Glow discharge mass spectrometry studies on nephrite minerals formed by different metallogenic mechanisms and geological environments

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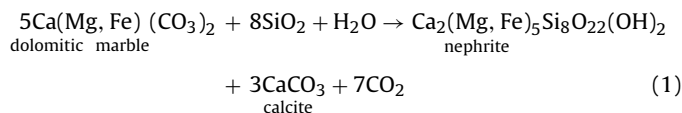[c] Fudan University, Shanghai 200433, PR China

ABSTRACT

Glow discharge mass spectrometry (GD-MS) was applied to study the nephrite minerals formed by different metallogenic mechanisms and geological environments from deposits in China, Canada, New Zealand and Russia. The GD-MS analysis and multivariate statistic analysis results indicated that two types of nephrite minerals of different metallogenic mechanisms could be classified by some typical elements. It was shown that serpentine-related nephrite minerals had higher concentrations of Cr, Co and Ni than dolomitic-marble-related nephrite minerals. Meanwhile, nephrite samples from Wenchuan had higher concentrations of Mn, V than other deposits and nephrite samples from Xiaomeiling had higher concentrations of Sr, K and Na than other deposits, which were consistent with their geological environments. These analytical results of nephrite samples by GD-MS showed that both metallogenic mechanisms and geological environments could affect the elemental concentrations in nephrite minerals.

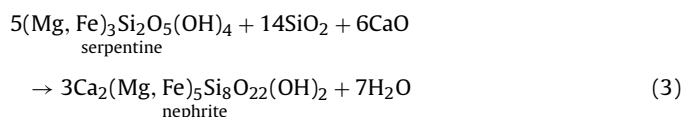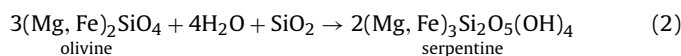© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Nephrite is a gemstone composed of tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$] and actinolite [$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$] [1]. Many nephrite deposits have been reported in many countries, such as China, Korea, Russia, New Zealand, Canada and so on [2,3]. In principle, nephrite minerals can be divided into two types by their different formation [4,5]. One type was formed by contact metasomatism between intermediate-acidic intrusive rocks and dolomitic marble. The typical reaction could be presented as the following equation:

$$5Ca(Mg, Fe)\,(CO_3)_2 + 8SiO_2 + H_2O \rightarrow Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$$
$$\underset{\text{dolomitic marble}}{} \qquad\qquad \underset{\text{nephrite}}{}$$
$$+ 3CaCO_3 + 7CO_2 \qquad (1)$$
$$\underset{\text{calcite}}{}$$

The other type was formed by contact metasomatism of serpentine or serpentinizing peridotite and more silicic rocks. There were two steps, first step was serpentine formation by metasomatism of ultramafic rocks (such as olivine) and low-medium temperature hydrotherm, the second step was metasomatic interaction of serpentine with more silicic rocks, and this process was promoted by

Ca-rich hydrous fluid-flow, the typical reactions could be presented as follows:

$$3(Mg, Fe)_2SiO_4 + 4H_2O + SiO_2 \rightarrow 2(Mg, Fe)_3Si_2O_5(OH)_4 \qquad (2)$$
$$\underset{\text{olivine}}{} \qquad\qquad\qquad \underset{\text{serpentine}}{}$$

$$5(Mg, Fe)_3Si_2O_5(OH)_4 + 14SiO_2 + 6CaO$$
$$\underset{\text{serpentine}}{}$$
$$\rightarrow 3Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2 + 7H_2O \qquad (3)$$
$$\underset{\text{nephrite}}{}$$

In recent years, various spectroscopic methods of analysis have been applied to the studies of nephrite. For example, X-ray fluorescence spectroscopy (XRF) and external beam proton-induced X-ray emission (PIXE) were used to determine the main elemental compositions of artifacts to identify their raw materials as nephrite [6–8]. Raman spectrometry and X-ray diffraction (XRD) were used to investigate their mineralogical identification and crystalline structure [9,10]. These previous studies mainly focused on the identification of the raw materials by major elements and the structures of nephrite jades. As the major elements of nephrite minerals from different deposits did not have remarkable differences, it was difficult to understand their geological settings only by major elements. Actually, the minor and trace elements in nephrite minerals played an important role in reflecting their geographic origins. Therefore, systematically analysis of the minor and trace elements of nephrite minerals from different deposits might provide important information of their metallogenic mechanisms and geological

environments. Furthermore, these investigations would promote the establishment of a geological database for nephrite minerals to solve some problems on geology, archaeology and so on.

