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Multiple Solutions of Ore-Forming Fluids of Carbonate Rock-Related Nephrites Constrained by the Hydrogen and Oxygen Isotopes

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Abstract: Hydrogen and oxygen isotopes of ore-forming fluid of nephrite deposit have always been changing due to mixings between different fluids and oxygen isotope exchanges between the ore-forming fluid and country rocks, resulting in that tremolites (or actinolite) have to constantly re-establish new isotope fractionation equilibriums with the dynamic fluid, which is of great significance to understand the genesis of hydrogen and oxygen isotopes of nephrites. Based on this, Taylor closed model and fluid mixing model are used to unravel the control of multi-stage evolution of ore-forming fluid on the δD and $\delta^{18}O$ of nephrite. Although Taylor closed model is conducive to interpreting the genesis of nephrite with light δD and $\delta^{18}O$, such as Vitim nephrite and Chuncheon nephrite, it is unable to be effectively used in other nephrites. The fluid mixing model can quantitatively constrain proportions of different fluids during different ore-forming stages. Multiple solutions of ore-forming fluids of carbonate rock-related nephrites result from the absence of external constraints, such as isotope compositions of intrusive rocks, carbonate rocks and meteoric water. Due to the generally heavy $\delta^{18}O$ of country rocks of carbonate rocks, a small amount of meteoric water that enters the hydrothermal system in the later ore-forming stage is insufficient to offset the $\delta^{18}O$ increment of nephrite caused by the oxygen isotope exchange between country rocks and water, which should be responsible for the abnormal heavy $\delta^{18}O$ of Luodian nephrite, Dahua nephrite, Sanchakou nephrite, Xiaomeiling nephrite, etc, not metamorphic water dominating their formation.

Keywords: Hydrogen and oxygen isotopes; nephrite; ore-forming fluid; Taylor closed model; fluid mixing model; multiple solutions

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1. Introduction

Hydrogen and oxygen isotopes of rocks and minerals are generally useful as isotopic tracers in analyzing the source and evolution of geological fluid [1]. Nephrite, a metamorphic rock composed of tremolite (or actinolite), has a natural advantage of using the δD and $\delta^{18}O$ to discuss the origin of its ore-forming fluid. In the past two decades, it is very prevalent to adopt the δD and $\delta^{18}O$ of nephrite to invert the origin of ore-forming fluid [2–7]. S-type nephrite occurred in serpentinite (or serpentinite mélange) has a wide range of δD and $\delta^{18}O$ [8,9], and sources of the ore-forming fluid are complex, involving the metamorphic water, seawater and meteoric water [9]. For C-type primary nephrites that is associated with carbonate rocks, the δD and $\delta^{18}O$ of nephrite from the same deposit are relatively convergent (Figure 1a) [2,4,5,7,10], but there are significant differences in δD and $\delta^{18}O$ among different nephrites, resulting in the diversity of interpretation on their ore-forming fluids [7,10].

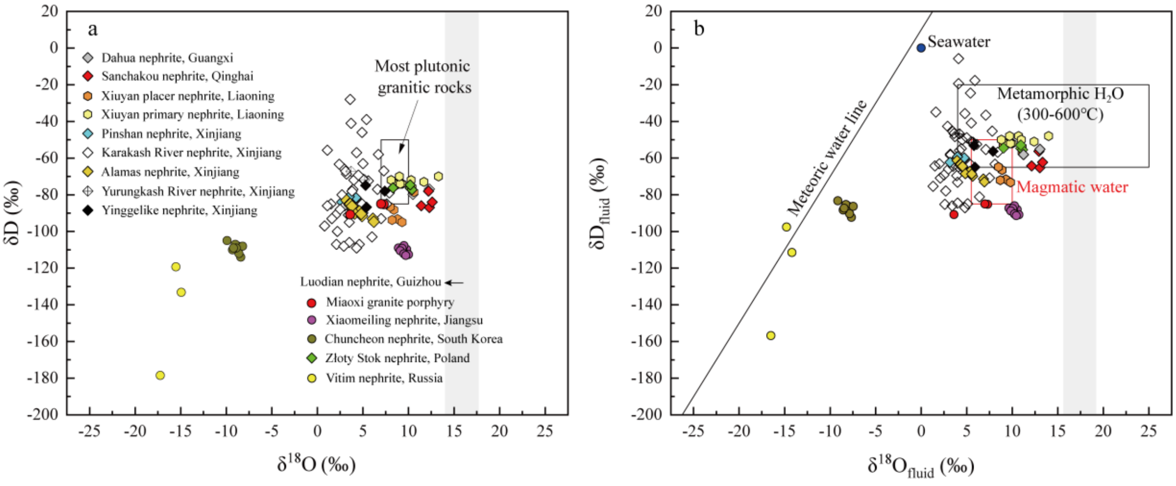

Figure 1. **(a)** δD and $\delta^{18}O$ of different nephrites. **(b)** δD and $\delta^{18}O$ of ore-forming fluids of different nephrites at 350°C. Isotopic range of most plutonic granitic rocks is from Taylor (1977) [1].

Traditionally, metamorphic water is considered as the source of ore-forming fluid of nephrites with heavy $\delta^{18}O$, such as Sanchakou nephrite ($\delta^{18}O$=+11.4-+12.6‰) [11], Dahua nephrite ($\delta^{18}O$=+10-+12.3‰) [12] and Luodian nephrite ($\delta^{18}O$=+14.1-+17.7‰) [13] (Table 1 and Figure 1). However, this assertion is not supported by the geological settings. These nephrites are formed by contact metasomatism between basic rocks and carbonate rocks, therefore the genesis of $\delta^{18}O$ anomaly of these nephrite is still a controversial issue. In addition, hydrogen and oxygen isotope compositions of parent rocks of nephrite are of considerable importance, because any composition in the system must be accounted for during the evolution of ore-forming fluids, otherwise it is difficult to determine actual causes of δD and $\delta^{18}O$ anomaly of nephrite, much less to trace sources of ore-forming fluids. But so far, researches on isotope compositions of parent rocks lag behind that of nephrites. Understanding how parent rocks control the isotope compositions of nephrite can contribute to the constraint of the origin and evolution of ore-forming fluids. Correspondingly, it is not comprehensive to determine the ore-forming fluids of nephrites only by the δD and $\delta^{18}O$ of tremolite. These questions motivate us to discuss the couplings between fluids, country rocks and tremolite, and re-deconstruct the source and evolution of ore-forming fluids of nephrites.

Table 1. Hydrogen and oxygen isotope compositions of different nephrites and the ore-forming fluids (‰).

