Scanning Microscopy

Volume 1 | Number 2 Article 8

1-21-1987

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Recommended Citation

Mao, H.; Hemley, R. J.; and Chao, E. C. T. (1987) "The Application of Micro-Raman Spectroscopy to Analysis and Identification of Minerals in Thin Section," *Scanning Microscopy*: Vol. 1 : No. 2 , Article 8.
Available at: https://digitalcommons.usu.edu/microscopy/vol1/iss2/8

Scanning Microscopy, Vol. 1, No. 2, 1987 (Pages 495-501)
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

THE APPLICATION OF MICRO-RAMAN SPECTROSCOPY TO ANALYSIS AND IDENTIFICATION OF MINERALS IN THIN SECTION

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(Received for publication April 20, 1986, and in revised form January 21, 1987)

Abstract

Micro-Raman spectroscopy is a useful analytical tool for studying minerals in thin section. The advantages of this technique as a structural probe for analysis of micron-size minerals are demonstrated with a study of polymorphism of SiO_2 and $MgSiO_3$. Three polymorphs of silica, α-quartz, coesite, and glass, in a thin section of Coconino sandstone were identified *in situ* with a Raman microprobe. The Raman spectra of these phases were compared to that measured for stishovite obtained from the same rock. Spectra of protoenstatite, orthoenstatite, and clinoenstatite, three polymorphs of $MgSiO_3$, are consistent with their similar pyroxene chain structures but different space groups. The characteristic Raman spectra in each instance could be used for "finger-printing" identification of the phases and their orientations.

Key Words: Micro-Raman spectroscopy, Raman microprobe, thin section, silica, stishovite, coesite, enstatite, clinoenstatite, orthoenstatite, protoenstatite.

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Introduction

The potential of using Raman spectroscopy for identification and structural analysis of minerals has long been recognized (Griffith, 1975, White, 1975). With the recent development of micro-Raman techniques (Dhamelincourt et al., 1979, Rosasco, 1980, Sharma et al., 1985), the Raman microprobe is emerging as an important tool in mineralogical and petrographic research.

Raman spectroscopy provides detailed structural information about site symmetry, short-range and long-range bonding, and lattice-vibrational properties. Macro-sampling Raman spectroscopy has been used as the main analytical method of studying the structures of silicate glasses quenched from various temperatures and pressure (Furukawa et al., 1981; Mysen et al., 1982, 1985; McMillan, 1984; Sharma et al., 1983). The method provides critical structural information such as the mechanism of pressure densification, the angles of Si-O-Si linkages, the number of non-bridging oxygens, and the effect of ion substitution. Raman spectra are also sensitive to slight differences in the symmetry of polymorphous mineral phases and to the ordering of cations. It has been used to investigate the classical crystal-chemical problems of order-disorder phenomena including distinguishing different forms of potassium feldspars, Al-Si ordering in cordierites, and cation ordering in spinels. The results compare favorably with and are complementary to those obtained by x-ray diffraction and transmission electron microscopy (Vodop'yanova et al., 1983; McMillan et al., 1984; Ishii et al., 1982).

The coupling of a research grade microscope to a Raman spectrometer has led to the capability of obtaining Raman spectra in micron size samples (Dhamelincourt et al., 1979; Adar, 1986; Beny-Bassez and Rouzaud, 1985), and there are numerous uses and developments of the technique. The application of Raman spectroscopy to mineralogy is no longer limited to large synthetic samples or gem-quality natural specimens. Practically any sample suitable for optical microscopy or electron microprobe analysis can be studied. The Raman microprobe has become an important tool for identifying fluid and crystalline inclusions in minerals (Dubessy et al.,1983; Dele-Dubois et al., 1980). Its