Glow discharge mass spectrometry (GD-MS) is a powerful tool for trace analysis of solid materials [11–13]. The glow discharge ion source has a capability of generating the stable analyte ion population directly from the solid sample, which could preclude the problems of dissolution, dilution and contamination that may arise for techniques requiring solution samples [14]. GD-MS also has the capability to analyze all the elements from major compositions to trace compositions, over a wide dynamic range (sub ppb to 100%) [15]. In a dc-GD-MS instrument, the sample must be conductive. Bulk metals are the most ideal samples even though non-conductive samples can also be analyzed. Soil, nuclear and radioactively contaminated environmental samples could also be analyzed by GD-MS [16–18]. In these cases, the samples were needed to be mixed with binder material or the technique of secondary cathode [15]. Another method to overcome the conductivity problem is using a radiofrequency (rf) source instead of dc-GD source. It is possible to sputter-atomize directly nonconductive solid samples such as glasses and ceramic samples [19–21].

In the present research work, GD-MS was used to determine the major, minor and trace elements of 23 nephrite samples from different deposits in China and other countries. Multivariate statistic analysis on some minor and trace elements was used to classify two types of nephrite minerals of different formation. Typical elements of nephrite samples from some specific deposits were found to separate them from nephrite samples of other deposits. The relationship between elemental concentrations of nephrite minerals and their geological settings was also discussed.

2. Experimental

2.1. Materials and sample preparation

Twenty three nephrite samples were studied in this work. Nineteen samples were collected from different deposits in China including Hetian, Qiemo and Manasi of Xinjiang province, Geermu of Qinghai province, Xiuyan of Liaoning province, Xiaomeiling of Jiangsu province, Wenchuan of Sichuan province, Xichuan of Henan province and Hualian of Taiwan province. The others were collected from Lake Baikal in Russia, British Columbia in Canada and Milford Sound in New Zealand. According to the previous reports [2,4,22], these samples could be divided into two groups by their metallogenic mechanisms: samples 1–17 were from dolomitic-marble-related nephrite deposits; samples 18–23 were from serpentine-related nephrite deposits, as listed in Table 1. The elemental compositions in Table 1 were determined by GD-MS in this study.

During the preparation process, all the samples were milled to powder of 200 meshes. High purity indium (>99.9999%) block was melted and made into pin (2 mm in diameter × 20 mm in length). Preliminarily, the indium pin was exposed to the glow discharge plasma to remove the surface contamination. Then the indium pin was rolled in the nephrite sample powder to make the pin coated with the sample powder [23]. While the small grains, which were not pressed tightly into the indium pin, were blown away by pure dry nitrogen gas. Finally, the indium pin with the powder was placed for 30 min for the following GD-MS analysis.

2.2. GD-MS experiments

The glow discharge mass spectrometry applied in this study was VG9000 glow discharge mass spectrometer (Thermo Elemental, UK). It was a double-focusing magnetic sector instrument

with reverse Nier-Johnson configuration. The cell of ion source used was a pin cell designed for pin-shaped samples, and it was pre-cooled down by liquid nitrogen at about −180 °C. Glow discharge samples were atomized by cathode sputtering in argon of high purity (>99.9999%), the pressure of the Ar is 1.10×10^{-4} mbar–1.15×10^{-4} mbar. The operation was carried out in a mode with discharge voltage of 1 kV at a constant 0.5 mA current. The accelerating voltage was set to 8 kV to extract ions in the glow discharge into mass spectrometer. The intensity of the ion beams was measured by a Daly photomultiplier for small current (10^{-19} to 10^{-13} A) and by a Faraday cup detector for large currents (10^{-13} to 10^{-9} A). For all the scans, the mass resolution was more than 4000. In the measurement of sample WC-2, the internal precision was in the range of 2.4% RSD ($n = 5$) for major element Ca (170,000 ppm wt., relative to Si) to 23% RSD ($n = 5$) for the trace element Zr (9.35 ppm wt, relative to Si), and the external precision for major elements was in range of 4.4%–9.2% RSD ($n = 4$), while precision of some trace elements was in range of 10%–40% RSD ($n = 4$). These results were shown in our previous study [24], which indicated that the precision and reproducibility were good enough for the following classification of nephrite minerals from different deposits.

The relative sensitivity factor (RSF) values used here were from commercial software of VG9000 glow discharge mass spectrometer; while we did some calibration on some major and minor elements (Mg, Ca, Si and Fe) using results of sample HTY-1 analyzed by PIXE, which was performed at the NEC 9SDH-2 Pelletron tandem accelerator in Fudan University, Shanghai, China. The elemental compositions were listed in the Table 1. The singular oxide forms are simplification in this paper to present the total elemental composition. According to the previous reports [25,26], ferric iron (Fe^{3+}) is rare in nephrite and ferrous iron (Fe^{2+}) is dominant. In general, total iron was usually expressed as ferrous iron (FeO) for simplification in the studies on nephrite [2,26]. In our work, FeO was also used to represent the total iron in nephrite minerals.