Nephrite deposit	Sample No.	δD	$\delta^{18}O$	δD_{H_2O}	$\delta^{18}O_{H_2O}$			References
					330°C	390°C	450°C	
Pishan, Xinjiang	392-1	-89.9	4.99	-68.2	5.48	6.11	6.51	[14]
	392-2	-81.8	4.27	-60.2	4.76	5.39	5.79	
	392-3	-84.0	2.67	-62.3	3.16	3.79	4.19	
	392-4	-82.4	3.63	-60.7	4.12	4.75	5.15	
	392-5	-82.4	3.89	-60.7	4.38	5.01	5.41	
	392-6	-83.0	3.92	-61.3	4.41	5.04	5.44	
	392-7	-81.6	4.24	-59.9	4.73	5.36	5.76	
	392-8	-81.0	3.50	-59.3	3.99	4.62	5.02	
Yingelike, Ruoqiang, Xinjiang	H-3	-74.9	5.3	-53.2	5.79	6.42	6.82	[4]
	H-4	-78.0	7.4	-56.3	7.89	8.52	8.92	
	H-5	-86.7	5.4	-65.0	5.89	6.52	6.92	
					350°C	400°C	450°C	
Xiaomeiling, Liyang, Jiangsu	LY-Q-13	-109.0	8.9	-87.3	9.64	10.10	10.42	This study

	LY-Q-14	-109.8	9.8	-88.1	10.54	11.00	11.32	
	LY-Q-16	-110.3	9.4	-88.6	10.14	10.60	10.92	
	LY-HL-3	-107.7	9.5	-86.0	10.24	10.70	11.02	
	LY-HL-7	-109.2	9.3	-87.5	10.04	10.50	10.82	
	LY-HL-10	-110.5	9.1	-88.8	9.84	10.30	10.62	
	LY-QB-3	-112.6	10.0	-90.9	10.74	11.20	11.52	
	LY-QB-12	-112.2	9.5	-90.5	10.24	10.70	11.02	
	LY-QB-21	-113.1	9.7	-91.4	10.44	10.90	11.22	
					293℃	350℃	400℃	
Alamas, Xinjiang	ABY-1	-86.7	3.8	-65.0	3.7	4.54	5.00	[3]
	ABY-1	-83.0	3.2	-61.3	3.1	3.94	4.40	
	AQB-1	-93.1	6.1	-71.4	6.0	6.84	7.30	
	AQB-2	-89.0	4.6	-67.3	4.5	5.34	5.80	
	AQB-3	-85.1	3.5	-63.4	3.4	4.24	4.70	
	AQB-4	-85.9	3.6	-64.2	3.5	4.34	4.80	
	AQB-6	-94.7	6.2	-73.0	6.1	6.94	7.40	
	AQY-1	-90.2	4.1	-68.5	4.0	4.84	5.30	
	AQY-2	-85.0	3.6	-63.3	3.5	4.34	4.80	
	AQY-3	-91.6	4.9	-69.9	4.8	5.64	6.10	
	AQY-4	-90.4	4.8	-68.7	4.7	5.54	6.00	
	AQY-5	-86.2	3.8	-64.5	3.7	4.54	5.00	
					330℃	350℃	430℃	
Yurungkash River, Xinjiang	ZY2	-71.8	5.2	-51.4	5.7	6.0	6.6	[15]
	ZY3	-67.3	3.7	-46.8	4.2	4.4	5.1	
Karakash River, Xinjiang	QZY4	-72.4	5.6	-52.5	6.1	6.3	7.0	
	QZY5	-55.7	1.1	-34.9	1.6	1.8	2.5	
	QZY6	-71.4	5.0	-51.0	5.5	5.7	6.4	
	QZY7	-65.7	2.9	-45.2	3.4	3.6	4.3	
	MY1	-68.7	3.2	-48.3	3.7	4.0	4.6	
	MY2	-63.3	2.4	-42.7	2.9	3.1	3.8	
	MY3	-69.3	4.5	-48.9	5.0	5.3	5.9	
	MY4	-67.1	3.1	-46.6	3.6	3.8	4.5	
					330℃	390℃	450℃	
Karakash River, Xinjiang	MYH1	-97	0.8	-75.4	1.3	1.9	2.3	[2]
	MYH2	-93	7.0	-70.8	7.5	8.1	8.5	
	MYH3	-107	4.6	-84.9	5.1	5.7	6.1	
	MYH4	-80	2.7	-57.9	3.2	3.9	4.2	
	MYH6	-63	5.0	-40.9	5.5	6.2	6.6	
	MYH7	-67	7.3	-45.3	7.8	8.4	8.8	
	MYH10	-46	4.9	-24.6	5.4	6.0	6.4	
	MYH11	-28	3.6	-5.8	4.1	4.7	5.1	
	MYH21	-39	5.4	-17.7	5.9	6.6	7.0	
	MYH24	-106	3.5	-84.5	4.0	4.6	5.0	
	MYH25	-41	3.7	-19.4	4.1	4.8	5.2	
	MYH30	-80	2.7	-58.4	3.2	3.8	4.2	
	MYH31	-85	7.6	-63.3	8.1	8.8	9.1	
	MYH32	-85	1.5	-63.1	2.0	2.6	3.0	
	MYH33	-86	1.1	-64.3	1.5	2.2	2.6	
	MYH34	-77	6.6	-55.3	7.1	7.8	8.2	
	MYH35	-91	2.0	-69.2	2.5	3.2	3.6	
	MYH36	-107	2.1	-85.2	2.6	3.2	3.6	
	MYH37	-91	3.4	-69.6	3.9	4.5	4.9	
	MYH38	-87	3.6	-64.8	4.1	4.7	5.1	
	MYH39	-58	6.7	-36.6	7.1	7.8	8.2	
	MYH40	-77	3.9	-54.8	4.4	5.0	5.4	
	MYH41	-78	3.8	-55.8	4.2	4.9	5.3	
	MYH42	-57	4.3	-35.7	4.8	5.4	5.8	
	MYH43	-108	2.9	-86.1	3.4	4.0	4.4	
	MYH44	-86	3.0	-64.5	3.5	4.1	4.5	