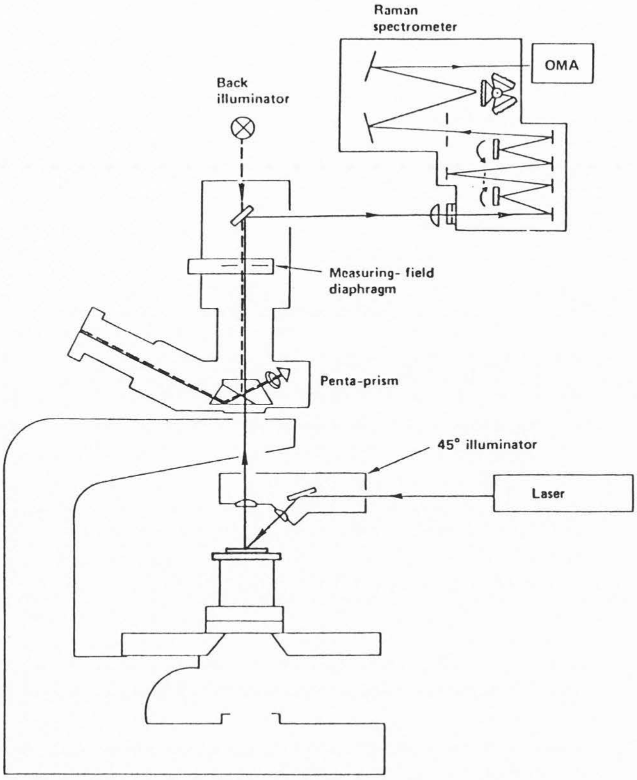

Fig. 1. Schematic of the micro-Raman spectrometer system.

applications to phase separation and to clay mineralogy have been demonstrated (Purcell and White, 1983; Boyer et al., 1985; Velde and Boyer, 1985; Haley et al., 1982). Recent developments in multichannel detectors matched with appropriate spectrographs have shortened measurement time from hours to seconds (Purcell and Etz, 1982, Grayzel et al., 1985). As a result, routine use of the Raman microprobe in mineralogical studies becomes practical.

In this article, we describe a Raman microprobe system which can be used as a routine petrographic tool comparable to a conventional petrographic microscope or an electron microprobe. High spatial resolution and rapid measurement can be obtained with standard doubly polished thin sections of rock. Case studies of polymorphs of SiO_2 and $MgSiO_3$ are presented to demonstrate the power of the system as a structural probe.

Instrumentation

The Raman Microprobe system used in this study is shown in Figure 1. A variety of lines from an argon ion laser (Spectra-Physics 165) are used as an excitation source. Plasma lines other than the principal excitation wavelength are filtered with a prism pre-monochromator (Applied Photophysics 2400). The output power of the laser is normally kept below 100 milliwatts to avoid damaging the epoxy resin holding the rock sample. This laser damage appears to involve oxidation of the resin, which in turn results in further absorption of the laser radiation and further damage, as well as causing a general deterioration in optical quality of the thin section.

The microscope portion of the system is designed so that petrographic thin sections can be handled routinely and so that the spatial resolution in the samples can be optimized. The basic component is a Leitz Ortholux I microscope with added polarizer and analyzer, similar to a petrographic microscope, for observing thin sections under crossed Nicols. The present system used a 45° incident light illuminator made by Leitz, instead of the 180° epi-illuminator commonly employed in other Raman microprobes. In epi-illumination, the laser light is partially reflected by a semi-transparent beam splitter and focused by a microscope objective onto the sample. The 180° (backscattered) Raman radiation is collected by the same objective, partially passes through the same beam splitter, and enters the spectrometer. The axial spatial resolution (depth of field scaled by the refractive index) is achieved with an aperture at an intermediate image plane. Because the illuminating laser beam and the Raman scattered radiation are coaxial, the depth of field is at least six times greater than the lateral spatial resolution (Clarke and Adar, 1983). Unwanted spectra of epoxy resins and the glass slide under the doubly-polished rock section are seen with greater depth of field and could interfere with the desired sample spectra (Boyer et al., 1985; Velde and Boyer, 1985). Interfering spectra from the epoxy resins may involve both fluorescence and Raman scattering.