2.3. Statistic analysis method

A multivariate statistic analysis was used to classify the two types of nephrite minerals. The statistic analysis was carried out by the principle component analysis method with the software "Statistical Product and Service Solutions ver15.0". Elemental concentrations of some minor and trace elements were selected for this calculation. The concentrations were standardized before the statistical calculation. Then statistic analysis result was plotted in a 3-dimensional graph with three principle component (Component 1, Component 2 and Component 3).

2.4. Semi-quantitative analysis

The concentrations of Mg, Ca, Si and Fe were calibrated by results of PIXE, while concentrations of other elements were obtained by "standard" RSF values in software of VG9000. Although it was a semi-quantitative result, it could provide significant elemental information of nephrite minerals. Moreover, the elemental concentrations data were standardized before the statistic analysis, and the influence of semi-quantitative results on the classification of nephrite minerals from different deposits could be negligible. More accurate quantitative results should be obtained by analysis of reference materials with similar matrices to get a suitable RSF values. However, GD-MS semi-quantitative analysis of nephrite minerals was proven to be simple efficient to perform the classification of nephrite minerals by their different metallogenic mechanisms and determine the nephrite minerals from some specific deposits.

Table 1
Elemental compositions of nephrite minerals analyzed by GD-MS.

No.	Label	Color	Metallogenic type	Deposit locality	Major compositions (wt.%)			Minor and trace compositions (ppm wt.)				
					MgO	SiO$_2$	CaO	Cr$_2$O$_3$	MnO	FeO	CoO	NiO
1	HTY-1	BW	Dolomitic-marble-related	Hetian	25.16	59.52	12.11	5.21	498	8810	1.50	28.3
2	HT-QB	BW	Dolomitic-marble-related	Hetian	24.35	59.55	12.97	99.3	839	8860	2.83	90.9
3	HTY-3	BG	Dolomitic-marble-related	Hetian	25.29	53.69	16.74	13.9	2110	24,600	6.28	187
4	QM-QB	BW	Dolomitic-marble-related	Qiemo	23.70	58.18	16.04	2.73	1390	10,100	3.12	576
5	09XJ-B1-B	BG	Dolomitic-marble-related	Qiemo	23.08	58.25	15.15	9.09	479	18,700	6.06	599
6	09XJ-H1	W	Dolomitic-marble-related	Qiemo	24.21	54.55	18.30	12.2	498	10,900	4.55	102
7	09XJ-H2	W	Dolomitic-marble-related	Qiemo	24.62	56.37	16.87	33.9	336	5970	3.83	356
8	QH-3	W	Dolomitic-marble-related	Geermu	26.69	54.39	18.64	25.9	83.2	690	4.58	83.1
9	QH-4	W	Dolomitic-marble-related	Geermu	24.01	59.93	15.30	9.17	63.1	2430	1.72	50.2
10	XML-2	BG	Dolomitic-marble-related	Xiaomeiling	23.64	61.31	12.90	48.3	300	3100	3.20	248
11	XML-3	BG	Dolomitic-marble-related	Xiaomeiling	24.40	59.48	13.94	53.0	167	1160	4.41	157
12	WC-1	W	Dolomitic-marble-related	Wenchuan	25.55	60.90	12.21	20.4	3440	1730	0.598	34.9
13	WC-2	BW	Dolomitic-marble-related	Wenchuan	24.70	59.17	14.72	54.5	4450	1970	1.50	92.8
14	XY-1	BG	Dolomitic-marble-related	Xiuyan	25.28	59.23	14.03	13.7	314	3210	0.888	185
15	XC-1	DG	Dolomitic-marble-related	Xichuan	22.79	55.74	16.77	29.7	541	32,500	12.5	599
16	ELS-3	W	Dolomitic-marble-related	Lake Baikal	26.69	56.05	15.70	24.2	149	1430	3.36	120
17	ELS-4	W	Dolomitic-marble-related	Lake Baikal	24.81	60.64	13.28	14.6	710	3520	1.58	65.5
18	MNS-1	DG	Serpentine-related	Manasi	22.82	58.85	12.47	2250	498	4100	67.4	1440
19	MNS-2	DG	Serpentine-related	Manasi	22.31	58.22	13.78	2430	684	42,800	55.5	1280
20	HL-1	DG	Serpentine-related	Hualian	22.04	53.74	15.75	4110	1600	36,400	53.4	1410
21	HL-2	DG	Serpentine-related	Hualian	20.72	55.52	17.20	4070	918	49,300	58.3	1660
22	JND-2	DG	Serpentine-related	British Columbia	23.28	57.08	13.41	2200	1620	46,700	58.3	1300
23	XXL-2	DG	Serpentine-related	Milford Sound	25.37	53.15	16.16	2200	639	31,100	54.4	1220

