglong-style mineralization stage II (average value of 2 potassium feldspar samples from 1 deposit)

It can be seen from Figure 5 that:

- The projection points of the main mineralization period of Jiaojia-type and Linglong-type gold deposits are located near the atmospheric precipitation evolution curve C and D at 250 – 300 ℃, which is quite different from the magmatic water evolution curve and is farther away from the magmatic water area.
- The sources of the ore-forming fluids in the mineralization stages I and II of the Jiaojia-type and Linglong-type gold deposits are basically the same, only the Linglong-type gold deposit has more atmospheric precipitation mixed in the ore-forming fluids in the mineralization stage III.
- The projection points of δD_{H2O} and $\delta^{18}O_{H2O}$ of the potassium feldspar samples of Jingwen Mao's Jiaojia and Linglong gold deposits are also located near C and D of the atmospheric precipitation evolution curves at 250 – 300 ℃, which is consistent with the results of the projection points of the 7 samples in Figure 1. It also shows that the source of the fluid that formed potassium feldspar is basically the same as the source of the ore-forming fluid in the second mineralization stage of the Jiaojia and Linglong gold deposits, which is very close to the research results of previous researchers using quartz as the target mineral, and is reasonable.
- The two projection points of δD_{H2O} and $\delta^{18}O_{H2O}$ of the sericite samples collected by Jingwen Mao from the Jiaojia-type and Linglong-type gold mines, and the projection points of the 25 samples in Figure 1, all fall within the range of the superposition of regional metamorphic water and magmatic water, indicating that the ore-forming fluid is more likely to come from metamorphic fluid. This result is very different from the large amount of research data of previous researchers using quartz as the target mineral.

Jingwen Mao believes that the ore-forming hydrothermal fluid is the result of the mixing of mantle-derived fluid and crustal fluid[1]. The only possible evidence is the δD_{H_2O} and $\delta^{18}O_{H_2O}$ data of sericite, but these data are completely unreliable. As mentioned above, there are a series of problems in using sericite as the target mineral to determine the δD_{H_2O} and $\delta^{18}O_{H_2O}$ values of ore-forming fluids, which is wrong and will not be repeated here.

What is certain is that this error is not seen from the final result, but the root cause has been planted at the beginning.

Selecting sericite as the target mineral to determine the δD_{H_2O} and $\delta^{18}O_{H_2O}$ of the ore-forming fluid is in itself a low-level common-sense mistake.

5 The sulfur isotope problem

When explaining the $\delta^{34}S$ distribution characteristics of sulfides in Jiaodong gold deposits, Jingwen Mao made the following description[1]:

Although there are several factors responsible for mineral deposition, the change of sulfur composition in the various types of gold deposits in the Jiaodong area can be closely related to fO_2. Wang and Yan[18] and Wang et al.[19] mentioned that $\delta^{34}S$ values of pyrite are higher in the gold deposits hosted in the large and open fracture system, and lower in those hosted in small-scale and relatively close fracture system[1].

To this end, Jingwen Mao specifically quoted the "$\delta^{34}S$ variation trend and structural relationship diagram of the Zhaoyuan-Yexian gold ore belt" (Figure 6) produced by Wang[19].