	MYH50	-85	4.9	-63.5	5.4	6.0	6.4	
	MYH51	-100	2.2	-77.9	2.7	3.3	3.7	
	MYH52	-79	7.9	-56.8	8.4	9.0	9.4	
	MYH54	-88	2.5	-66.0	3.0	3.7	4.1	
	MYH55	-103	6.0	-81.1	6.4	7.1	7.5	
	MYH56	-95	3.5	-73.2	4.0	4.6	5.0	
	MYH57	-109	4.3	-87.1	4.8	5.5	5.9	
	MYH58	-72	4.0	-50.1	4.5	5.1	5.5	
	MYH59	-93	1.6	-70.9	2.1	2.7	3.1	
					350°C	400°C	450°C	
Dahua, Guangxi	D-4	-76.9	12.3	-55.2	13.04	13.50	13.82	[16]
	D-8	-79.8	10.5	-58.1	11.24	11.70	12.02	
Luodian, Guizhou	LDS		15.8		16.54	17.00	17.32	[17]
	LDW1		16.4		17.14	17.60	17.92	
	LDW5		15.4		16.14	16.60	16.92	
	LDGW-1		17.7		18.44	18.90	19.22	
	LDW6		15.2		15.94	16.40	16.72	
	LDLG4		15.8		16.54	17.00	17.32	
Luodian, Guizhou	LMBT-13-2		15.3		16.04	16.50	16.82	[18]
	LMTC08-7		14.3		15.04	15.50	15.82	
	11KY080		15.6		16.34	16.80	17.12	
	11KY181		16.5		17.24	17.70	18.02	
	ETC05-2-5		14.7		15.44	15.90	16.22	
	ETC05-2-6		14.5		15.24	15.70	16.02	
	ETC05-4		14.1		14.84	15.30	15.62	
	ETC05-6		14.6		15.34	15.80	16.12	
	ETC05-8		15.5		16.24	16.70	17.02	
	ETC05-23		16.3		17.04	17.50	17.82	
					350°C	400°C	650°C	
Sanchakou, Qinghai	QH-176	-86	11.4	-64.3	12.13	12.60	13.35	[19]
	QH-177	-87	12.3	-65.3	13.03	13.50	14.25	
	QH-001	-78	12.2	-56.3	12.93	13.50	14.15	
	QHSH-001	-84	12.6	-62.3	13.33	13.80	14.55	
					330°C	390°C	450°C	
Xiuyan placer nephrite, Liaoning	LHM15-1	-88.23	8.40	-66.53	8.89	9.52	9.92	[20]
	LHM15-2	-75.2	8.50	-53.5	8.99	9.62	10.02	
	LHM15-3	-93. 29	8.80	-71.59	9.29	9.92	10.32	
	LHM15-4	-94.95	9.30	-73.25	9.80	10.42	10.82	
	LHM15-5	-78.51	10.60	-56.8	11.09	11.72	12.12	
	LHM15-6	-93.78	8.20	-72.07	8.69	9.32	9.72	
	LHM15-7	-86.58	8.00	-64.88	8.49	9.12	9.52	
					350°C	400°C	450°C	
Xiuyan, Liaoning	Y-1	-70	10.0	-48	10.7	11.20	11.52	[21]
	Y-3	-74	9.3	-52	10	10.50	10.82	
	G-3	-74	8.5	-52	9.2	9.70	10.02	
	G-6	-72	8.1	-50	8.8	9.30	9.62	
	W-1	-70	13.3	-48	14	14.50	14.82	
	W-2	-73	11.7	-51	12.4	12.90	13.22	
	S-1a	-76	10.4	-54	11.1	11.60	11.92	
	S-1b	-72	10.3	-50	11	11.50	11.82	
	S-3a	-74	9.1	-52	9.8	10.30	10.62	
	S-3b	-70	9	-48	9.7	10.20	10.52	
Chuncheon, South Korea	NE1	-108	-8.7	-86.3	-7.96	-7.50	-7.18	[5]
	NE2	-114	-8.4	-92.3	-7.66	-7.20	-6.88	
	NE3	-105	-9.9	-83.3	-9.16	-8.70	-8.38	
	NE4	-107	-9	-85.3	-8.26	-7.80	-7.48	
	NE5	-108	-8.2	-86.3	-7.46	-7.00	-6.68	
	NE6	-112	-8.6	-90.3	-7.86	-7.40	-7.08	
	NE7	-109	-8.9	-87.3	-8.16	-7.70	-7.38	

	NE8	-110	-9.3	-88.3	-8.56	-8.10	-7.78	
	NE9	-109	-9.2	-87.3	-8.46	-8.00	-7.68	
Złoty Stok, Poland	A	-76.4	10.2	-54.7	10.94	11.40	11.72	[22]
	B	-76.2	8.3	-54.5	9.04	9.50	9.82	
	C	-77.2	10.4	-55.5	11.14	11.60	11.92	
	D	-74.6	10.2	-52.9	10.94	11.40	11.72	
Vitim, Russia		-119.3	-15.52	-97.6	-14.78	-14.32	-14.00	
		-178.5	-17.24	-156.8	-16.50	-16.04	-15.72	[6]
		-133.2	-14.93	-111.5	-14.19	-13.73	-13.41	

δD_{H_2O} and $\delta^{18}O_{H_2O}$ that are not given in references can be calculated by the hydrogen and oxygen isotope equilibrium fractionation equations between tremolite and water. Oxygen isotope equilibrium fractionation equation is $1000\ln\alpha_{Tr\text{-}Water}=3.95\times10^6/T^2-8.28\times10^3/T+2.38$ [23]. Hydrogen isotope equilibrium fractionation equation is $10^3\ln\alpha_{Tr\text{-}Water}=-21.7\pm2$ [24]. T is the absolute temperature.

2.δ. D and δ^{18}O of Different Rocks in C-Type Nephrite Deposits

2.1.δ. D and δ^{18}O of C-Type Nephrite

Although the contact metasomatism between intrusive rocks and carbonate rocks dominates the formation of most C-type nephrites, such as C-type nephrites widely distributed in the southern margin of Tarim Basin [3,4,25,26], Sanchakou nephrite [11], Xiaomeiling nephrite [27], Vitim nephrite [6,28], Chuncheon nephrite [5], Złoty Stok nephrite [22], Dahua nephrite [12], Luodian nephrite [13], etc, significant differences in the δD and δ^{18}O between different nephrites suggest that their ore-forming fluids have different evolutionary processes.

Meteoric water is considered to be participated in the ore-forming processes of Vitim nephrite [6,28], Chuncheon nephrite [5] and Xiaomeiling nephrite (Figure 1b), and their δD and δ^{18}O domains are independent of each other and do not overlap with other nephrites (Figure 1a), making them highly recognizable. Paradoxically, the δD of Xiaomeiling nephrite is much the same as that of Chuncheon nephrite, which could be attributed to meteoric water participating in the growth of tremolite, but the δ^{18}O far exceeding that of its parent rock (Miaoxi granite porphyry) indicates the existence of other heavy δ^{18}O material in the Xiaomeiling nephrite deposit (Figure 1a and Table 1). The anomaly is difficult to be explained from previous studies about the ore-forming fluid of nephrite.

For Pishan nephrite, Alamas nephrite, Yinggelike nephrite and Złoty Stok nephrite, their δD and δ^{18}O domains and their ore-forming fluids are concentrated in and around that of most plutonic granitic rocks and that of magmatic water (Figure 1), indicating that magmatic water from intrusive rocks plays an important role in their ore formation processes. There is a significant difference between Xinjiang primary nephrites (Pishan nephrite, Alamas nephrite and Yinggelike nephrite) and Xinjiang secondary nephrites produced from Yurungkash and Karakash River. The δD and δ^{18}O of Xinjiang primary nephrites are slightly less than those of most plutonic granitic rocks [1], and the range of ore-forming fluids is relatively narrow and closer to magmatic water (Figure 1) [3,4,26]. The range of δD and δ^{18}O of secondary nephrites is much broader (Figure 1) [2]. indicating that the weathering related to low-temperature water-rock interactions may dominate the evolution of δD and δ^{18}O of secondary nephrites (Figure 1). The δ^{18}O range of Xiuyan placer nephrite overlaps with that of Xiuyan primary nephrite, while its δD is generally lighter (Figure 1), which could be the result of weathering. Consequently, the influence of Earth's surface geochemical processes on the δD and δ^{18}O of secondary nephrite is also a noteworthy issue.

