

## MICROSTRUCTURAL VARIATIONS OF A PYROPE INCLUSION IN DIAMOND, AS REVEALED BY A MICRO-RAMAN SPECTROSCOPIC STUDY

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### ABSTRACT

Using a micro-Raman technique, two microstructural variations of a syngenetic pyrope inclusion in diamond from Liaoning, China, have been recognized, the degeneration of long-range order and the existence of a structural hydrous component. These experimental results provide direct evidence for the existence of a crystalline-to-amorphous transition, the incorporation of "mantle water" into the structure of a magnesium silicate, and the genetic correlation of these two phenomena in the specific range of conditions in the upper mantle in which diamond forms.

**Keywords:** mineral inclusion, diamond, degeneration of long-range order, hydrous component, micro-Raman spectroscopy, Liaoning, China.

### SOMMAIRE

Nous documentons, au moyen de la spectroscopie micro-Raman, deux propriétés micro-structurales d'une inclusion de pyrope syngénétique dans un cristal de diamant provenant de Liaoning (Chine): 1) la dégénérescence de l'ordre atomique à longue échelle, et 2) l'existence d'une composante hydratée dans le grenat mantellique. Les résultats expérimentaux fournissent des évidences directes d'une transition de l'état cristallin à l'état amorphe, l'incorporation de l'eau mantellique dans une structure d'un silicate magnésien, et la corrélation de ces deux phénomènes dans une région du manteau dans le champ de stabilité du diamant.

(Traduit par la Rédaction)

**Mots-clés:** inclusion minérale, diamant, dégénérescence de l'ordre atomique à longue échelle, composante hydratée, spectroscopie micro-Raman, Liaoning, Chine.

### INTRODUCTION

A great deal of attention has been devoted to the study of mineral inclusions in diamond since Meyer's pioneering work in 1967. Increasing attention has been attracted to this field because diamond, as the host of mineral inclusions, is regarded as a metastable phase that has remained unreactive since emplacement; the mineral in-

clusions, on the other hand, are considered the deepest unaltered sample of the upper mantle, which thus can provide very important information on the processes in the interior of the Earth. Moreover, the results of a thousand chemical analyses of mineral inclusions in diamond (Meyer 1987) have revealed two major geochemical environments in the upper mantle important for diamond formation, peridotitic and eclogitic. Therefore, the topic of this study has significance both with respect to mantle geology and exploration for diamond.

To date, no structural features of the mineral inclusions in diamond have been reported. In 1980, the micro-Raman spectroscopic method was used to identify mineral inclusions still sealed in a diamond host (Dele-Dubois *et al.* 1980a,b). This technique can undoubtedly be used to detect material enclosed in such a transparent medium. However, the high index of refraction of diamond and the complicated shape of the crystals commonly give rise to diminished intensities of the incident laser beam and the Raman signal. It is also not rare for fluorescent radiation from the host diamond to cover the weak Raman signal from the inclusion. Actually, it is hard to acquire, from a spectrum with rather poor signal-to-noise ratio, any detailed information on structural features of a mineral inclusion sealed in diamond.

Micro-Raman spectroscopy is, however, the most suitable technique (Delhaye & Dhamelincourt 1975) for the study of structural features of mineral inclusions in cases where they can be exposed through cracking of the host diamond. This approach is thus a method of micro-zone analysis with a 1- $\mu$ m spatial resolution, which appears to be much smaller than the size of ordinary mineral inclusions in diamond. Furthermore, it does not require sample preparation, so that mineral grains can be put on a glass slide and measured immediately. Also, its nondestructive nature permits other types of analysis, such as with an electron microprobe and by infrared absorption spectroscopy.



FIG. 1. Photo of the diamond grain (3 x 2.1 mm), showing the seven pyrope inclusions.

### SAMPLE AND EXPERIMENT

The diamond grain (3 × 2.1 mm) contains seven pyrope inclusions (Fig. 1); it was selected from the No. 50 kimberlitic pipe of Liaoning, China. In order to take out these inclusions for analysis, the diamond was cracked by means of a "cracker" designed by Professor Meyer.

The electron-microprobe analysis of one of these pyrope inclusions was carried out on a Cameca SX50 instrument (20 kV, 20 nA). The results of the analysis and the calculated chemical formula are given in Table 1.