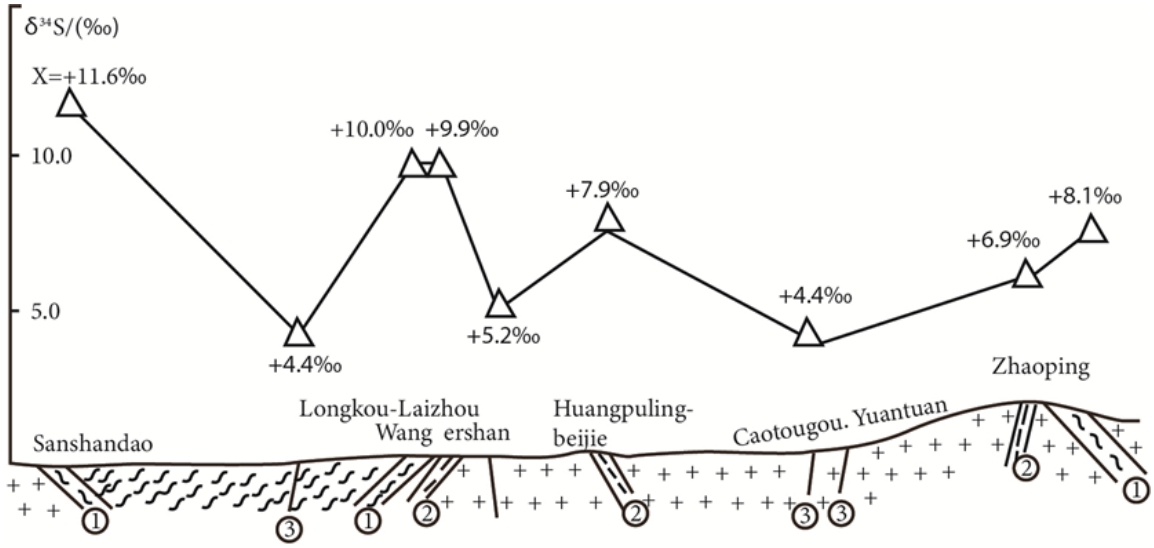

Figure 6. $\delta^{34}S$ changes along the Sanshandao-Linglong gold deposits section depending on the ores-hosted fractures (Jingwen Mao quoted from Figure 4 in Wang et al's original work[19])

Note: ① Regional ductile shear zone; ② Shear zone; ③ Subsidiary fracture.

Author's note of this paper: In Wang et al's original work[19], ① is regional brittle-ductile-shear zone; ② is ductile shear zone; and ③ is subsidiary control fracture

Regarding this statement by Jingwen Mao, we interpret it as follows:

- In different types of gold deposits in the Jiaodong area, the changes in the sulfur isotope composition of sulfides are closely related to the oxygen fugacity fO_2.
- Pyrite formed in the tectonic background of large-scale tensional (open) fault systems (note: relatively high oxygen fugacity) has a higher $\delta^{34}S$ value.

- Pyrite formed in the tectonic background of small-scale relatively closed fault systems (note: relatively low oxygen fugacity) has a lower $\delta^{34}S$ value.

In short, Jingwen Mao believes that the $\delta^{34}S$ value of sulfides and oxygen fugacity (fO_2) are positively correlated in the Jiaodong gold mining area. This view is completely wrong and completely distorts the academic view of Wang et al.[19].

According to Ohmoto's $\log fO_2$ - pH sulfur isotope evolution diagram, namely Figure 7 in this paper (1972), when $\delta^{34}S_{\Sigma S}$ = 0‰ and pH ≤ 7, the $\delta^{34}S_{Py}$ value is basically negative. When $\log fO_2 \geq -38$, $\delta^{34}S_{Py} = -0.3$. As $\log fO_2$ continues to increase, the $\delta^{34}S_{Py}$ value instantly becomes a large negative value, which can be as large as -24 to -26[20]. Obviously, Jingwen Mao's understanding that the above-mentioned sulfide $\delta^{34}S$ value and oxygen fugacity (fO_2) are positively correlated is completely opposite to the research results of Ohmoto[20].