Some nephrites are considered to be products of regional metamorphism, such as Xiuyan primary nephrite [29], Mastabia nephrite [30], Scortaseo nephrite [31], Luanchuan nephrite and Longxi nephrite. Previous researches suggested that the ore-forming fluid of Xiuyan primary nephrite could be the Si-rich hydrotherm produced by regional metamorphism and migmatitization [29,32]. Metamorphic water can be responsible for Xiuyan primary nephrites with heavy δ^{18}O (Figure

1), but the source of metamorphic water with heavy δ^{18}O directs the crux of the problem to the country rock.

The ore-forming fluid hardly has the hydrogen isotope exchange with country rocks of carbonate rocks without hydrogen element, implying that the process controlling the δD and δ^{18}O evolution of tremolite is not synchronous. The δD evolution of ore-forming fluid in the hydrothermal system can be considered as a process only controlled by the initial and external fluid, and with the increase of the proportion of external fluid, the δD of final ore-forming fluid evolves towards the external fluid. Vitim nephrite and Chuncheon nephrite are typical examples of the ore-forming fluid evolving towards meteoric water.

2.2.δ. D and δ^{18}O of Intrusive Rocks and Country Rocks

The fluid, no matter what its source, first reacts with country rocks, then tremolite crystallizes from the fluid, which determines an important significance of country rocks in constraining intermediate states of fluid evolution. As a consequence, it is necessary to investigate isotope compositions of intrusive rocks, carbonate rocks and siliceous rocks associated with the ore formation of nephrites (Table 2 and 3). The heavy δ^{18}O anomalies of nephrites are difficult to be explained by the δ^{18}O of basic rocks and granitic rocks, because the δ^{18}O of basic rocks is between +5.5 and +7.4‰ [33] and the δ^{18}O of intrusive rocks associated with the ore formation of nephrites is not significantly different from the most plutonic granitic rocks (+7 to +10‰) (Table 2) [1].

Table 2. Oxygen isotope compositions of intrusive rocks and siliceous rocks in different nephrite deposits (‰).

Nephrite deposit	Sample No.	Rock	δD	δ^{18}O	Reference
Xiaomeiling, Jiangsu	γ-3	Minaxi Granite porphyry	-90.8	3.6	This study
	γ-4		-85.2	7.3	
	γ-5		-85.0	7.0	
Khaita, Vitim, Russia		Granite		4.16	[6]
Kavokta, Vitim, Russia				9.93	
Luodian, Guizhou	11YK2100	Siliceous rock		22.4	[18]

Due to alteration, the δD and δ^{18}O of γ-3 are lighter than those of unaltered γ-4 and γ-5. Xiaomeiling nephrite is formed by contact metasomatism between Miaoxi granite porphyry and Qixia Formation limestone.

Table 3. Oxygen isotope compositions of carbonate rocks in different nephrite deposits (‰).

Nephrite deposit	Sample No.	δ^{18}O	Sample No.	δ^{18}O*	Reference
Xiaomeiling, Jiangsu	P-1	19.5	C-2	15.2	This study
	P-3	20.7	C-3	14.8	
	P-5	19.9	C-4	16.4	
Chuncheon, South Korea	D-1	18.2	D-18	2.4	[5]
	D-2	18.0	D-19	4.1	
	D-3	15.0	D-20	3.8	
	D-4	14.3	D-21	7.4	
	D-5	18.2			
	D-6	13.7			
	D-7	15.1			
	D-8	15.9			
	D-9	14.7			
	D-10	17.6			
	D-11	15.5			
	D-12	15.5			
	D-13	16.9			
	D-14	14.0			
	D-15	14.4			
	D-16	17.8			
	D-17	14.2			
Golyube, Vitim, Russia		28.4		22.36	[6]

Xiuyan, Liaoning	9872	22.6		[34]
Alamas, Xinjiang	S-1	6.1		
Luodian, Guizhou	EC-4B2	20.2		[18]

δ^{18}O* is the δ^{18}O of carbonate rock after the oxygen isotope exchange between the carbonate rock and fluids. For Alamas nephrite, it cannot determine whether the +6.1‰ of S-1 is the δ^{18}O value after the oxygen isotope exchange.

Generally, country rocks of carbonate rocks associated with the ore formation of nephrites have quite heavy δ^{18}O (Table 3), which is in accord with carbonate rocks formed in the geological history [35]. The δ^{18}O of marble metamorphosed from Qixia Formation limestone exceeds that of Xiaomeiling nephrite and the δ^{18}O of marble (C-2, C-3 and C-4) at the mining pit is lighter than that of marbles (P-1, P-3 and P5) far away from the mining pit (Table 3). For Chuncheon nephrite, the δ^{18}O range of dolomite without oxygen isotope exchanges in the mining area is between +13.7 and +18.2‰, while that of dolomite after exchanges is between +2.4 and +7.4‰ [5]. Compared with the dolomite in Vitim nephrite deposit, the δ^{18}O of newly formed calcite is lighter (Table 3) [10]. In the area of Passo Bondolo, the δ^{18}O of dolomite in metasomatic veins decreases from +23‰ before exchange to +12.5‰ after exchange [36]. Oxygen isotope exchanges between carbonate rocks and water can cause the δ^{18}O depletion of carbonate rocks and the δ^{18}O enrichment of fluid, and it is conceivable that tremolites crystallized from the fluid will inherit the heavy δ^{18}O characteristic of carbonate rocks.

One particular concern is that the δ^{18}O of siliceous rocks is heavier than that of the contemporaneous carbonate rocks [35], making siliceous rocks another important material source for heavy δ^{18}O nephrites. The δ^{18}O of siliceous rock (11YK2100) in contact with Luodian nephrite is up to +22.4‰ and slightly heavier than the EC-4B2 carbonate rock in contact with it (Table 2 and 3) [18]. In addition, the δ^{30}Si range of Luodian nephrite coincides exactly with that of siliceous rocks in carbonate rocks but distinctly differ from that of diabase in the mining area (Table 4) [18], which illustrate that the siliceous rock is the vital source of Si element for Luodian nephrite. In field, Luodian nephrite is always interbedded with banded siliceous rocks in carbonate rocks, while carbonate rocks without siliceous rocks often do not produce nephrites. In similar fashion, the δ^{18}O enrichment of Dahua nephrite is also possibly related to siliceous rocks in carbonate rocks. Therefore, the abnormal heavy δ^{18}O of Luodian nephrite and Dahua nephrite should arise out of complex oxygen isotope exchanges between carbonate rock, siliceous rock, water and tremolite.

Table 4. Silicon isotope compositions of nephrite, diabase and siliceous rock in Luodian deposit (‰).