Another pyrope inclusion was chosen for the micro-Raman experiment. It is 100 × 250 μm in size, wine red in color, and has a bumpy surface (Fig. 2). This pyrope grain was immediately sealed, without any preparation, by using two concave slides after extraction from the host diamond.

TABLE 1. ELECTRON-MICROPROBE DATA ON THE PYROPE INCLUSION

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	MnO	Na <sub>2</sub> O	Total
41.2	0.06	14.3	12.3	6.41	22.9	3.0	0.39	0.003	100.6
chemical formula		(Mg <sub>12.27</sub> Ca <sub>0.23</sub> Mn <sub>0.23</sub> Fe <sub>2.27</sub> (Al <sub>1.21</sub> Ti <sub>0.005</sub> Cr <sub>1.20</sub> Fe <sub>0.20</sub> Si <sub>1.20</sub> Al <sub>0.20</sub> O <sub>12</sub> )							

Composition is expressed in weight % oxides.



FIG. 2. Photo of the pyrope inclusion (100 × 250 μm) chosen for micro-Raman study.

Then, after removal of one of the slides, it was placed directly under the laser beam on the microscope stage of the Raman spectrometer for analysis.

The micro-Raman spectrometer used in this experiment is a double-monochromator Jobin-Yvon instrument (model U1000) with a photomultiplier as monochannel detector. The slits of the spectrometer were fixed at 400 μm, and a 50× long-working-distance objective was used to introduce the laser beam and to collect scattered radiation. The 514.5 nm line of an argon ion laser (Spectral Physics, model 2000) was used as exciting source. In order to give precisely the polarization direction of the exciting radiation, a Spectral Physics rotating polarizer was mounted at the output terminal of that laser. In this way, the polarization of laser radiation can be made to turn to any direction on the plane perpendicular to the laser beam, and at the same time to mark that direction with an angle  $\theta$  in the range of 0 to 720°. When the  $\theta$  angle of the polarizer changes 90° from any value, the polarization of laser radiation will be perpendicular to its original polarization.

### RESULTS AND DISCUSSIONS

The Raman spectrum in the fundamental vibration region of this pyrope inclusion is shown in Figure 3. In order to discuss its spectral features, the Raman spectra of four megacrystic samples of pyrope are given in Figure 4. Among them, No. 1 and No. 19 were selected from the Victory 1 kimberlitic pipe, in Shandong; samples 31 and 53 have a non-kimberlitic origin. The spectrum of the pyrope inclusion (Fig. 3) shows features similar to

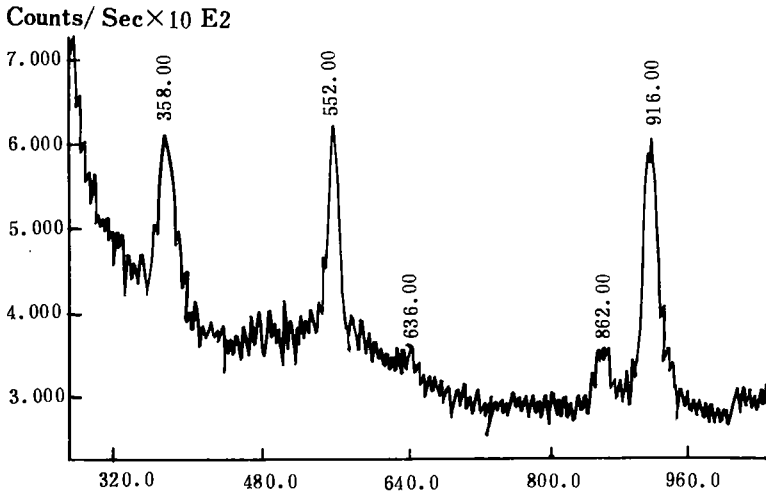


FIG. 3. Raman spectrum of the pyrope inclusion: fundamental vibrations of  $\text{SiO}_4$ .