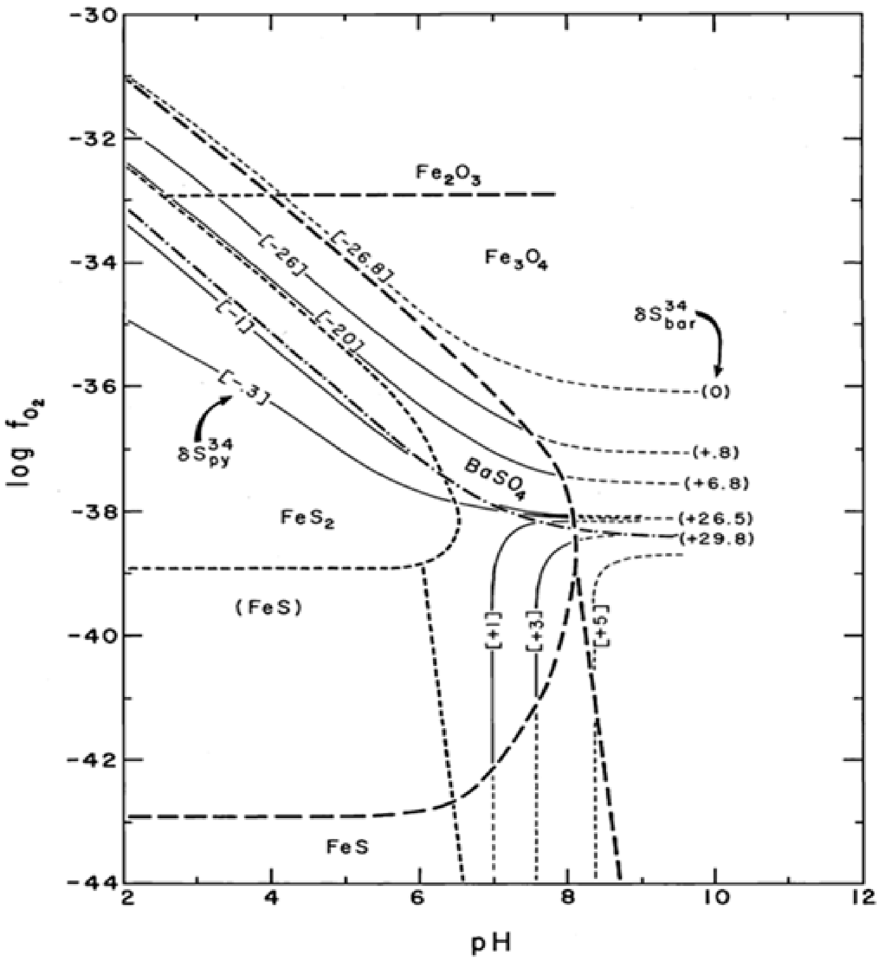

Figure 7. Comparison of the positions of $\delta^{34}S_i$ contours with the stability fields of Fe-S-O minerals and barite (T = 250 °C and I = 1.0)[20]

Note: ~……: $\delta^{34}S_i$ contours. Values in [ ] and ( ) are respectively for pyrite and barite at $\delta^{34}S_{\Sigma S}$ = 0‰; ———: Fe-S-O mineral boundaries at $\sum S$ = 0.1 moles/kg H_2O; - - - - : Fe-S-O mineral boundaries at $\sum S$ = 0.001 moles/kg H_2O; -•-•-: barite soluble/insoluble boundary at $m_{Ba+2}.m_{\sum S} = 10^{-4}$ (Under these T and I conditions, an increase of m_{Ba+2} or $m_{\sum S}$ value by 1 order of magnitude drops the boundary by about 0.5 $\log fO_2$ units)

Wang et al. (2002) set that when T = 250 °C and I = 1.0, pH = 4.3 - 7.2, $\delta^{34}S_{\Sigma S}$ = 10‰, based on the mineral paragenesis combination research and theoretical calculation, it was determined that the $\log fO_2$ of quartz vein-type gold deposits is relatively high (-34 - -37), and the $\log fO_2$ of altered rock-type gold deposits is relatively low (-34 - -40)[19].

According to the relationship between $\delta^{34}S_{Py}$ of sulfide and logfO_2, the $\delta^{34}S_{PY}$ of pyrite in Jiaodong area ranges from 5.0‰ to 11.0‰, among which the quartz vein type gold deposit is 5.0‰ to 8.0‰, and the altered rock type gold deposit is 8.0‰ to 11.0‰. However, as the logfO_2 performance continues to increase, $\delta^{34}S_{PY}$ changes sharply towards the negative value direction. Further, under the background of overall enrichment of ^{34}S in Jiaobei terrane, Wang et al. analyzed the relationship between the sulfur isotope composition of regional gold deposits and the level, mechanical properties and occurrence of ore-controlling structures based on the control of regional structure on $\delta^{34}S$ of the ore fields. Generally, gold deposits distributed along the main fault surface or its hanging and foot walls (mainly the foot wall) in regional primary and secondary brittle-ductile shear zones with a gentle inclination (generally less than 45 degrees) are characterized by relatively enriched ^{34}S. The ^{34}S of gold deposits located in the third and fourth order brittle faults (mostly steep ones) far away from the main fault zone is relatively low. That is, the order and nature of the ore-controlling structure are closely related to the ^{34}S of the deposit. This has resulted in the spatial pattern of alternating distribution of four ^{34}S high-value zones and three ^{34}S low-value zones of sulfur isotopes in the Zhaoyuan-Yexian gold deposit belt. It is based on the above research results that Wang et al. (2002) produced Figure 6[19].