Nephrite deposit	Sample No.	Rocks	δ^{30}Si	Reference
Luodian, Guizhou	11YK2100	Siliceous rock	1.4	[18]
	LMBT-13-2	Nephrite	1.3	
	LMTC08-7		1.2	
	11KY080		1.2	
	11KY181		1.1	
	ETC05-2-5		1.4	
	ETC05-2-6		1.7	
	ETC05-4		1.4	
	ETC05-6		1.3	
	ETC05-8		1.1	
	ETC05-23		1.2	
Luodian, Guizhou	LDS	Nephrite	0.3	[17]
	LDW1		0.8	
	LDW5		0.7	
	LDGW-1		0.3	
	LDW6		0.7	
	LDLG4		0.8	
	LKT001-C	Siliceous rock	0.5	
	LKT002		0.4	
	LJGL-1	Diabase	0.2	

LJGL-2	0.0
LJGL-4	0.1

3. Multi-Stage Water/Rock Interactions

3.1. Isotope Exchanges Between Water and Minerals

Before the crystallization of tremolite, the isotope exchange between the initial fluid (W^1) and country rocks is the first predictable process (I). There is only the oxygen isotope exchange for the initial fluid, no the hydrogen isotope exchange, and the initial fluid can be magmatic water, metamorphic water or any other hydrothermal fluid. Equilibrium fractionation equations between mineral and water can be used to calculate the $\delta^{18}O$ of fluid (W^2) after oxygen isotope exchanges (Table 5). If the $\delta^{18}O$ of initial fluid is lighter than that of country rock, the $\delta^{18}O$ of W^2 only depends on reaction temperatures and the $\delta^{18}O$ of country rock. When the temperature is 350°C, the $\delta^{18}O$ of W^2 calculated by oxygen isotope equilibrium fractionation equations of quartz-water, dolomite-water and calcite-water is +17.10‰, +13.76‰ and +16.23‰, respectively (Table 5), which are generally higher than $\delta^{18}O$ values of ore-forming fluids calculated by the $\delta^{18}O$ values of tremolite (Table 1).

Table 5. Oxygen isotope compositions of W^2 and Tr^* at different temperatures (‰).

Stage	Mineral-water	$\delta^{18}O^i$ of country rocks	$\delta^{18}O$ of W^2		
			350℃	400℃	450℃
I	Qtz-W^1	22.4	17.10	18.34	19.34
	Dol-W^1	20.0	13.76	14.94	15.88
	Cal-W^1	20.0	16.23	17.25	18.07
			$\delta^{18}O$ of Tr^*		
II	W^2-Tr		16.36	17.14	17.83
	W^2-Tr		13.02	13.73	14.36
	W^2-Tr		15.50	16.05	16.56

W^2 is the fluid after the oxygen isotope exchange between W^1 and country rocks. The $\delta^{18}O$ of W^1 is set to the left boundary of magma water (+5.5‰). The $\delta^{18}O$ and δD of Tr^* can be calculated by the isotope equilibrium fractionation equation between W^2 and tremolite. Dolomite, limestone and siliceous rock are three kinds of country rocks that are most closely related to the formation of nephrite, so dolomite, calcite and quartz as main minerals of these rocks can be used for the calculation of oxygen isotope exchange reactions. The initial $\delta^{18}O$ values of quartz, calcite and dolomite are set to +22.4‰ (the $\delta^{18}O$ value of siliceous rock in Luodian nephrite deposit in Table 2), +20.0‰ (approaching the average $\delta^{18}O$ value of P series marbles in Xiaomeiling nephrite deposit) and +20.0‰ (for the comparison with nephrites related to the limestone), respectively. Oxygen isotope equilibrium fractionation equations of quartz-water (Qtz-Water), dolomite-water (Dol-Water) and calcite-water (Cal-Water) are $1000\ln\alpha_{Qtz\text{-}Water}=3.38\times10^6/T^2-3.40$ [37], $1000\ln\alpha_{Dol\text{-}Water}=3.2\times10^6/T^2-2.00$ [38] and $1000\ln\alpha_{Cal\text{-}Water}=2.78\times10^6/T^2-3.39$ [39], respectively.

The second predictable process (II) is the crystallization of tremolite from W^2, and isotope compositions of tremolite are bound to be affected by W^2. Assuming that all the initial fluid is converted to W^2 and then tremolites have isotope exchange reactions with W^2, the $\delta^{18}O$ values of tremolites (Tr^*) after the reaction with W^2 under three country rocks conditions are +16.36‰, +13.02‰ and +15.50‰, respectively (Table 5). The genesis of almost all nephrites with heavy $\delta^{18}O$ that have been found so far can be explained by $\delta^{18}O$ values of Tr^*. And yet, the $\delta^{18}O$ values of most nephrites are always lighter than that of Tr^*, indicating that there are other factors controlling isotopic compositions of tremolite.

The $\delta^{18}O$ of $Tr^*_{Dol\text{-}Water\text{-}Tr}$ is significantly lighter than that of $Tr^*_{Qtz\text{-}Water\text{-}Tr}$ and $Tr^*_{Cal\text{-}Water\text{-}Tr}$ at the same temperature (Table 5), which could be an important reason why the $\delta^{18}O$ of nephrite associated with dolomite is relatively light, such as Alamas nephrite, Yinggelike nephrite and Pishan nephrite (Figure 1a), whereas the $\delta^{18}O$ of nephrite associated with limestone and siliceous rock is always heavier, such as Dahua nephrite, Xiaomeiling nephrite and Luodian nephrite (Table 1 and Figure 1a). The δ^{18}O range of Luodian nephrite highly coincides with that of Tr*$_{\text{Qtz-water-Tr}}$ (+16.36‰) (Figure 2b), indicating that almost all of magmatic water from diabase has oxygen isotope exchanges with country rocks. Due to the fact that basic rocks can only release a small amount of magmatic water, country rocks with heavy δ^{18}O can fully exchange with the magmatic water, which is also conducive to explaining why the δ^{18}O enrichment is a common feature of Dahua nephrite, Luodian nephrite and Sanchakou nephrite.

Different from basic rocks, granitic rocks can produce more magmatic water, but perhaps not all of magmatic water can have oxygen isotope exchanges with country rocks. The δ^{18}O of whole hydrothermal fluid will be closer to that of initial magmatic water with the increase of unexchanged magmatic water, which is one possible reason for the δ^{18}O of most nephrites associated with granitic rocks less than the δ^{18}O of Tr*. Meteoric water is another important factor that can cause the evolution of δD and δ^{18}O of ore-forming fluid towards low values, such as Chuncheon nephrite and Vitim nephrite. If δD and δ^{18}O of unaltered Miaoxi granite porphyry are regarded as isotope compositions of initial fluid (W^1), the Tr* should be at the dotted circle (Figure 2a). The evolution direction from the dotted circle to Xiaomeiling nephrite is in sync with the evolution of Miaoxi granite porphyry altered by meteoric water, indicating that meteoric water did participate in the formation of Xiaomeiling nephrite. Therefore, both the impact of internal and external fluids on the evolution of ore-forming fluid and the isotope re-equilibration between the mixed fluid and tremolite should not be ignored.