those of the kimberlitic pyrope: 1) the relative intensities of three main bands, near 920, 560 and  $360\text{ cm}^{-1}$ , reach almost the same level, 2) some distinguishable distortions can be seen in the bandwings, 3) all bandwidths increase, and 4) the background of the spectrum appears to be higher. The spectra have been discussed in detail in another study (Wang 1987); these Raman spectral features were found to reflect a microstructural variation in the pyrope structure, *i.e.*, the degeneration of long-range order (Brawer 1975) due to the appearance of the anomalous structural elements, which appear to be mainly in the form of irregularly polymerized tetrahedra ( $\text{SiO}_4$ ) (McMillan 1984) or, in other words, the amorphous structural elements ( $\text{SiO}_2$ )<sub>n</sub>. The pressure-induced crystalline-to-amorphous transition has been documented recently using a diamond anvil cell, X-ray diffraction and micro-Raman spectroscopy (Hemley *et al.* 1988). It suggests that the temperature at which amorphization can be made to proceed is low relative to the activation energy barrier for the transformation to a thermodynamically stable crystalline phase, so that the structural elements of the crystal distort and gradually break down at high pressure to accommodate a more efficient packing of ions. The documentation of an amorphous component in undisputed mantle-derived pyrope indicates that this transition actually does occur in the interior of the Earth. Moreover, according to general occurrences of diamondiferous kimberlites, in the central part of old cratons, characterized by a stable high pressure and a relatively low temperature, it can be postulated that the amorphization, to various degrees, could possibly be a special structural

character of mantle-derived pyrope syngenetic with diamond.

Figure 5 shows the high-frequency region of the Raman spectrum of this pyrope inclusion. Similar to infrared absorption results (Aines & Rossman 1984a, b), this Raman spectrum precludes the possibility of molecular water introduced through surface absorption or contamination in experimental operations. As can be seen, the three bands at  $3719$ ,  $3647$  and  $3575\text{ cm}^{-1}$ , which represent the symmetric stretching vibration of the O-H bond, indicate the existence of a structurally bound hydrous component. Besides, the photo of the host diamond (Fig. 1), which is devoid of cracks, demonstrates that the pyrope studied obviously could only be a primary inclusion, or at least a syngenetic one, which crystallized with its structurally bound hydrous component in the upper mantle at a depth probably greater than 150 km. The presence of a structurally bound hydrous component in pyrope of suspected mantle origin was reported earlier (Aines & Rossman 1984a, b), but their data were all based on megacrysts from kimberlites. Therefore, this pyrope inclusion in diamond, with its undisputed mode of occurrence, provides the most direct evidence of the existence of water in the region of the upper mantle where diamond formed, and of its incorporation, at that depth, into the structure of a magnesium silicate that is nominally anhydrous. The existence of stable hydrous magnesium silicate at that depth also corresponds to the decrease in water fugacity at the bottom of the low-velocity zone (Ringwood 1975).

On the other hand, the existence of a structurally bound hydrous component in pyrope provides a

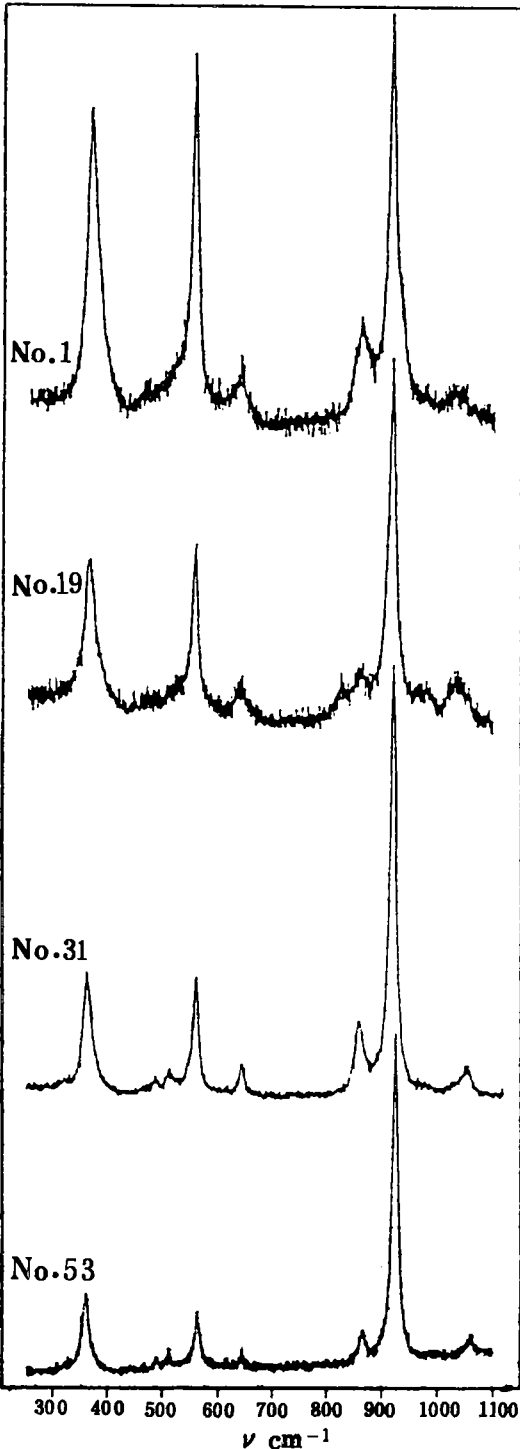
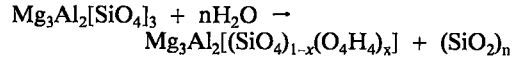