In the case of 45° illumination, the laser is reflected by a total reflection front-surface mirror, and then focused by an objective onto the thin section at 45°. The resulting 135° scattered radiation is collected by another objective at right angles to the thin section, and enters the spectrometer without going through an additional, semi-transparent, beam splitter. Only the sample volume at the intersection of the illuminating cone and the Raman scattering cone is detected. The axial spatial resolution is equal to the lateral resolution and the spectrum of the substrate in the thin section is eliminated completely. An additional advantage of the 45° geometry is to avoid the decrease in both laser and Raman scattering intensities resulting from the use of a semitransparent beam splitter. A commonly used beamsplitter, for example, would introduce losses of 50% in both the excitation and scattered light levels. In the present design the intensity of scattered Raman radiation is thus increased by a factor of four over epi-illumination using this type of beamsplitter with the same laser intensity. A disadvantage of the 135° geometry is that there is less flexibility for adjusting the polarization with the excitation and scattered light on nonorthogonal axes.

The lateral spatial resolution is a function of the characteristics of the microscope objectives and the intermediate aperture. The objectives designed for the 45° illuminator are of the Leitz UM or UT series with magnifications from 5X to 40X. This type of objective has a relatively long working distances (16mm), and can be used for samples with great depth, such as samples in diamond anvil cells (Sharma et al., 1985).

A segment of a Leitz MPV microphotometer system is adapted in this microscope for controlling the intermediate aperture and for viewing. The aperture consists of a rectangular diaphragm with continuously and independently adjustable side lengths. The viewing part consists of a trinocular microscope head that contains a pentaprism and a beam splitter. The intermediate aperture can be back-illuminated and its image projected to the eyepieces. The image of the back-projected aperture is thus overlapped with the image of the sample and the exact area and position of sampling can be determinedd precisely. The MPV system is designed to measure spectra on a 0.7 micron sample when a high-magnification, short-working distance objective (Leitz PL 80X/0.95) is used. In the configuration of the present system, high-quality spectra can be obtained from 1-2 micron rectangular areas of a grain in thin section.

The scattered radiation that passes through the intermediate aperture is fully collected by a 50 mm Micro-Nikkor camera lens, and is focused to the entrance slit of a Spex Industries Triplemate^R Raman spectrometer. The Triplemate consists of a 0.22 m double subtractive filter stage spectrograph and a second-stage 0.6 m single dispersive spectrograph. An intensified 700-channel optical scanning multichannel analyzer (OSMA, Princeton Instruments, Inc.) is mounted at the exit of the Triplemate^R to collect the entire spectrum dispersed during a scan period (smallest unit, 33 msec.). Typically, a 10 sec. exposure is sufficient to obtain a usable Raman spectrum in thin section. Longer exposure times or the average of multiple measurements may be needed in some instances to improve the signal-to-noise ratio for weak Raman spectra.

Polymorphs of SiO_2 in Shock-Metamorphosed Coconino sandstone

Two high-pressure polymorphs of silica, coesite and stishovite, were first synthesized in the laboratory by Coes (1953) and by Stishov and Popova (1961). They were first discovered as naturally occurring minerals in the shock-metamorphosed Coconino sandstone at Meteor Crater, Arizona (Chao et al., 1960; Chao et al., 1962). The rock also contains two other polymorphs of silica, the original α-quartz grains and a shock-produced silica glass. The nature of the shock-wave compression process produced by meteor impacts has generated considerable interest (Kieffer, 1971; Stoffler, 1971). The properties of the high-pressure polymorphs and the shock textures of the rock have been used to interpret the impact processes. It would be preferable to study the high-pressure phases *in situ* in thin section, but before availability of micrograin techniques, the positive identification of fine-grain coesite and other high-pressure phases was made only on extracts. Critical textural information was lost.