3.2. Taylor Closed Model

Yui and Kwon (2002) used Taylor open model to discuss the significance of water/rock interaction for the origin of Chuncheon nephrite. Results suggest that Chuncheon nephrite is formed at high W/R ratios and low X_{CO_2} (<0.01-0.1), and the ore-formation fluid is the circulating meteoric water induced by Chuncheon granite, which provides a new insight into the contribution of water/rock interaction to the abnormal δ^{18}O and δD of nephrite. In view of the fact that most of nephrites are not significantly affected by meteoric water, the ore-forming system for most of nephrites should be relatively closed. Consequently, Taylor closed model can be used to discuss the evolution of ore-forming fluid of nephrite whose δ^{18}O value is lower than that of Tr*. Assuming all meteoric water enters the closed hydrothermal system at once, the interactions between Tr* and meteoric water can be expressed by the following equation [1], which is the third water/rock interaction (III):

$$\mathrm{W/R} = \frac{\delta^f_{Tr} - \delta^i_{Tr}}{\delta^i_{H_2O} - \left(\delta^f_{Tr} - \Delta\right)} \tag{1}$$

where i is the initial value, $\delta^i_{H_2O}$ is the δD and δ^{18}O of meteoric water, δ^i_{Tr} is the δD and δ^{18}O of Tr*, f is the final value after exchange, $\Delta = \delta^f_{Tr} - \delta^f_{H_2O}$, W and R are the atom percents of oxygen and hydrogen of meteoric water and tremolite in the total system, respectively. Based on Equation (1), the evolution curve of δD and δ^{18}O of Tr* can be obtained at different W/R ratios (Figure 2).

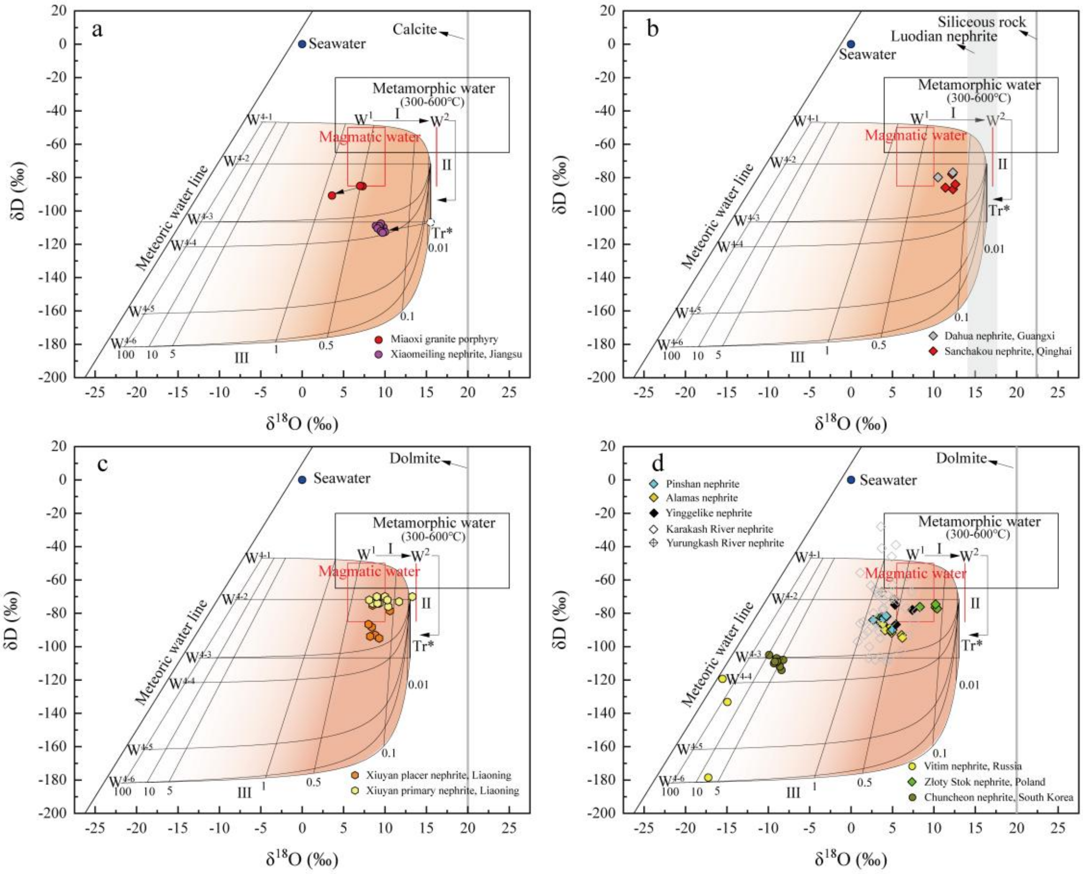

Figure 2. Plot of δD and $\delta^{18}O$ of nephrites versus evolution curves of Tr* interacted with meteoric water in the Taylor closed model. If the δD range of magmatic water is taken as that of initial fluid, W^2 is a red line segment that the abscissa is a constant value, and Tr* is a black line segment parallel to the W^2. δ^i_{Tr} in Equation (1) is set to the upper and lower endpoints of Tr*, and $\delta^i_{H_2O}$ can be set to the different meteoric water (W^4). The δD and $\delta^{18}O$ of W^{4-1}, W^{4-2}, W^{4-3}, W^{4-4}, W^{4-5} and W^{4-6} are (-25, -4.38), (-50, -7.50), (-80, -11.88), (-100, -13.75), (-140, -18.75) and (-160, -21.25), respectively. In fact, W^4 can be any point in the meteoric water line [40]. If the δD range of $\delta^i_{H_2O}$ is consistent with that of magmatic water, the calculated δD of Tr* will be constrained in the region composed of W^{4-2} straight line and W^{4-3} straight line.

The $\delta^{18}O$ of Xiaomeiling nephrite indicates that W/R ratios are between 0.1 and 0.5, much higher than 0.01 reflected by its δD, revealing the inconsistency of W/R ratios in explaining the interaction between meteoric water and Tr* (Figure 2a). The W/R ratios reflected by the $\delta^{18}O$ of Sanchakou nephrite, Dahua nephrite and Złoty Stok nephrite are between 0.1 and 0.5, indicating that a proportion of meteoric water is relatively low in the whole system (Figure 2a and 2d). The W/R ratios reflected by the $\delta^{18}O$ of Alamas nephrite, Pishan nephrite and Yinggelike nephrite (Xinjiang primary nephrite) are between 0.5 and 1, indicating that meteoric water plays an important role in the formation of these nephrites (Figure 2b, 2c and 2d), but the δD values of these nephrites are incapable of accurately constraining the W/R ratios due to a lack of δD of initial fluid and meteoric water. On the other hand, δD values of these nephrites are between the W^{4-2} straight line and the W^{4-3} straight line, implying that the effect of meteoric water on these nephrites should be not significant. If meteoric water participates in the ore formation of Xiuyan nephrite, the W/R ratios will be between 0 and 0.5 (Figure 3c). The W/R ratios of Chuncheon nephrite are more than 5 and there is no inconsistency in the revelation of $\delta^{18}O$ and δD on W/R ratios (Figure 2d), indicating that the ore-forming fluid is mainly composed of meteoric water. Moreover, the range of δD and $\delta^{18}O$ of meteoric water during the formation of Chuncheon nephrite is likely to be between W^{4-3} and W^{4-3} in the meteoric water line [40] (Figure 2d). The W/R ratios of Vitim nephrite are relatively discrete, indicating that the range of δD and $\delta^{18}O$ of meteoric water is relatively broad.