FIG. 4. Raman spectra of four megacrystic samples of pyrope.

condition for the appearance of the amorphous structural elements discussed above:



Inasmuch as these microstructural variations have already been found independently in the structure of megacrystic pyrope of suspected mantle origin (Aines & Rossman 1984a, b, Wang 1987), their coexistence in a mantle-derived pyrope inclusion provides first of all experimental evidence for their genetic correlation in the upper mantle environment.

More detailed Raman experiments could evaluate the structural role of that hydrous component in pyrope. Since McConnell (1942) first postulated the isomorphous substitution of  $(\text{O}_4\text{H}_4)^{4-}$  for  $(\text{SiO}_4)^{4-}$  to resolve discrepancies between analytical data and structural concepts observed in several minerals, numerous studies have been performed using X-ray and neutron diffraction as well as infrared absorption spectroscopy to study the possibility of this substitution in garnet. The earlier work concentrated on the hydrogrossular series. Cohen-Addad *et al.* (1967) suggested that the structural entity  $(\text{O}_4\text{H}_4)^{4-}$  does not form; they proposed instead that the polyhedra were either  $\text{Al}(\text{OH})_6$  or  $\text{AlO}_{6-x}(\text{OH})_x$ . But Foreman's study (1968) on a deuterated hydrogrossular documented the existence of  $(\text{O}_4\text{H}_4)^{4-}$ , and questioned the interpretation of Cohen-Addad *et al.* In addition, the most recent structural refinement (Lager *et al.* 1989) also revealed that the substitution of  $(\text{O}_4\text{H}_4)^{4-}$  for  $(\text{SiO}_4)^{4-}$  is the usual form of the structurally bound hydrous component in the garnet structure. Four O-H bonds surrounding a vacancy at site  $d$  ( $d$  is the Wyckoff notation for the site  $S_4$ , which has  $\bar{4}$  symmetry in space group  $Ia3d$ ) form a tetrahedron. The position of the oxygen atoms is slightly displaced from their position in the  $(\text{SiO}_4)^{4-}$  tetrahedron, and H atoms are located outside the tetrahedral volume, with their positions not being strongly dependent on OH content. Because the displacement vectors of the oxygen atoms are approximately parallel to the  $d$ -O directions in the tetrahedron, the  $(\text{O}_4\text{H}_4)^{4-}$  tetrahedron is larger than  $(\text{SiO}_4)^{4-}$  in size, but does not differ in shape or orientation. Therefore, as a first approximation, the  $(\text{O}_4\text{H}_4)^{4-}$  unit will keep the  $T_d$  structural symmetry; an analysis by group theory suggests that it should have 18 normal vibrational modes. They are as follows:

$$\Gamma_{\text{vib.}}^{(\text{O}_4\text{H}_4)^{4-}} = 2A_1(R) + 2E(R) + F_1(\text{In}) + 3F_2(R, \text{IR})$$

Only one  $A_1$  (Raman active) and one  $F_2$  (Raman and infrared doubly active) are the modes related

