THE RELATIONSHIP BETWEEN CONTENT, VALENCE STATE OF Fe AND COLOUR IN XIUYAN JADE

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ABSTRACT

Having beautiful colours and fine features, Xiuyan jade is famous in the world. Mineralogically, Xiuyan jade is serpentine jade. XRD, IR and TEM studies indicate that the jade consists mainly of antigorite ($m\{Mg_{3(1-1/m)}[Si_2O_5](OH)_{1+3(1-2/m)}\}$) with a minor amount of chrysotile. Two favourite samples (P_{xA}, P_{x1-1}), chosen for research on ^{57}Fe Mossbauer spectra, are only antigorite. Studies indicate that: a. iron ion in antigorite enters the lattice as impurity; b. Fe^{2+} and Fe^{3+} substitute for Mg in the coordination octahedron; and c. the colour of jade is related to content of Fe, and $Fe^{2+}/Fe^{3+} \leqslant 1$ is favourite for colour-forming.

Keywords: Xiuyan jade Antigorite Mössbauer spectra

1 INTRODUCTION

Xiuyan jade is named after its origin in Xiuyan county, Liaoning Province. For being colourful, sparkling and fine, it is famous at home and abroad, and becomes one of the major jades in China.

Mineralogically, Xiuyan jade known as serpentine jade, belongs to silicate mineral. It is distributed in Xiuyan, Fengcheng and Kuangdian of Liaoning province, and occurs in Proterozic dolomite marble of Dashiqiao formation of Liaohe group. Some researchers, Zhang Guangrong, Wan Pu, Xu Rongqi, Li Qingshen, Ke Zhaixi and Zussman have researched the jade and obtained some achievements.[1-4] Nevertheless, there are still some problems and blank areas.

In this paper, Xiuyan jade samples have been studied by XRD, IR, OAS and TEM, then researches by means of ^{57}Fe Mössbauer spectra have been carried out in order to relate valence state, occupation with colouration of Fe-ion in the jade.

2 MINERAL ASSOCIATION, CHEMICAL COMPOSITION AND CRYSTAL STRUCTURE

Xiuyan jade is an aggregate of serpentine in colloid-cryptocrystalline with many

kinds of beautiful colours, mainly bright green and yellow. The favourite jade is that which is fresh green, transparent, and big but no rift.[5]

The results of XRD, IR and TEM study show the essential mineral of Xiuyan jade is antigorite, the high quality jade is almost pure antigorite, auxiliary mineral is chrysotile which appears in fibrous form among antigorites and sometimes involves minor magnesite, tremolite and talc that badly affect the quality of jade. Under a microscope, antigorite is in foliated aggregate and forms foliated interpenetration structure. Electron micrographs of its fragments are lath-shaped, with its long axis parallel to C-axis. In E.D. pattern, antigorite shows typical super-structure and $a = 41 \times 10^{-10}$ m, whose value is very similar to that ($a = 43.325 \times 10^{-10}$ m) reported by Zhang Guangrong *et al.*

Table 1

Chemical composition of Xiuyan jade

Composition	Ideal serpentine	P_{XA}	P_{X1-1}	Xiuyan jade[2]
SiO_2	43.48	44.51	44.55	45.00
Al_2O_3		0.28	0.57	0.09
Fe_2O_3		1.74	1.95	0.61
FeO		0.54	0.29	0.50
TiO_2		0.07	0.09	-
P_2O_5		0.14	0.27	-
MnO		0.02	0.02	0.036
MgO	43.48	40.17	39.08	42.62
CaO		0.16	0.47	0.03
K_2O		0.04	0.07	0.06
Na_2O		0.13	0.33	0.076
Cr_2O_3		0.003	-	0.003
H_2O^+	13.04	12.36	12.32	11.88
Total	100.00	100.16	99.95	100.91

Antigorite belongs to a subgroup of tri-octahedral phyllosilicate mineral. The ideal chemical formula is $Mg_3[Si_2O_5](OH)_4$. Consideration of joining of two components, which are a brucite layer (0.54 nm × 0.92 nm) and a tridymite layer (0.50 nm × 0.87 nm), will probably involve appreciable mis-matching, the several ways in which the two components can match better may occur in different serpentine minerals. Antigorite achieves matching by means of internating wave structure, i.e., in an ideal model of internating wave, 9 tetrahedra point to upper (positive semiwave) and 8 tetrahedra point to down (reversal semiwave) among total 17 Si-O tetrahedra, opposed case for adjacent cell, thus they form a wave-shaped structure[6] (radius of curvature 7.5 nm) and force the sites of M_1 and M_2 to tend to equal. For ideal internating structure ($a = 43.3 \times 10^{-10}$ m), its corresponding formula is $Mg_{2.8235}[Si_2O_5](OH)_{3.547}$, however, in natural crystal, the number of tetrahedra (m) may not be 17 (usually 10 ~ 20), so a ($m \times 2.55 \times 10^{-10}$) varies corresponding with chemical formula (commonly