As shown in Figure 6, the structural belt numbered ① has four high-value $\delta^{34}S$ belts in Sanshandao, Longkou-Laizhou, and Zhaoping area. On the contrary, the structural belt numbered ③ has three low-value $\delta^{34}S$ belts in Tenjia, Chijia, Wasunjia, Qiansunjia, Caotouguo, and Yuantuan areas.

However, Jingwen Mao's interpretation of Figure 6 is completely opposite to Wang et al's[19]. He believes that the tectonic belt numbered ① belongs to a tensile (open) fault system, i.e., an environment with relatively high oxygen fugacity. If so, the $\delta^{34}S$ of its sulfide should be a low-value belt, not a high-value belt. Similarly, Mao believes that the tectonic belt numbered ③ belongs to the tectonic background of a small-scale relatively closed fault system, i.e., an environment with relatively low oxygen fugacity. And under the mineralization conditions of low fO_2, the $\delta^{34}S$ of its sulfide should be a high-value belt, not a low-value belt[1]. Obviously, Jingwen Mao's understanding not only violates the original intention and conclusion of Wang et al.[19], but also violates the basic principle of Ohmoto (1972) on the evolution of sulfur isotopes under logfO_2 - pH conditions[20].

Wang et al. also conducted more detailed research on the control of regional structure on $\delta^{34}S$ of the ore fields[19]. For example, he concluded that the Jiaojia Fault Zone, which controls super-large gold deposits such as Jiaojia and Xincheng, is a brittle-ductile shear zone with a gentle dip angle, and is a regional class I ore-controlling fault zone. The fault zone was mainly plastically deformed in the early stage, and superimposed with brittle deformation in the late stage. This medium-deep semi-closed thermodynamic environment is conducive to the exchange equilibrium of sulfur isotopes, so the gold deposits controlled by this fault zone are all characterized by high $\delta^{34}S$ values. For example, in the Linglong ore field, the Taishang gold deposit, which is located in the Potouqing Fault Zone and is controlled by the main fault surface, has a $\delta^{34}S$ = 8.0‰, and the Fushan gold mine has a $\delta^{34}S$ = 8.3‰.

This shows that the closer to the main fault zone (brittle-ductile shear zone) controlling the ore in the region, the greater the probability of the occurrence of altered rock-type gold deposits, and the higher the $\delta^{34}S$ of sulfides. The quartz vein-type (Linglong-type) gold deposits in the brittle faults far away from the main fault surface in the footwall of the main fault have the lowest $\delta^{34}S$. The above-mentioned $\delta^{34}S$ high-value belt (area) controlled by regional structure, from west to east, the $\delta^{34}S$ of Sancang ore field is 11.6‰, the $\delta^{34}S$ of Jiaoxin ore field is 9.6‰, the $\delta^{34}S$ of Lingbei ore field is 7.9‰, the $\delta^{34}S$ of Linglong ore field is 6.9‰, and the $\delta^{34}S$ of Xia (dian)-Jiu (dian) ore field (southern section of Zhaoping fault) is 7.3‰.

On the contrary, the $\delta^{34}S$ of the Tengjia and Chijia gold deposits between the Sanshandao Fault and the Jiaojia Fault is 3.7‰ - 5.8‰, which is characterized by low $\delta^{34}S$. The Wa Sunjia and Qian Sunjia gold deposits distributed along the secondary faults of the Jinhuashan-Wa Sunjia fault zone between the Wangershan Fault and the Ling-Bei Fault are also characterized by low $\delta^{34}S$ = 2.8‰ - 5.3‰.

These specific data once again prove that the above academic views of Wang et al.（2002）are correct[19].

Wang et al. (2002) studied the relationship between $\delta^{34}S$ and logfO_2 of sulfides from the perspective of how redox conditions affect the conversion between H_2S and SO_4^{2-}, and pointed out that the sulfur isotopes of gold mines in the Zhaoyuan-Yexian area are characterized by rich $\delta^{34}S$[18].