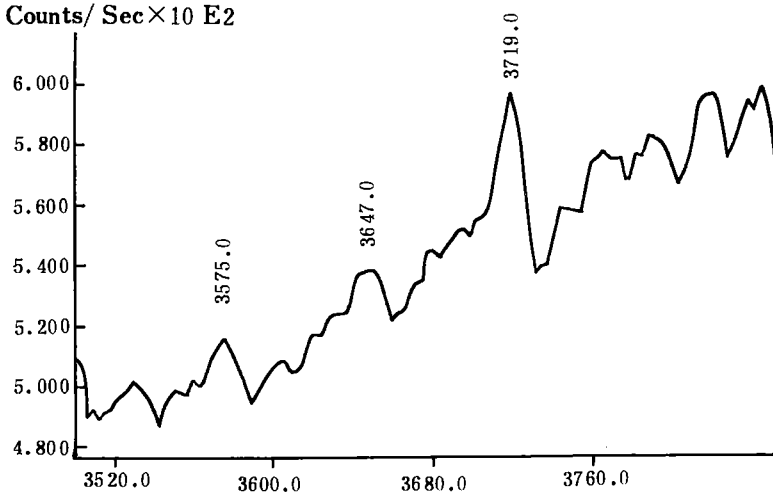


FIG. 5. Raman spectrum of the pyrope inclusion: stretching vibration of OH.

with the stretching vibration of O-H bond (Table 2), whose frequencies are located in the 3500-3800  $\text{cm}^{-1}$  region. Because the  $(\text{O}_4\text{H}_4)^{4-}$  tetrahedron occupies the  $S_4$  site in the pyrope structure, the  $F_2$  triply degenerate mode further splits into two modes, belonging to the B and E species, which are all doubly active modes (Table 3). In addition, the factor group splitting can be neglected, because less than one  $(\text{SiO}_4)^{4-}$  tetrahedron can be replaced by a  $(\text{O}_4\text{H}_4)^{4-}$  group per unit cell in the structure of pyrope (Lager *et al.* 1989); therefore, interactions among neighboring  $(\text{O}_4\text{H}_4)^{4-}$  tetrahedra can be

ignored (Table 3). In general, on the basis of this analysis, we speculate that a hydrous pyrope garnet (rich in the pyrope component) will exhibit three Raman bands and two infrared absorption bands in the OH stretching vibration region 3500-3800  $\text{cm}^{-1}$ . They are:

$$\Gamma^{(\text{O}_4\text{H}_4)^{4-}}_{\text{stretching vib.}} = A(R) + B(R,IR) + E(R,IR)$$

This speculation is approximately coincident with the experimentally observed findings. Both the result of Aines & Rossman (1984b) and the result of our experiment (Wang 1988) on a

TABLE 2. FUNDAMENTAL VIBRATION MODES OF  $(\text{O}_4\text{H}_4)^{4-}$

	OH symmetry	site symmetry	molecular symmetry
	$C_{\infty v}$	$C_{3v} - N=4$	$T_d$
$\Gamma_{\text{inter vib.}}$	$\sum^1 (R,IR)$ symmetric stretching	$A_1(R,IR)$	$A_1(R)$ $F_2(R,IR)$
$\Gamma_{\text{trans.}}$		$A_1(T_z)$ $E(T_x, T_y)$	$A_1(R)$ $E(R)$ $F_1(In)$ $F_2(R,IR)$ $- F_2(T_x, T_y, T_z)$
$\Gamma_{\text{lib.}}$		$E(R_x, R_y)$	$E(R)$ $F_1(In)$ $F_2(R,IR)$ $- F_1(R_x, R_y, R_z)$
$\Gamma_{\text{vib.}}^{(\text{O}_4\text{H}_4)^{4-}} = 2A_1(R) + 2E(R) + F_1(In) + 3F_2(R,IR)$			

TABLE 3. STRETCHING VIBRATION MODES OF  $(O_4H_4)^{4-}$  IN THE PYROPE STRUCTURE

molecular symmetry	site group splitting	factor group splitting
$T_d$	$S_4$	$O_h$
$A_1(R)$	$A(R)$	could be neglected
$F_2(R,IR)$	$B(R,IR)$	
	$E(R,IR)$	