In this study, doubly-polished thin sections from an original specimen of Coconino sandstone studied by Chao et al. (1962) were examined with the Raman microprobe, and the spectra are shown in Figure 2. The sandstone sample contains mostly α-quartz and silica glass, but with up to 25% coesite and 0.5% stishovite. α-Quartz can be identified instantly on the basis of its intense Raman line at 464 cm^{-1}. Fine-grained crystals (less than 15 microns) of coesite were easily identified *in situ* by their characteristic Raman lines at 521, 425, 355, and 271 cm^{-1}. The strongest line at 521 cm^{-1} has been assigned to a symmetric Si-O-Si stretching mode, correlating with the 464 cm^{-1} mode of α-quartz (see Hemley, 1987). The rock also contains trace amounts of zircon, which appears similar to coesite under the optical microscope in terms of size, shape, relief, and birefringence. Coesite and zircon can be distinguished readily on the basis of their Raman spectra, as shown in Figure 2. The Raman spectrum of zircon is consistent with previous large sample measurements (White, 1975).

The Raman spectrum of silica glass in the thin section shows a strong, broad band at 440 cm^{-1}, with weaker features at 800 and 1000 cm^{-1}. The spectrum is similar to that of synthetic fused silica glass (see Hemley et al., 1986a), but the spectrum of the natural sample appears to be more diffuse. For example, the bands at 490 and 605 cm^{-1} (the so-called D_1 and D_2 defect bands) are not resolved. Hemley et al. (1986a) observed that the 440 cm^{-1} band of silica glass sharpened and shifted to higher frequency irreversibly when quenched from pressures higher than 80 kbars at room temperature. The lack of such a change in the Coconino silica glass indicates that either the shock pressure was lower than 80 kbars or that the temperature was high enough to anneal the glass after the pressure dropped below 80 kbars. In fact, a slight broadening relative to that observed in synthetic silica glass is observed. This broadening may arise from a widened distribution of Si-O-Si angles in the shocked material.

Stishovite occurs only in trace amounts (less than 0.5%) and submicron fine-grain size in these samples, and thus *in situ* identification was unsuccessful. It was possible to extract grains of stishovite from the Coconino sandstone by dissolving other phases in concentrated HCl and HF (Fahey, 1964). Stishovite was identified by powder x-ray diffraction to have the rutile-type structure with Si in six-fold coordination with oxygen. A previous study on the stishovite extracts reported Raman spectrum totally inconsistent with the rutile-type pattern, however, and suggested that the natural stishovite did not have the ideal rutile structure (Nicol et al., 1980). In a more recent study (Hemley et al., 1986b) new batches of stishovite were extracted by the acid leaching process, and the spectrum was measured with the Raman microprobe. As shown in Figure 3, the spectrum contains at least three of the four sharp fundamental bands that were observed in the spectrum of the synthetic sample (*i.e.*, the B_{1g}, E_g, and A_{1g} bands at 231, 589, and 753 cm^{-1}, respectively). These bands are indicative of a rutile-type structure.

A notable difference between the spectra of the natural and synthetic stishovite is the broad band at 475 cm^{-1}. This feature may indicate the existence of residual glass, other contaminants, or shock-produced structural disorder giving rise to a multiphonon band in stishovite (Hemley et al., 1986b). The spectrum of the natural sample is also considerably weaker owing to the fine-grain nature of the material. It is also useful to point out two distinct types of spurious fluorescence tended to interfere with the Raman measurements of the two stishovite samples. This problem was alleviated by tuning the argon ion laser to longer wavelengths (514.5 nm) for the measurement of the natural sample and to shorter wavelengths (457.9 nm) for that of the synthetic stishovite.