According to the analysis results of inclusion composition, the sulfur in the fluid during the mineralization period of Jinchiling gold deposit is mainly H_2S, with only trace amounts of SO_4^{2-}. In the temperature range of 150 - 300 ℃, pyrite $\delta^{34}S$ (4.75‰) basically represents the $\delta^{34}S$ of hydrothermal fluid. The $\delta^{34}S$ of sphalerite in Shilipu silver mine varies from -2.12‰ to -4.6‰. The reason for the decrease in sphalerite $\delta^{34}S$ may be the increase in hydrothermal fO_2 during the polymetallic mineralization stage, which leads to the transformation of $H_2S \rightarrow SO_4^{2-}$.

This indicates that the difference in sulfur isotopes is due to the increase in oxygen fugacity during fluid evolution, which causes part of H_2S to be converted into SO_4^{2-}, and SO_4^{2-} is enriched in heavy sulfur. For example, at 250 ℃, 4% of H_2S in the hydrothermal fluid is converted into SO_4^{2-}, and the $\delta^{34}S$ of sphalerite decreases by about 1‰ in Jinchiling Gold Mine. 20% of H_2S in the hydrothermal fluid is converted into SO_4^{2-}, and the $\delta^{34}S$ of sphalerite decreases by about 7‰ in Shilipu Silver Mine. For another example, among the deposits in the study area, the oxygen fugacity (fO_2) of Liukou Gold Mine is as high as -33 - -34, and its $\delta^{34}S_{py}$ can reach as low as -14.2‰, with an average of 4.3‰ for 7 samples[18]. The above facts show that the $\delta^{34}S$ of sulfides in hydrothermal endogenous metal deposits is closely related to the oxygen fugacity (fO_2) under mineralization conditions, but it is not a positive correlation, but a reverse increase and decrease.

Jingwen Mao consulted the paper by Wang et al. (2002)[19], but he did not understand it. In order to explain the distribution characteristics of $\delta^{34}S$ of sulfides in the Jiaodong gold mining area, which has four high-value bands and three low-value bands as shown in Figure 6, Jingwen Mao not only completely reversed right and wrong, but also attributed this error to Wang[18] and Wang et al.[19]. This is not only an unethical academic behavior, but also shows that Jingwen Mao does not understand the basic knowledge of sulfur isotope geochemistry.

Sulfur isotopes are one of the important means to study the source of ore-forming materials and the genesis of ore deposits. The relevant contents discussed by Ohmoto, Wang, and Wang etc. should be familiar to ore geologists[18-20]. But Jingwen Mao turned right and wrong upside down. In the field of scientific research, such behavior of pretending to know is intolerable.

What is even more despicable is that Jingwen Mao linked his own erroneous views with Wang et al.[18]. For this reason, we consulted Wang et al.'s paper[18]. In their paper, Wang et al. did not mention any relationship between the $\delta^{34}S$ value of sulfides and ore-controlling structures in the Jiaodong gold mining area. Jingwen Mao completely fabricated and imposed his views on others.

6 Conclusions

As can be seen from the above discussion, in order to determine the source of the ore-forming fluid of the Jiaodong gold deposit and explore the genesis of the deposit, Jingwen Mao chose sericite as the target mineral, extracted water from sericite by crushing, and determined the hydrogen and oxygen isotope composition of the ore-forming fluid, which is completely wrong.

In the absence of the oxygen isotope fractionation coefficient relationship between sericite and water, Jingwen Mao used the oxygen isotope fractionation coefficient relationship between muscovite and water instead, which is a mistake on top of a mistake.

When explaining the relationship between the high and/or low changes in the $\delta^{34}S$ values of sulfides in different types of Jiaodong gold deposits and $\log fO_2$, Jingwen Mao believed that the high or low changes in the $\delta^{34}S$ values of sulfides were positively correlated with $\log fO_2$, which completely contradicted the research results of Ohmoto.

In the field of stable isotope geochemistry, Jingwen Mao's paper with frequent errors was published in *Ore Geology Reviews*, which had a wide impact and a very bad effect. As an ore geologist, he made such a low-level mistake in such a conventional research field, which is a shame for the Chinese geological community.

Science pursues truth as its ultimate goal, and scientists take benefiting mankind as their responsibility. This sacred mission does not tolerate any form of fraud, pretending to know, or making up stories. This bad behavior that is completely contrary to the professional ethics of scientific workers must be exposed.

The author has not conducted any research on the Jiaodong gold mine, but the purpose of this article is to clarify matters and get to the bottom of things.

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