$N < 1$

$$\Gamma_{stretching\ vib.}^{(O_4H_4)^{4-}} = A(R) + B(R,IR) + E(R,IR)$$

megacrystic garnet rich in the pyrope component, taken from a kimberlite from Liaoning, China, indicate two overlapping infrared absorption bands near 3640 and 3560  $cm^{-1}$ ; the Raman measurement for the same pyrope particle demonstrates, as predicted, three bands, near 3730, 3640, and 3560  $cm^{-1}$  (Fig. 6a). Therefore, the two doubly active bands near 3640 and 3560  $cm^{-1}$  have been assigned to the B,E modes, whereas the Raman-active band near 3730  $cm^{-1}$  must be the symmetric stretching vibrational mode A of the  $(O_4H_4)^{4-}$  group.

However, in turning the polarizer at the output terminal of the  $Ar^+$  laser, it was found that the Raman band near 3730  $cm^{-1}$  has a polarization behavior opposite to that of the symmetric stretching vibrational mode of  $(SiO_4)^{4-}$  group near 920  $cm^{-1}$ , which also belongs to the A species (Wang 1987). In general, the Raman bands that belong to a same symmetric species will reach their maximum under a unique polarization direction of exciting radiation. But Figure 6 shows that the band

near 3730  $cm^{-1}$  and that near 920  $cm^{-1}$  reach their maxima separately under two different conditions of polarization (polarizer angle  $\theta = 600^\circ$ , and  $\theta = 690^\circ$ , i.e., perpendicular to each other), although they both belong to the A species. This experimental anomaly poses a question concerning the real structural role of the hydrous component in pyrope.

Assuming that the hydrous component takes on structural forms other than the  $(O_4H_4)^{4-}$  entity (Cohen-Addad *et al.* 1967), or it occupies sites other than  $S_4$  (Basso *et al.* 1984), group-theory analysis indicates that it will always have a Raman-active mode that belongs to A (or  $A_1$ ,  $A_g$ ,  $A_{1g}$ ) species representing the symmetric stretching vibration of the O-H bond. In fact, none of the Raman bands in 3500–3800  $cm^{-1}$  region has the same polarization behavior as the band near 920  $cm^{-1}$  ( $A_{1g}$  species). Moreover, the number of infrared and Raman bands derived from the above assumptions (Table 4) also differs from the experimental results. We

TABLE 4. STRETCHING VIBRATION MODES OF OH IN THE PYROPE STRUCTURE WITH DIFFERENT MODES OF SUBSTITUTION

substitute for	form of molecular group	OH site in molecular group	symmetry of molecular group	site in pyrope	$\Gamma_{vib.}^{OH}$	number of IR bands (in 3500–3800 $cm^{-1}$ )	number of Raman bands (3500–3800 $cm^{-1}$ )
SiO <sub>4</sub>	(O <sub>4</sub> H <sub>4</sub> )	C <sub>3v</sub>	T <sub>d</sub>	S <sub>4</sub>	A(R)+B(R,IR)+E(R,IR)	2	3
	SiO(O <sub>3</sub> H <sub>3</sub> )	C <sub>s</sub>	C <sub>3v</sub>	D <sub>3</sub>	A <sub>1</sub> (R)+E(R,IR)	1	2
	SiO <sub>2</sub> (O <sub>2</sub> H <sub>2</sub> )	C <sub>2v</sub>	C <sub>2v</sub>	S <sub>4</sub>	A(R)+B(R,IR)	1	2
	SiO <sub>3</sub> (OH)	C <sub>3v</sub>	C <sub>3v</sub>	D <sub>3</sub>	A <sub>1</sub> (R)	0	1
AlO <sub>6</sub>	Al(OH) <sub>6</sub>	C <sub>4v</sub>	O <sub>h</sub>	S <sub>6</sub>	A <sub>g</sub> (R)+E <sub>g</sub> (R) +A <sub>u</sub> (IR)+E <sub>u</sub> (IR)	2	2
MgO <sub>8</sub>	Mg(OH) <sub>8</sub>	C <sub>3v</sub>	O <sub>h</sub>	D <sub>2</sub>	2A(R)+2B <sub>1</sub> (R,IR)+ 2B <sub>2</sub> (R,IR)+2B <sub>3</sub> (R,IR)	6	8

\* The factor group splitting was ignored in all cases.