$Mg_{3(1-1/m)}[Si_2O_5](OH)_{1+3(1-2/m)}$). No matter what number of m is, the practical value of Mg and (OH) are lower than and Si is higher than theoretical estimates value in antigorite. Two samples (P_{xA}, P_{x1-1}) for Mössbauer spectra analysis are high grade antigorite jade, among them the former is dark green, the latter is green. Their chemical compositions are listed in Tab.1.

3 RESULTS AND DISCUSSION

Samples for study are examined under a microscope and hand-picked when necessary to remove impurities, then ground into fine powder. Sample volume is 100mg, absorber holder is 1.3cm in diameter. Mössbauer spectrum was taken at room-temperature on constant acceleration velocity spectrometer with a 512 channel analyser. The γ -ray source was ^{57}Co diffused into Pd foils having intensity of 1.11×10^9 Bq. The zero point and velocity increment are calibrated against metallic-Fe foil. The velocity increment per channel is 0.0188 mm/s. The linewidth of the third and the fourth peaks of α -Fe is 0.244 mm/s, baseline counts exceede 1.8×10^6 per channel. Mössbauer parameters are determined by Newton-Goss's one dimension searching programme installed on GW0520A microcomputer.

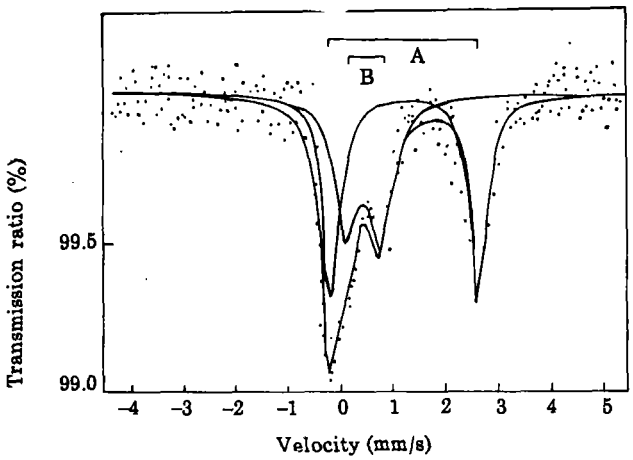

Fig.1 Mössbauer spectrum of P_{xA} of Xiuyan jade

The shapes of Mössbauer spectra of the two samples are very similar. Their experimental spectra are like the one shown in Fig.1. Two sets of quadrupole doublets can be fitted on the computer, and their parameters are listed in Tab.2. For the two samples, isomer shifts (IS or δ) of the first set of quadrupole doublet (A) are approximately the same as 1.12 mm/s. The peak is regarded as a result from of high-spin of Fe^{2+}. Their quadrupole splits (QS or $\triangle$) are quite the same as 2.732 mm/s and 2.716 mm/s. Whether for the isomorphism (Fe^{2+} and Mg are the most common isomoric pair-element) or for the crystal structure (only Mg-O octahedra can be entered) or for the comparison with Mössbauer spectra data that we have known (also

see Tab.2), the doublet should be assigned to Fe^{2+} of Mg–O octahedron. The two coordination octahedra M_1 and M_2 in antigorite couldn't be distinguished, so the doublet is named as Fe^{2+} of octahedron (the quadrupole split corresponds to that of M_2 in other serpentine minerals). The linewidth (Γ), which expresses the common feature (small and steady) in serpentine, is reasonable.

Table 2

Mössbauer parameters of Xiuyan jade and antigorite (mm/s)

Sample	Fe^{2+} (Oct.)				Fe^{3+} (Oct.)				Fe^{3+}/Fe^{2+}		
	δ	$\triangle$	Γ	$A/\Sigma A$	δ	$\triangle$	Γ	$A/\Sigma A$	Moss.	Chem.	Ref.
P_{XA}	1.124	2.732	0.384	0.528	0.364	0.632	0.545	0.472	0.90	1.45	
$P_{X1\ 1}$	1.119	2.716	0.358	0.565	0.351	0.546	0.602	0.435	0.78	3.83	
	1.12	2.70	0.35		0.36	0.70	0.84		0.47	0.50	
	1.13	2.73	0.35		0.38	0.70	1.14		0.47		
Antig-	1.13	2.70	0.40		0.43	0.80	0.80		0.65	0.40	
orite	1.14	2.74	0.31		0.34	0.76	0.52		0.25	0.08	
	1.15	2.75	0.41		0.42	0.70	0.52		0.19		[7]
	1.24	2.72	0.49	0.72	0.46	0.59	0.35	0.28	0.39		
	1.25	2.72	0.29	0.41	0.43	0.87	0.52	0.59	1.40		
	1.27	2.75		0.90	0.51	0.73		0.10	0.11		