No.	Label	Minor and trace compositions (ppm wt)													Fe/(Fe + Mg)
		B$_2$O$_3$	Na$_2$O	Al$_2$O$_3$	P$_2$O$_5$	SO$_3$	Cl	K$_2$O	TiO$_2$	V$_2$O$_5$	ZnO	SrO	Y$_2$O$_3$	ZrO$_2$	
1	HTY-1	45.3	486	20,800	43.6	117	45.0	783	324	33.5	39.1	3.50	3.30	12.0	0.019
2	HT-QB	37.7	605	18,900	968	205	70.7	470	118	21.5	36.4	3.68	15.4	3.88	0.020
3	HTY-3	20.5	643	13,600	96.0	624	110	244	284	23.2	126	11.4	12.4	12.3	0.052
4	QM-QB	10.7	328	7040	198	190	129	569	225	16.9	86.6	6.48	9.50	2.70	0.023
5	09XJ-B1-B	29.2	655	12,800	690	211	175	681	111	11.6	42.2	8.97	7.68	2.57	0.043
6	09XJ-H1	9.24	758	15,400	37.0	170	45.5	592	516	37.3	179	7.47	12.7	31.3	0.025
7	09XJ-H2	15.0	823	12,800	18.2	147	44.2	517	326	9.99	36.7	6.70	4.59	16.8	0.013
8	QH-3	19.0	544	711	11.2	343	61.6	195	32.9	9.53	24.6	7.71	4.93	2.12	0.001
9	QH-4	18.5	348	2200	16.3	1310	744	227	66.4	6.11	53.7	9.60	0.530	0.827	0.006
10	XML-2	64.7	3580	11,000	23.8	120	186	2230	275	20.4	33.3	228	4.16	10.9	0.007
11	XML-3	50.8	3830	12,100	24.8	257	397	2830	293	50.3	22.9	381	3.07	19.7	0.003
12	WC-1	43.4	500	5470	965	309	339	168	92.2	217	65.2	10.5	3.43	1.67	0.004
13	WC-2	15.2	472	4360	1930	109	114	144	86.9	230	80.3	19.8	4.03	3.62	0.004
14	XY-1	49.6	375	8900	335	221	207	640	48.2	13.9	21.6	9.85	5.64	1.59	0.007
15	XC-1	14.9	655	11,500	25.6	169	81.6	628	109	4.93	36.5	11.7	3.79	3.05	0.074
16	ELS-3	18.8	1190	11,100	18.6	517	59.1	583	72.0	109	19.0	12.6	100	2.24	0.003
17	ELS-4	8.63	314	7150	85.0	162	89.0	360	157	5.1	25.5	15.9	1.20	3.08	0.008
18	MNS-1	29.0	210	9140	80.6	353	60.3	139	129	28.9	21.7	8.23	0.401	0.764	0.092
19	MNS-2	44.9	240	8660	68.4	172	113	196	55.0	18.2	37.2	10.1	3.04	1.14	0.097
20	HL-1	14.8	508	39,900	4.75	255	55.8	178	96.5	34.6	74.2	3.94	9.22	2.24	0.085
21	HL-2	69.2	662	7810	22.3	309	164	203	125	67.5	111	3.87	40.6	6.67	0.118
22	JND-2	22.4	215	9440	21.3	216	56.9	166	89.3	37.3	41.8	2.81	0.970	1.10	0.101
23	XXL-2	30.6	414	16,900	33.3	155	92.4	191	96.2	17.6	34.5	9.62	0.950	2.58	0.064

BW, bluish white; BG, blue green; W, white; DG, dark green.

3. Results and discussion

3.1. GD-MS studies on the elements Mg, Fe of nephrite

At the beginning of our work, some major and minor elements of 23 nephrite samples were analyzed by GD-MS. The results of concentrations were listed in Table 1. In previous reports, molar ratio of Fe/(Mg + Fe) was often used in classification of nephrite minerals. It indicated isomorphous substitution of Fe^{2+} and Mg^{2+}, and Fe/(Mg + Fe) ratio increases with the increase of element Fe in the nephrite minerals. Commonly, Fe/(Mg + Fe) ratios of serpentine-related nephrite minerals were higher than those of dolomitic-marble-related nephrite minerals [26,27]. Fe/(Mg + Fe) ratios were also considered in our work, as shown in Fig. 1. The results were mainly consistent with previous reports: most of Fe/(Mg + Fe) ratios of serpentine-related samples were higher than those of dolomitic-marble-related samples. It means that serpentine-related samples had more Fe than dolomitic-marble-related samples.