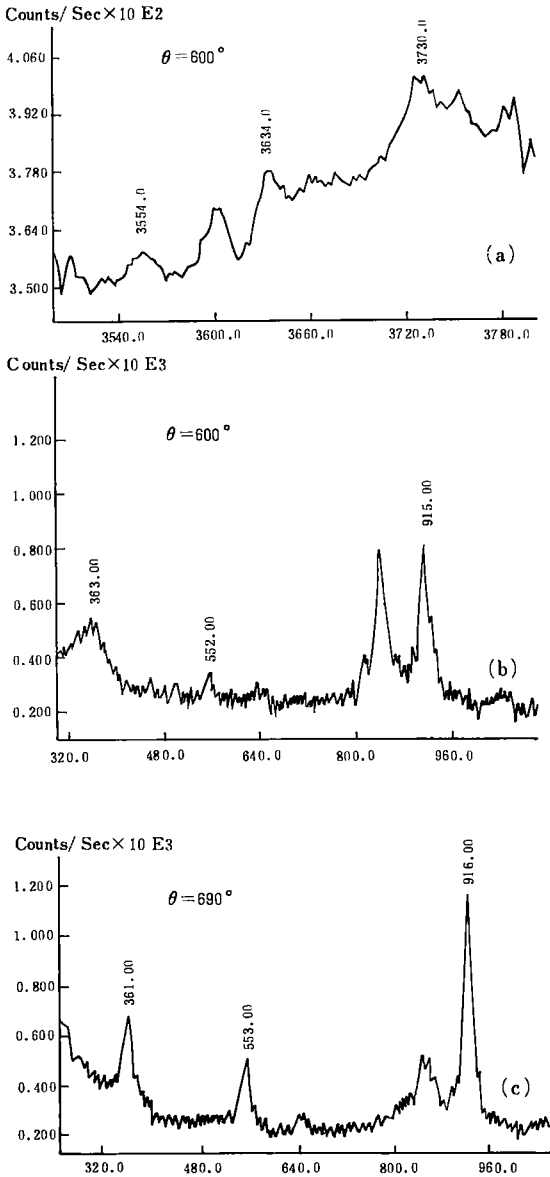


FIG. 6. Raman spectra of a megacrystic garnet (rich in pyrope component): a) OH stretching vibration bands with the angle of polarizer  $\theta = 600^\circ$ . b)  $\text{SiO}_4$  fundamental vibration bands with the angle of polarizer  $\theta = 600^\circ$ . c)  $\text{SiO}_4$  fundamental vibration bands with the angle of polarizer  $\theta = 690^\circ$ .

must preclude the possibility of other modes of substitution.

The experimental anomaly shown in Figure 6 can be explained if the different directions of atomic

displacements of the O-H stretching mode ( $\sim 3730 \text{ cm}^{-1}$ ) and that of  $(\text{SiO}_4)^{4-}$  stretching mode ( $\sim 920 \text{ cm}^{-1}$ ) are considered. The atomic displacements in a stretching vibrational mode are known always to occur along the bonding direction. However, the structural refinements (Lager *et al.* 1989, Cohen-Addad *et al.* 1967) reveal that the O-H bonds in a substituting polyhedron, present as  $(\text{O}_4\text{H}_4)^{4-}$  or in other forms, do not parallel the Si-O bonds in an equivalent  $(\text{SiO}_4)^{4-}$  tetrahedron. The calculated angle between O-H and O-Si directions in hydrogarnet structures varies from about  $45$  to  $82^\circ$ . It is thus very possible that the stretching band of O-H bond will reach its maximum under a polarization direction ( $\theta = 600^\circ$ ) that is perpendicular to the direction ( $\theta = 690^\circ$ ) approximately suitable for the stretching mode of the  $(\text{SiO}_4)^{4-}$  group.