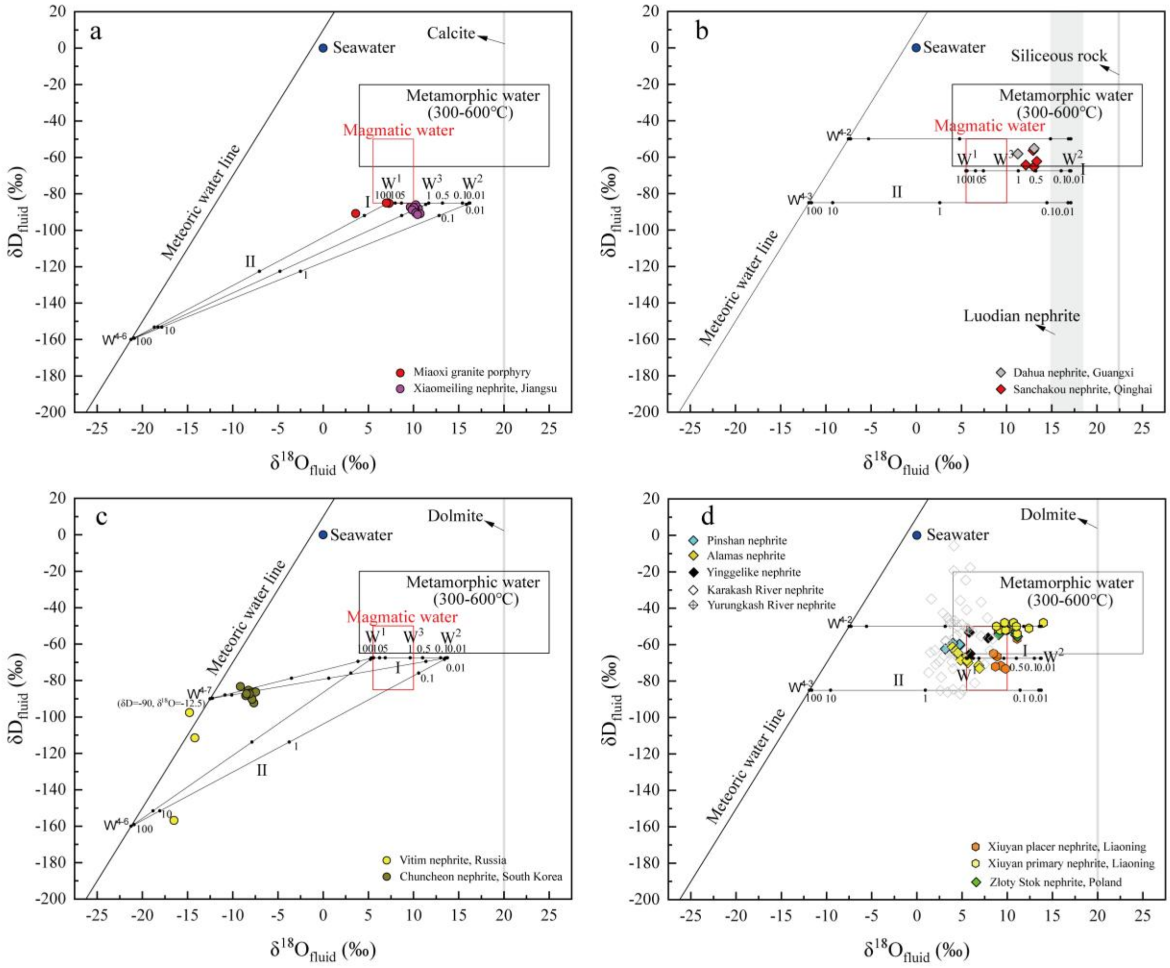

Figure 3. Plot of ore-forming fluids versus the two-stage mixing of ore-forming fluid. Due to the lack of isotope compositions of magmatic water, the δD and δ^{18}O of W^1 in Figure 3b, 3c and 3d are set to -67.5 and +5.5‰, respectively.

An implicit condition in Equation (1) is that meteoric water is the only fluid participating in the water-Tr* interactions, which is responsible for the inconsistency of W/R ratio. In fact, it is difficult to determine that all the initial fluid has oxygen isotope exchanges with country rocks. If there is still part of the initial fluid without oxygen isotope exchanges in the hydrothermal system, and/or not all of W^2 transforms into the constitution water of tremolite in the II process, mixings between the residual initial fluid, W^2 and meteoric water will inevitably cause the $\delta^{i}_{H_2O}$ in Equation (1) to no longer be just meteoric water, but a mixed fluid, which inevitably has an impact on the subsequent evolution of δ^{18}O and δD of tremolite. As a consequence, if there is no way to determine the intermediate states of ore-forming fluid, the evolution of ore-forming fluid of nephrite cannot be truly reflected.

3.3. Fluid Mixing Model

Except isotope exchanges between fluids and country rocks, another process that can effectively affect the δD and δ^{18}O of tremolite is the mixing between different fluids. From magmatic to meteoric water, the evolution of ore-forming fluid can be divided into two mixing processes. The first process (I) is the mixing between the residual initial fluid (W^1) and exchanged fluid (W)^2 at high temperatures, producing the first mixed fluid (W^3). The δD and δ^{18}O of W^3 are only affected by the mixing of W^1 and W^2 due to the absence of meteoric water in the hydrothermal system. W^2 has continuously mixed with the residual initial fluid since its formation. The second process (II) is the mixing between W^3 and meteoric water (W^4) at relatively low temperatures, which produces the second mixed fluid (W^5).

The II process can be regarded as the last effective mixing between different fluids and the isotope re-equilibration between late tremolites and W^5 determines the δD and $\delta^{18}O$ of nephrite. Based on the principle of mass balance, the δD and $\delta^{18}O$ of mixed fluid can be calculated as follows:

$$W^1\delta^1_{H_2O} + W^2\delta^2_{H_2O} + \cdots W^n\delta^n_{H_2O} = W^{n+1}\delta^{n+1}_{H_2O} \qquad (2)$$

where δ_{H_2O} is the isotope value and W is the mass of fluid in the system.