In general, the Fe in dolomitic-marble-related nephrite minerals mainly came from dolomitic marble (Eq. (1)). Actually, the concentration of Fe in dolomitic marble was relatively low, which also remained in this type of nephrite minerals. The Fe in serpentine-related nephrite minerals mainly came from serpentine (Eq. (3)), while serpentine was produced from ultramafic rocks (such as olivine, as shown in Eq. (2)) with plenty of Fe. As a result, serpentine-related nephrite minerals commonly had more Fe than dolomitic-marble-related nephrite minerals.

However, Fe/(Mg + Fe) ratios of dolomitic-marble-related sample XC-1 (sample 15) was a little higher than the Fe/(Mg + Fe) ratio of a certain serpentine-related sample. It was possibly caused by the geological environment: the mineral was too close to wall rock, which led to much Mg^{2+} substituted by Fe^{2+} during the mineralization.
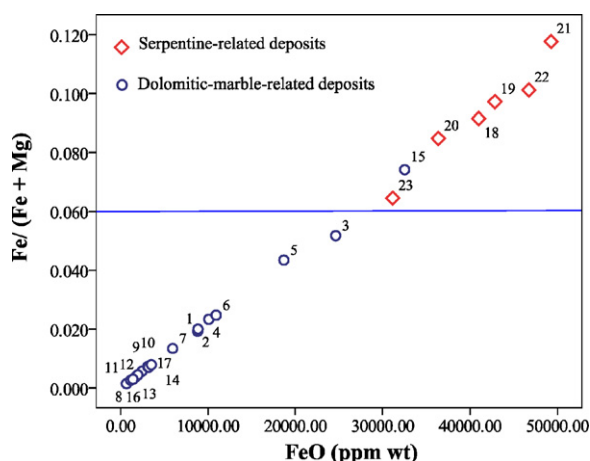
Fig. 1. FeO versus Fe/(Fe + Mg) plot of nephrite minerals.

At this case, nephrite minerals of two types could not be separated completely only by the Fe/(Fe + Mg) ratio. More elements including some minor, trace elements should be taken into consideration.

3.2. GD-MS studies on the elements Cr, Co, Ni of nephrite

To further completely distinguish two types of nephrite, some other minor and trace elements (Cr, Co, Ni) concentrations were determined by GD-MS. As shown in Table 1, the serpentine-related samples had higher concentrations of Cr, Co, Ni than dolomitic-marble-related samples.

For Fe, Mn, Cr, Co and Ni elements were related to each other in the minerals, these elements were chosen for the following statistic calculations. The statistical results by principle component analysis method were listed below:

$$\text{Component} \quad 1 = 0.492 \times ZCr_2O_3 + 0.490 \times ZFeO + 0.507 \times ZCoO$$
$$+ 0.509 \times ZNiO \tag{4}$$

$$\text{Component} \quad 2 = 0.047 \times ZCr_2O_3 + 0.998 \times ZMnO + 0.010 \times ZFeO$$
$$- 0.020 \times ZCoO - 0.035 \times ZNiO \tag{5}$$

$$\text{Component} \quad 3 = -0.67 \times ZCr_2O_3 + 0.02 \times ZMnO + 0.74 \times ZFeO$$
$$- 0.09 \times ZCoO + 0.03 \times ZNiO \tag{6}$$

ZCr_2O_3, $ZMnO$, $ZFeO$, $ZCoO$ and $ZNiO$ were standardized values of Cr_2O_3, FeO, MnO, CoO and NiO concentrations.

23 nephrite samples were plotted in (Component 1, Component 2 and Component 3) coordinates in 3-dimentional graph (Fig. 2). These results suggested that two types of nephrite samples could be well distinguished by Component 1. The Component 1 was related to concentrations of Fe, Cr, Co, Ni elements as indicated in Eq. (4). Especially for the sample XC-1 (sample 15), it was difficult to distinguish it from serpentine-related nephrite samples by Fe/(Fe + Mg) ratio as mentioned above. However, sample XC-1 could be easily distinguished by Component 1. Thus, statistical analysis suggested that Cr, Co and Ni could be recognized as typical elements to differentiate two types of nephrite minerals. The possible reason was that a large amount of Cr, Co and Ni coexisted with Fe in ultramafic protolith of serpentine-related deposits, so that serpentine-related nephrite minerals retained more Cr, Co, Ni from their protolith than dolomitic-marble-related nephrite minerals.
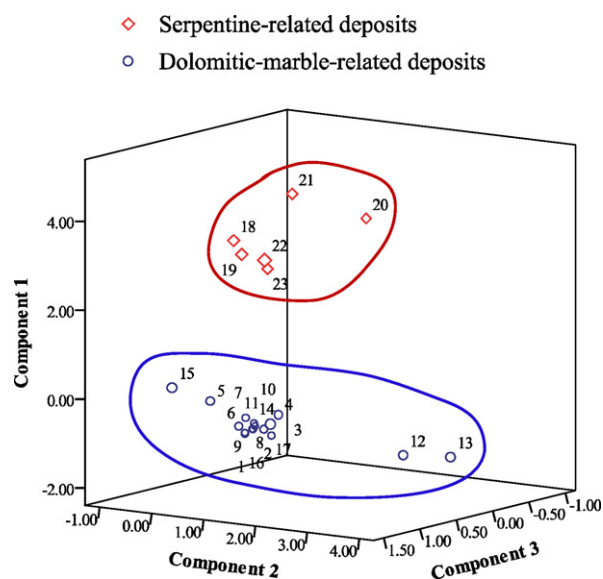