$MgSiO_3$ Enstatites

The four polymorphs of $MgSiO_3$ have a similar basic enstatite chain structure, but differ slightly in space group symmetry. They are protoenstatite (Pbcn), orthoenstatite (Pbca), high temperature clinoestatite (C2/c), and low temperature clinoenstatite ($P2_1/c$). Their phase relations are very sensitive to temperature, cooling rate, pressure, and shear stress (Boyd and England, 1965; Smith, 1969; Smyth, 1974). Their regions of stability, their pseudomorphism, and their twinning structures have been used extensively as indicators to interpret conditions of formation for rocks and meteorites (Raleigh et al., 1971; Komatsu, 1980; Ohashi, 1984). The similarity of their x-ray diffraction patterns and complications caused by twinning phenomena associated with sub-solidus conversions in enstatite, however, frequently pose a problem of phase identification.

Synthetic untwinned single crystals of proto-, ortho-, and clinoenstatite (low temperature $P2_1/c$) originally synthesized by Ito (1975) were used for Raman studies. The crystals were needle like, their dimensions approximately 0.1 x 1 mm, with the long direction parallel to the c axis. Three spectra were taken from each crystal at different orientations with the 135° scattering configuration shown in Figure 1. The results are shown in Figure 4. The effect of orientation of the c axis with respect to the plane of the laser and scattered light is pronounced.

The spectra of the three polymorphs of enstatite are similar in major features but distinctive in details. Orientation dependencies and the relative intensities of the symmetric Si-0 stretching bands at 1,000-1,050 cm^{-1} are characteristic in all enstatites and even in other pyroxenes, as are the symmetric stretching bands of the chain bridging oxygens at 650-680 cm^{-1} (assigned by White, 1975).

These strong bands reflect the general nature of the pyroxene chain. The peak splitting and the exact position of these bands caused by the minor differences in the chains, however, are distinctively different among the three polymorphs. The lower frequency bands (50-500 cm^{-1}), especially below 200 cm^{-1} which are in the lattice phonon region, differ substantially among the three enstatite polymorphs. These characteristic features can thus be used for "finger-printing" identification of the enstatite phases and their orientations *in situ* in thin section. Quantitative interpretations of the differences in the spectra in terms of structural effects await accurate calculations of the vibrational force fields of these phases.

Summary

Similar to the electron microprobe, the Raman microprobe is a convenient petrographic tool for routine and rapid determinations of micron-size grains in regular thin section. No special sample preparation is