## CONCLUSION

By means of a micro-Raman investigation, two microstructural variations, the degeneration of long-range order and the existence of structurally bound hydrous component, have been documented in a pyrope inclusion in diamond. They provide the direct evidence of the existence of crystalline-to-amorphous transition in a mantle-derived crystal, the incorporation of "mantle water" into the structure of a magnesium silicate that is nominally anhydrous, and the possible genetic correlation of these two phenomena under the physical and chemical conditions in the upper mantle where diamond forms.

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## REFERENCES

- AINES, R.D. & ROSSMAN, G.R. (1984a): The hydrous component in garnets: pyrope. *Am. Mineral.* **69**, 1116-1126.

- \_\_\_\_\_ & \_\_\_\_\_ (1984b): Water content of mantle garnets. *Geology* **12**, 720-723.
- BASSO, R., CIMMINO, F. & MESSIGA, B. (1984): Crystal chemistry of hydrogarnets from three different microstructural sites of basaltic metaroddingite from Voltri massif (western Liguria, Italy). *Neues Jahrb. Mineral. Abh.* **148**, 245-258.
- BRAWER, S. (1975): Theory of the vibrational spectra of some network and molecular glasses. *Phys. Rev.* **B11**, 3173-3194.
- COHEN-ADDAD, C., DUCROS, P. & BERTAUT, E.F. (1967): Étude de la substitution du groupement  $\text{SiO}_4$  par  $(\text{OH})_4$  dans les composés  $\text{Al}_2\text{Ca}_3(\text{OH})_{12}$  et  $\text{Al}_2\text{Ca}_3(\text{SiO}_4)_{2.16}(\text{OH})_{3.36}$  de type grenat. *Acta Crystallogr.* **23**, 220-230.
- DELE-DUBOIS, M.L., DHAMELINCOURT, P. & SCHUBNEL, H.J. (1980a): Etude par spectroscopie Raman d'inclusions dans les diamants, saphirs et émeraudes 1. *Revue de Gemmologie* **63**(juin), 11-15.
- \_\_\_\_\_, \_\_\_\_\_ & \_\_\_\_\_ (1980b): Etude par spectroscopie Raman d'inclusions dans les diamants, saphirs et émeraudes 2. *Revue de Gemmologie* **64** (sept.) 13-17.
- DELHAYE, M. & DHAMELINCOURT, P. (1975): Raman microprobe and microscope with laser excitation. *J. Raman Spectrosc.* **3**, 33-38.
- FOREMAN, D.W. (1968): Neutron and X-ray diffraction study of  $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$ , a garnetoid. *J. Chem. Phys.* **48**, 3037-3041.
- HEMLEY, R.J., JEPHCOAT, A.P., MAO, H.K., MING, L.C. & MANGHNANI, M.H. (1988): Pressure-induced amorphization of crystalline silica. *Nature* **334**, 52-54.
- LAGER, G.A., ARMBRUSTER, T., ROTELLA, F.J. & ROSSMAN, G.R. (1989): OH substitution in garnets: X-ray and neutron diffraction, infrared, and geometric-modeling studies. *Am. Mineral.* **74**, 840-851.
- MCCONNELL, D. (1942): Graphite, a hydrophosphate garnetoid. *Am. Mineral.* **27**, 452-461.
- McMILLAN, P. (1984): Structural studies of silicate glasses and melts - applications and limitations of Raman spectroscopy. *Am. Mineral.* **69**, 622-644.
- MEYER, H.O.A. (1967): Inclusion in diamond. *Carnegie Inst. Washington Year Book* **66**, 446-450.
- \_\_\_\_\_ (1987): Inclusion in diamond. In *Mantle Xenoliths* (P.H. Nixon, ed.). John Wiley Sons Ltd., Chichester, England.
- RINGWOOD, A.E. (1975): *Composition and Petrology of the Earth's Mantle*. McGraw-Hill, New York.
- WANG, ALIAN (1987): *Application de la microspectrométrie Raman à l'étude de quelques problèmes intéressant le domaine de la géologie*. Thèse de doctorat, Université des Sciences et Techniques de Lille Flandres Artois, Lille, France.
- WANG, WUYI (1988): *Statistical and Mineralogical Characteristics of Pyropes from Chinese Major Diamondiferous Kimberlites*. M.Sc. thesis, Chinese Academy of Geological Sciences, Beijing, China.

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