Fig. 2. Three-dimensional diagram of principle component analysis on nephrite minerals of different formation.

3.3. GD-MS studies on the elements Mn, V, Sr, K and Na of nephrite

Moreover, Mn, V, Sr, K and Na elements concentrations determined by GD-MS were discussed in this study. Fig. 2 showed that nephrite samples 12 and 13 from Wenchuan district were obviously separated from the others by Component 2, which was mainly related to concentration of Mn element by Eq. (5).

Apart from concentrations of Mn, the concentrations of V element of nephrite samples from Wenchuan were also different from that of other places. Classification of these nephrite samples using Mn and V elements was shown in Fig. 3. The figure indicated that Mn and V were typical elements of nephrite minerals from Wenchuan to separate them from nephrite minerals of other deposits.

Due to the substitution of Fe^{2+} in nephrite by abundant Mn^{2+}, the Mn concentration in nephrite samples from Wenchuan was quite high. It was reported that there is a polianite (MnO_2) deposit located in Heishui, Sichuan province, which is close to Wenchuan. The high Mn concentration in samples from Wenchuan might be influenced
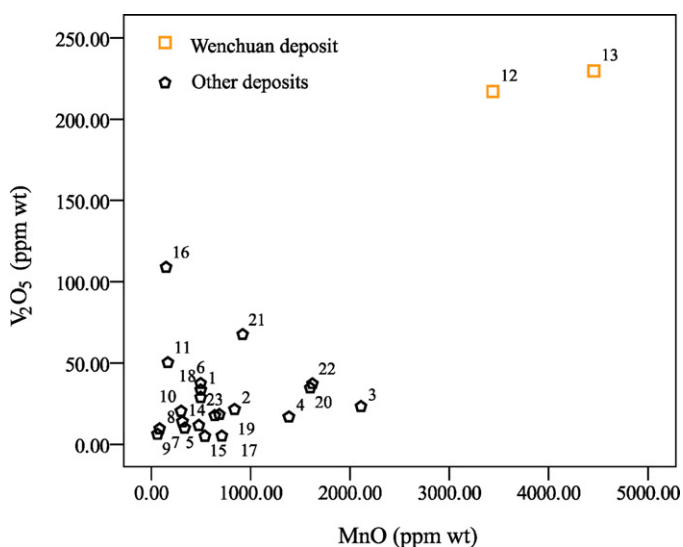

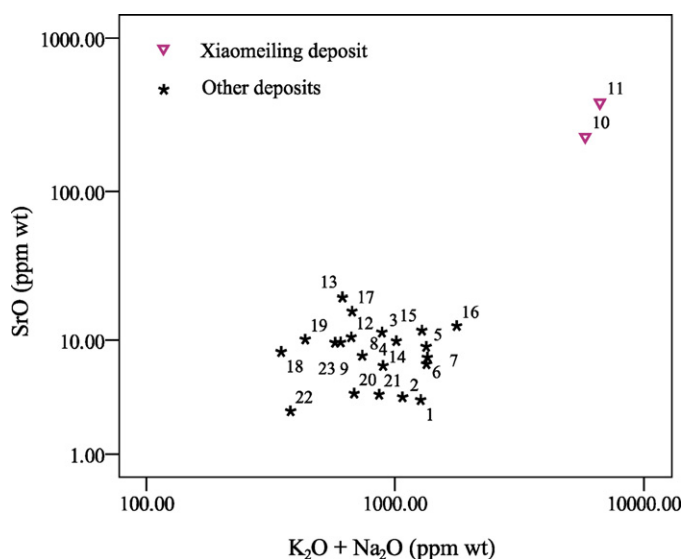**Fig. 3.** Nephrite minerals from Wenchuan deposit.