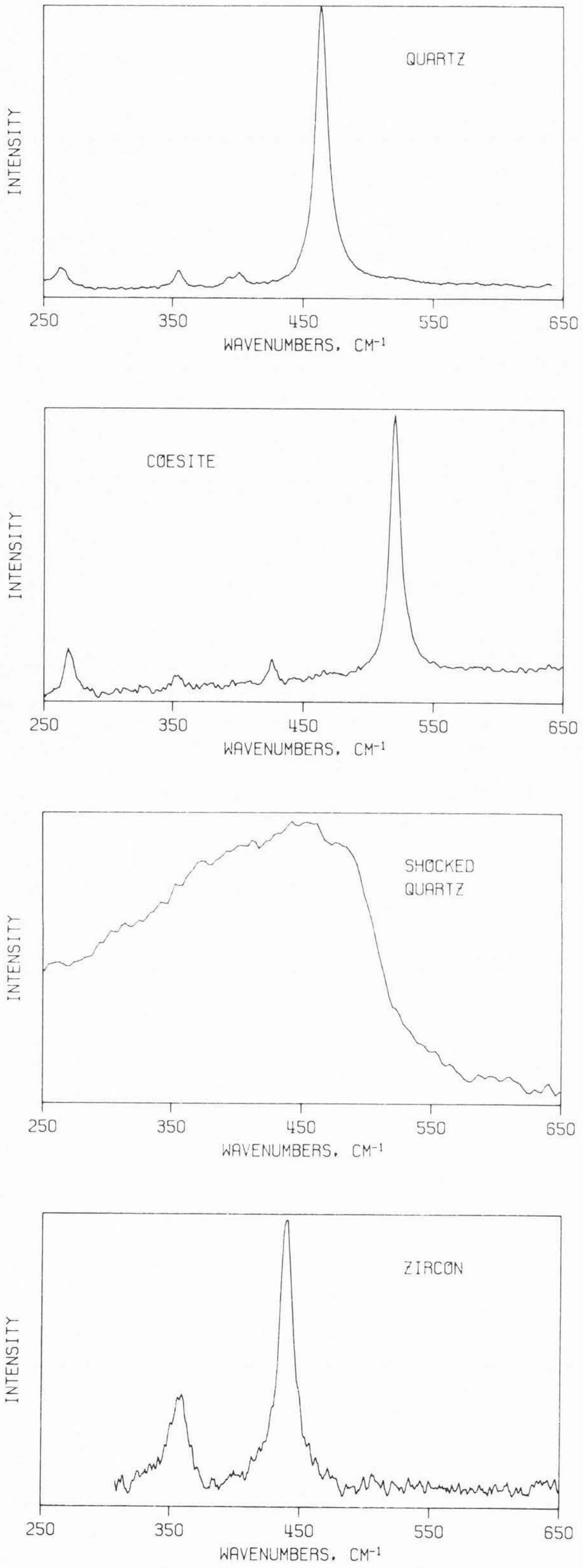

Fig. 2. Micro-Raman spectra of phases present in a thin section of shocked Coconino sandstone: α-quartz, coesite, glass, and zircon. Only the mid-frequency range (250-650 cm^{-1}) is shown.

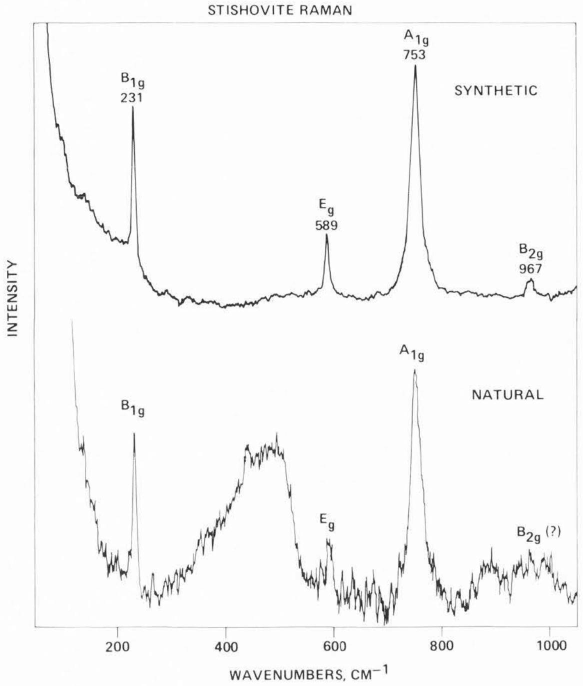

Fig. 3. Comparison of Raman spectra obtained from synthetic stishovite and natural stishovite from Coconino sandstone (Hemley et al., 1986b).

needed. Unlike the electron microprobe which is limited to analysis on the surface of the sample, the Raman microprobe with well-defined depth resolution can be focused on internal grains beneath the surface of a thin section. Even for submicron-size grains of stishovite in a rock, high-quality Raman spectra can still be obtained on aggregates of extracted grains. The study of zircon, α-quartz, coesite, and silica glass in thin sections of Coconino sandstone also demonstrates that the technique can be used to distinguish polymorphs of identical chemical composition, as well as minerals of different compositions.

In addition to "finger-printing" identification, Raman spectroscopy yields sophisticated structural information. Raman spectra of protoenstatite, orthoenstatite, and clinoenstatite reflect differences in the nature of their pyroxene chains and space groups. The broadening of the 440 cm^{-1} Raman band in the glassy silica phase produced from shocked quartz may be indicative of pressure densification and a wider distribution of Si-O-Si angles relative to that of synthetic fused silica glass. The additional band in the Raman spectrum of stishovite may reflect shock-produced structural disorder. Obtaining this crystal-chemical information for minerals *in situ* in thin section is critical to understanding the history and the process of rock formation.