If $W^{4\text{-}6}$ is taken as a starting point, extending towards coordinates of ore-forming fluids of Xiaomeiling nephrite and intersecting with the W^1-W^2 fluid mixing line (Figure 3a), the range of intersection points represents W^1/W^2 ratios in the I mixing process. The W^1/W^2 ratios of Xiaomeiling nephrite approach 1, indicating only half of magmatic water from Miaoxi granite porphyry had the oxygen isotope exchange with Qixia Formation limestone (Figure 3a). As a consequence, the $\delta^{18}O$ of Xiaomeiling nephrite much less than that of $Tr^{*}_{Cal\text{-}Water\text{-}Tr}$ (+15.50‰) should be attributed to the residual magmatic water, not meteoric water. The less than 0.1 of W^4/W^3 ratios indicate that the amount of meteoric water is only one-tenth of that of initial magmatic water at most, but it is this less than 10% of meteoric water that significantly reduces the δD of Xiaomeiling nephrite, resulting in the δD almost at the same level with that of Chuncheon nephrite (Figure 1a). If meteoric water in Equation (2) shifts from $W^{4\text{-}6}$ to $W^{4\text{-}3}$, intersection points will shift to W^2, and the contribution of residual magmatic water to the $\delta^{18}O$ of nephrite will decrease, but the contribution of meteoric water to the $\delta^{18}O$ and δD of nephrite is just the opposite.

It is almost certain that oxygen isotope exchanges between country rocks, fluid and tremolite give rise to the high $\delta^{18}O$ of Sanchakou nephrite, Luodian nephrite and Dahua nephrite. However, due to the δD of their ore-forming fluids overlapped with that of magmatic water, there are two possible situations that need to be discussed. Assuming that the formation of these three nephrites is irrelevant to meteoric water, W^1/W^2 ratios of Luodian nephrite are a little more than 0.1 (Figure 3b), indicating that the vast majority of magmatic water from basic rocks had oxygen isotope exchanges with country rocks, whereas W^1/W^2 ratios of Dahua nephrite and Sanchakou nephrite indicate that about one-third to one-half of magmatic water had the oxygen isotope exchange (Figure 3b). If meteoric water participates in their formation, the δD of these nephrites will decrease with the increase of W^4/W^3 ratios, unless the δD of meteoric water during the crystallization of tremolite is consistent with that of magmatic water. If that happens, the proportion of meteoric water in W^5 is slightly less than 10% for Luodian nephrite and slightly more than 10% for Dahua nephrite and Sanchakou nephrite (Figure 3b), respectively, which means that a small amount of meteoric water mixed into the system is insufficient to offset the $\delta^{18}O$ increment of nephrite caused by the oxygen isotope exchange between country rocks and magmatic water.

It is difficult to determine W^1/W^2 ratios of Vitim nephrite and Chuncheon nephrite, and can only roughly know that the total amount of meteoric water is almost ten times that of magmatic water for Chuncheon nephrite and more than ten times for Vitim nephrite, respectively (Figure 3c). If the slope from W^1 to the coordinates of these ore-forming fluids is less than that of meteoric water line, the intersection point of extension line and meteoric water line can represent the lower limit of meteoric water during the crystallization of late tremolite, and the extension line from W^2 to the coordinates of these ore-forming fluids can be used to determine the upper limit. The range of meteoric water during the ore formation of Chuncheon nephrite is relatively narrow, while that of Vitim nephrite is much broader (Figure 3c). In fact, the absence of δD and $\delta^{18}O$ of intrusive rocks and $\delta^{18}O$ of carbonate rocks make it impossible to determine isotope compositions of W^1 and W^2 as well as meteoric water.

Multiple solutions are complicated for nephrites with ore-forming fluids close to magmatic water (Figure 3d). First, assuming that the formation of these nephrites has no relevance to meteoric water, W^1/W^2 ratios of Yinggelike nephrite are between 1 and 100 (Figure 3d), indicating that the residual magmatic water accounts for a high proportion in the ore-forming fluid. The W^2 is the main component of ore-forming fluids of Xiuyan primary nephrite and Złoty Stok nephrite, but a wide range of W^1/W^2 ratios indicates that W^1 is not evenly mixed with W^2 (Figure 3d). Pishan nephrite and most of Alamas nephrite are situated on the left side of magmatic water (Figure 3d), but it is not certain whether this is caused by meteoric water, the low $\delta^{18}O$ intrusive rocks or low $\delta^{18}O$ carbonate rocks (Table 3). On the other hand, if the δD range of meteoric water participating in the growth of late tremolite is consistent with that of magmatic water, there are few differences in the δD between the final hydrothermal fluid and magmatic water. The W^4/W^3 ratios of Pishan nephrite are close to 1 (Figure 3d), indicating that the amount of meteoric water approaches that of initial magmatic water . For Alamas nephrite, Pinshan nephrite and Yinggelike nephrite, the amount of meteoric water is less than half of W^5, while W^4/W^3 ratios of Xiuyan primary nephrite and Złoty Stok nephrite are lower (Figure 3d), implying that only a large amount of meteoric water can offset the impact of residual magmatic water and the oxygen isotope exchange between magmatic water and country rocks on the $\delta^{18}O$ of nephrite, otherwise it is easy to cause a misjudgment that magmatic water or metamorphic water is the source of their ore-forming fluid.

4. Conclusions

Hydrogen and oxygen isotope compositions of nephrite are results of multi-stage water/rock interactions and the $\delta^{18}O$ evolution of nephrite is not synchronous with the δD evolution. Multiple solutions of ore-forming fluids of C-type nephrites result from a lack of constraints about isotope compositions of parent rocks and meteoric water during the growth of late tremolite. In this study, Taylor closed model and fluid mixing model are used to reveal the intermediate processes of evolution of ore-forming fluid of nephrite. Due to the influence of multicomponent fluids on the δD and $\delta^{18}O$ of ore-forming fluid of nephrite, the application range of Taylor closed model is limited. Fluid mixing model can calculate the proportion between different fluids step by step and is conducive to quantitatively constraining the evolution of ore-forming fluid of primary nephrite.

Oxygen isotope exchanges between the magmatic water from basic rocks and country rocks with heavy $\delta^{18}O$ should be responsible for the formation of nephrite with heavy $\delta^{18}O$, such as Sanchakou nephrite, Luodian nephrite, Dahua nephrite etc. In the absence of meteoric water, the ratio of initial fluid to exchanged fluid in the first mixed fluid determines the $\delta^{18}O$ shift direction of nephrite. For Luodian nephrite, the initial magmatic water from basic rocks has almost completely oxygen isotope exchange with country rocks, while the proportions for Sanchakou nephrite and Dahua nephrite are increased to about one-third to one-half of the initial magmatic water. If the δD of meteoric water is consistent with that of magmatic water, it is difficult to determine whether meteoric water participates in the formation of these nephrites. In such circumstances, only when the $\delta^{18}O$ of ore-forming fluid of nephrite is less than the left boundary of magmatic water, otherwise any $\delta^{18}O$ value from W^2 to the left boundary of magmatic water hardly indicates the existence of meteoric water in the hydrothermal system. Due to meteoric water in the hydrothermal fluid exceeding several times that of the initial magmatic water, the influence of meteoric water masks the oxygen isotope exchange between magmatic water and country rocks during the ore-forming processes of Vitim nephrite and Chuncheon nephrite.

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