Fig. 4. Nephrite minerals from Xiaomeiling deposit.

by geological environment with abundant Mn. Meanwhile, there are many Vanadium deposits in Sichuan province accounting for 63% of Vanadium reserve in China, and there is a Vanadium deposits in Wangcang which is close to Wenchuan. Geological environment with abundant V might result in the high V concentration in samples from Wenchuan.

Besides, as shown in Table 1, the Sr concentration of samples from Xiaomeiling was significantly higher than those from other places. The Na and K concentrations in these two samples were also higher than those from other places. Then Sr concentration was plotted versus sum of Na and K concentrations, as shown in Fig. 4. The result revealed that Sr, K and Na could be typical elements of nephrite samples from Xiaomeiling to separate them from nephrite minerals of other deposits.

For the ionic radii and chemical characteristics of Sr^{2+} and Ca^{2+} were similar to each other, Sr replacement of Ca in calcium-rich minerals usually occurs. The high concentration of Sr in samples from Xiaomeiling might result from hydrotherm formed in mineralization process of a celestite ($SrSO_4$) deposit at Aijing Hill in Lishui, Jiangsu province, which is close to Xiaomeiling. The high concentrations of K and Na might also be influenced by ion substitution of these elements from their surrounding wall rock.

These studies indicated that geological environments could have influence on the elemental compositions of nephrite minerals. Moreover, typical elements of nephrite minerals formed in specific geological environments were observed by GD-MS studies, which could provide some important information for the determination of their provenances.

4. Conclusions

GD-MS technique was used to investigate two types of nephrite minerals of different metallogenic mechanisms (dolomitic-marble-related and serpentine-related). The GD-MS studies and statistical analysis indicated that two types of nephrite minerals formed by different metallogenic mechanisms were well separated by elemental concentrations of Cr, Co and Ni. Meanwhile, nephrite minerals from Wenchuan could be distinguished from the others by concentrations of Mn, V elements, and nephrite minerals from Xiaomeiling could be distinguished from the others by concentrations of Sr, K and Na elements. The results revealed that the difference of elemental composition of nephrite minerals was possibly caused by both of their different metallogenic

mechanisms and geological environments. While previous studies mainly focused on the major elements and structure of nephrite, the GD-MS results of nephrite minerals in this study provided much information on minor and trace elements, which would be very important to study on geological origin of nephrite minerals. The direct analysis of solid samples by GD-MS could avoid contamination from dissolution, dilution and transfer that might arise for some techniques requiring solution samples. The low temperature ($-180\,^\circ$C) of discharge cell and high resolution magnet sector greatly reduced the interferences in the analysis. The GD-MS method also allowed us to determine the non-metallic elements with low concentrations such as S, P and Cl in the nephrite minerals. These studies indicated that GD-MS was an effective method to distinguish nephrite minerals of different geological origin and it had great potential on the determination of their provenance. Further studies in this area are under way in our laboratory.