IS of doublet (B) in the second set are 0.36 mm/s, and 0.35 mm/s respectively, obviously come from Fe^{3+}. Consideration of structure of internating wave in antigorite, the possibility of Fe^{3+} entering Si–O tetrahedron entirely is very small and IS is more than 0.3 mm/s, that doesn't match that of Fe^{3+} in $[SiO_4]$ (usually 0.21 mm/s or so, less than 0.3mm/s), we assign the doublet of Fe^{3+} of Mg–O octahedron. Their QS is 0.63mm/s and 0.55 mm/s respectively, that are low compared with those of antigorite now available. The linewidth of the doublet is a little wide and that is the common case in serpentine group. Some scholars believe that it is created by relaxation effect.

Fe^{3+}/Fe^{2+}: Because both of Fe^{3+} and Fe^{2+} occupy the sites of Mg–O octahedra, their recoilless factors may be basically the same. The ratio of Fe^{3+}/Fe^{2+} can be calculated by ratio ($A/\Sigma A$) directly, they are 0.90 and 0.78, respectively. Obviously, the amount of Fe^{2+} is a little more than that of Fe^{3+} in the two samples. The proportion indicates that Xiuyan jade is not only formed in weak reducing environment but also related to colours of jade directly.

The mineral and chemical compositions of Xiuyan jade show that its colour is related to the content of Fe-ion in antigorite and that some content of Fe is the base of colour-forming. The less the content is, the lighter the colours are (the white mainly); the more the content is, the harder the colours are, and the worse the transparency is. However, a suitable value (about 1–3%) of TFe_2O_3 is a major factor of bright green. The optical absorption spectra (OAS) of three samples indicate that major absorpting peak occurs between 14600–14450 cm^{-1} (685–692 nm) and that a very

weak peak between 24210–22780 cm^{-1} appears in only one yellow–green sample. The former is created by Fe^{2+}–Fe^{3+} charge–transfer transition in octahedron and shows bluish green–green and the latter is d–d transition and shows yellow. The transition energy of Fe^{2+} in crystal field is in infrared band and nothing to colour–forming. Therefore, the frequency and intensity of Fe^{2+}–Fe^{3+} charge–transfer transition are a major factor of green–forming; and they are related directly to the value of Fe^{3+}/Fe^{2+}. When the value is less than or near 1, the intensity approaches maximum and the d–d transition will disappear or become very weak. In respect of Fe^{3+}/Fe^{2+}, the ratio from Mössbauer spectrum is more precise than that from wet–state chemical analysis.

4 CONCLUSION

Conclusions obtained mainly from Mössbauer spectra are as follows:

a. The essential mineral of Xiuyan jade is antigorite. The high quality jade almost consists of antigorite. The feature of Mössbauer spectrum, which reveals one Fe^{3+} doublet and one Fe^{2+} doublet, is only for antigorite.

b. The Fe–ion of Xiuyan jade enters crystal lattice. It isn't physical mixture.

c. The Fe–ions substitute partially Mg–ions in antigorite. Fe^{3+} and Fe^{2+} occupy the sites of Mg–O octahedra.

d. The colour of jade is related to the content of Fe. $Fe^{3+}/Fe^{2+} \leqslant 1$ is a major factor of bright green forming.

REFERENCES

[1] Wan Pu. *Non – Metallic* (in Chinese), 1990, (1):10.

[2] Zhang Guangrong, Tang Chongguang, Cao Xuenbo. The Geology of Building–Materials. 1989, (5):16.

[3] Ke Zaixi. Liaoning Geology, 1982, 2:152.

[4] Rozenson L, Bouminger R. Amer Mineral, 1979, 64(78):893.

[5] Luan Bingao. Gemstone and jade in China. Urumqi: Xinjiang People Publishing House, 1982.

[6] Dear WA, Howie RA, Zussman J. Sheet silicate. In: Rock–forming minerals. London: Longmans, 1962. Vol.3.

[7] Jiang Saoyin. The mineralogy and property determination of serpentine. Beijing: Geological Publishing House, 1987.