Finally, it should be pointed out that absorption of the excitation laser and Raman signal by colored materials is often mentioned as an important limitation of Raman techniques (Rosasco, 1980). Laser absorption can result in either fluorescence, which may interfere with the Raman measurement, or decomposition of the sample. As demonstrated for the measurements on stishovite, however, it is possible to circumvent these problems by a judicious choice of laser wavelengths to avoid absorption and/or fluorescence bands of the sample. In addition, with the use of sensitive multichannel detectors, high-quality Raman spectra can be obtained from absorbing samples with very low laser power (*e.g.*, a few milliwatts) in order to minimize decomposition.

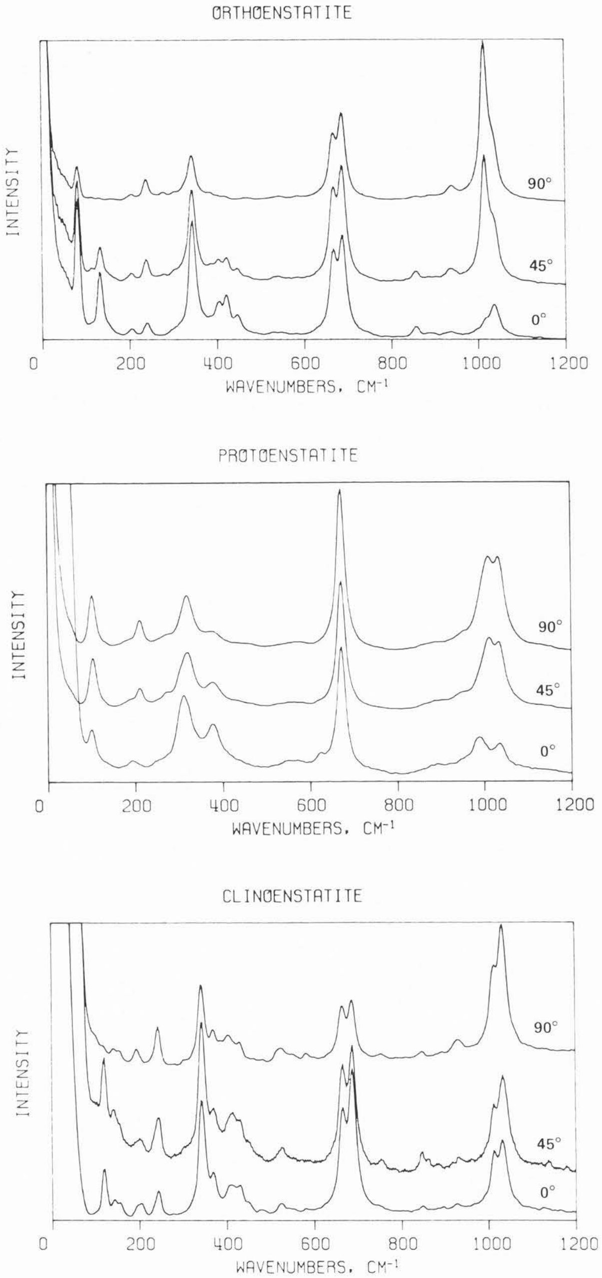

Fig. 4. Raman spectra of enstatite polymorphs. For each polymorph, measurements at three orientations are shown: bottom, the plane of laser beam and Raman scattered beam parallel to the c axis; middle, the plane at 45° to c; top, the plane perpendicular to c.

We are encouraged by the success of these approaches in recent Raman studies on opaque Fe-bearing minerals (Hemley and Mao, unpublished), phases in which sample absorption, fluorescence, and decomposition (including oxidation) have been particularly severe problems in previous optical work.

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Editor's Note: All of the reviewers' concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.