Acknowledgement

References

[1] J.G. Douglas, J.C. Yang, Materials and technology of Chinese jades dating to the Western Zhou period (1050-771 BCE), Sci. China Ser. E 51 (2008) 467–480.
[2] J. Deng, Y. Liu, G.H. Shi, T.J. Lu, H.Y. He, Y.N. Ng, C.H. Shen, L.Q. Yang, Q.F. Wang, Chemical zone of nephrite in Alamas, Xinjiang, China, Resour. Geol. 60 (2010) 249–259.
[3] T.F. Yui, S.T. Kwon, Origin of a dolomite-related jade deposit at Chuncheon, Korea, Econ. Geol. 97 (2002) 593–601.
[4] G.E. Harlow, S.S. Sorensen, Jade (nephrite and jadeitite) and serpentinite: metasomatic connections, Int. Geol. Rev. 47 (2005) 113–146.
[5] Z.W. Zhang, F.X. Gan, H.S. Cheng, PIXE analysis of nephrite minerals from different deposits, Nucl. Instrum. Meth. B 269 (2011) 460–465.
[6] H.S. Cheng, Z.Q. Zhang, B. Zhang, F.J. Yang, Non-destructive analysis and identification of jade by PIXE, Nucl. Instrum. Meth. B 219 (2004) 30–34.
[7] T.H. Chen, T. Calligaro, S. Pages-Camagna, M. Menu, Investigation of Chinese archaic jade by PIXE and µ Raman spectrometry, Appl. Phys. A Mater. 79 (2004) 177–180.
[8] J.G. Douglas, A review of some recent research on early chinese jades, in: Scientific Examination of Art: Modern Techniques in Conservation and Analysis, from the Arthur M. Sackler Colloquia of the National Academy of Sciences, The National Academies Press, Washington DC, 2005, pp. 206–214.
[9] F. Casadio, J.G. Douglas, K.T. Faber, Noninvasive methods for the investigation of ancient Chinese jades: an integrated analytical approach, Anal. Bioanal. Chem. 387 (2007) 791–801.
[10] F.X. Gan, J.Y. Cao, H.S. Cheng, D.H. Gu, G.Y. Rui, X.M. Fang, J.Q. Dong, H.X. Zhao, The non-destructive analysis of ancient jade artifacts unearthed from the Liangzhu sites at Yuhang, Zhejiang, Sci. China Technol. Sci. 53 (2010) 3404–3419.
[11] N.E. Sanderson, E. Hall, J. Clark, P. Charalambous, D. Hall, Glow-discharge mass-spectrometry - a powerful technique for the elemental analysis of solids, Mikrochim. Acta 1 (1987) 275–290.
[12] F.L. King, J. Teng, R.E. Steiner, Glow-discharge mass-spectrometry - trace-element determinations in solid samples, J. Mass Spectrom. 30 (1995) 1061–1075.
[13] J. Pisonero, B. Fernandez, D. Gunther, Critical revision of GD-MS, LA-ICP-MS and SIMS as inorganic mass spectrometric techniques for direct solid analysis, J. Anal. At. Spectrom. 24 (2009) 1145–1160.
[14] M. Betti, Isotope ratio measurements by secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS), Int. J. Mass spectrom. 242 (2005) 169–182.
[15] W. Schelles, R. VanGrieken, Quantitative analysis of zirconium oxide by direct current glow discharge mass spectrometry using a secondary cathode, J. Anal. At. Spectrom. 12 (1997) 49–52.
[16] D.C. Duckworth, C.M. Barshick, D.H. Smith, Analysis of soils by glow-discharge mass-spectrometry, J. Anal. At. Spectrom. 8 (1993) 875–879.
[17] C.M. Barshick, S.A. Barshick, M.L. Mohill, P.F. Britt, D.H. Smith, Elemental and organometallic analyses of soil using glow discharge mass spectrometry and

gas chromatography/mass spectrometry, Rapid Commun. Mass Spectrom. 10 (1996) 341–346.

[18] M. Betti, L.A. de las Heras, Glow discharge spectrometry for the characterization of nuclear and radioactively contaminated environmental samples, Spectrochim. Acta B 59 (2004) 1359–1376.

[19] F.L. King, J.N. Robertson-Honecker, N. Zhang, A. Pavkovich, Direct chromium speciation in solid state materials - a GDMS approach, J. Anal. At. Spectrom. 23 (2008) 1508–1517.

[20] A. Sanz-Medel, J. Pisonero, J.M. Costa, R. Pereiro, N. Bordel, A radiofrequency glow-discharge-time-of-flight mass spectrometer for direct analysis of glasses, Anal. Bioanal. Chem. 379 (2004) 658–667.

[21] M.R. Winchester, R. Payling, Radio-frequency glow discharge spectrometry: a critical review, Spectrochim. Acta Part B At. Spectrosc. 59 (2004) 607–666.

[22] C.J. Adams, R.J. Beek, H.J. Campbell, Characterisation and origin of New Zealand nephrite jade using its strontium isotopic signature, Lithos 97 (2007) 307–322.

[23] C.M. Barshick, Glow discharge mass spectrometry, in: C.M. Barshick, D.C. Duckworth, D.H. Smith (Eds.), Inorganic mass spectrometry: Fundamentals and Applications, Marcel Dekker, New York, 2000.

[24] R. Siqinbilige, S.J. Qian, F.X. Zhuo, Gan, Studies on the element characteristics of nephrite minerals from different deposits by GD-MS, Chin. J. Chem. 29 (2011) 1251–1255.

[25] C.J. Wilkins, W.C. Tennant, B.E. Williamson, C.A. McCammon, Spectroscopic and related evidence on the coloring and constitution of New Zealand jade, Am. Miner. 88 (2003) 1336–1344.

[26] Y. Iizuka, H.C. Hung, P. Bellwood, Noninvasive Mineralogical Study of Nephrite Artifacts from the Philippines and Surroundings: The Distribution of Taiwan Nephrite and the Implications for the Island Southeast Asian Archaeology, in: J. Douglas, P. Jett, J. Winter (Eds.), Scientific Research on the Sculptural Arts of Asia-Proceedings of the Third Forbes Symposium at the Freer Gallery of Art at Smithsonian Institution, Archetype Publications, London, 2007.

[27] G. Wen, Z.C. Jing, Chinese neolithic jade: a preliminary geoarchaeological study, Geoarchaeology 7 (1992) 251–275.