A STRESS INDICATOR FOR MINERALS BY MICRO-RAMAN SPECTROSCOPY;
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We applied micro-Raman spectroscopy to evaluating the residual stress in minerals. The technique measures very small shifts in the wavenumber position of a Raman line due to the residual stress in minerals. The residual stress gives physical constraints on the formation of minerals which have some stress histories such as static or shock deformations. In this paper, we successfully detected small shifts in the wavenumber position of Raman lines of olivine and quartz due to the residual stress and show that the method is useful for estimating the residual stress around 1 μm area within a mineral grain.

Method: Raman spectra were measured with a JASCO micro-Raman spectrometer of a triple monochromator (60 cm). The 488 nm line of an argon laser was focused to an area of about 1 μm diameter on the sample surface through a microscope (the backscattering (180^{o}) geometry). The laser power was about 4 mW on the surface of a sample. A multichannel detector was used to measure precisely the relative change of the position of a Raman line, because the mechanical scanning of monochromator is not required unlike a usual Raman spectrometer with a photomultiplier. The spectra were accumulated for 1-3 minutes and the peak position of a Raman line was determined by using the Lorentzian fitting of the spectra. Spectral slit width was about 1 cm^{-1} and the change of room temperature was within ±0.1 ^{o}C.

Results: Olivine shows strong Raman lines near 856 and 824 cm^{-1} and quartz does 466 cm^{-1}. Twenty spectra were measured for the same point of olivine (San Carlos), resulting the standard deviation (σ) of about 0.04 cm^{-1}. Although a wavenumber resolution corresponding to an element of the multichannel detector is 0.27 cm^{-1}, a practical resolving power is fairly enhanced because the peak position of a Raman line is determined by the Lorentzian fitting.

In order to detect the residual stress, we measured Raman spectra of the vicinity of an indentation on the sample surface made by a micro-Vickers hardness testing machine (Fig. 1). The diagonal length of the base of the indentation whose shape is a quadrangular pyramid is about 5 μm for olivine and about 4 μm for quartz. Raman spectra were measured at intervals of 1 μm outward from the midpoint of the edge of the base of the quadrangular pyramid. The shifts in the wavenumber position of Raman lines are shown in Fig. 2, as a function of the distance from the edge of the indentation. For olivine, both Raman lines shift to larger wavenumbers within 3 μm area around the indentation compared with those far from the indentation. For quartz, the Raman line also shifts within 2 μm area. Because the peak position of Raman lines shifts toward a larger wavenumber, the vicinity of the indentation is compressive stress fields, as expected from the indentation made by a Vickers hardness testing machine.

This technique is similar to that recently developed in the semiconductor research for evaluating the quality of Si (e.g., 1). It is known that the 520 cm^{-1} line of Si shifts at a rate of 1 cm^{-1} per 250 MPa. The technique of the stress analysis by micro-Raman spectroscopy has the following characteristic features: (1) spatial resolution is about 1 μm, comparable to the chemical analysis by an electron probe microanalyzer,

(2) no sample preparation is required, because of the 180° scattering geometry; direct measurement of crystal faces, fracture surfaces, and thin sections is possible, and (3) the time required for a measurement is short (a few minutes are enough). This method can be easily applied to Raman lines of other minerals and seems to be useful for analyzing residual stress distributions within a grain in statically deformed or shocked rocks and meteorites.

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References: (1) Kobayashi K., Inoue Y., Nishimura T., Arima H., Hirayama M., and Matsukawa T. (1987) Extended abstract of the 19th Conference on Solid State Devices and Materials, Tokyo, pp. 323-326.

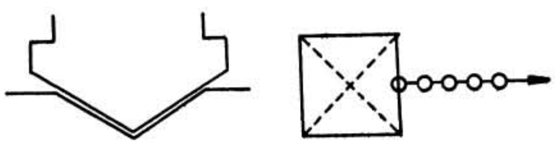
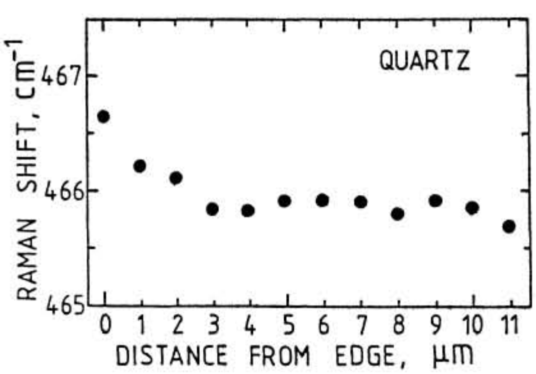


Fig. 1. Schematic diagram of indentation and measurement.
Open circles: measured points (1 μm interval), a square: the base of a quadrangular pyramid made by a micro-Vickers hardness testing machine.



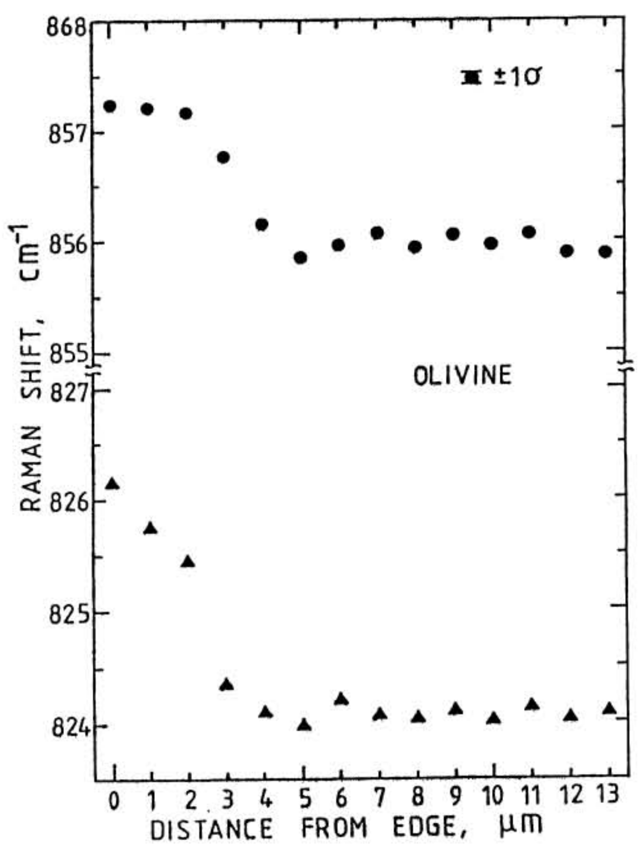


Fig. 2. Shifts in the wavenumber position of Raman lines of quartz (left) and olivine (right) due to the residual stress as a function of the distance from the edge of the indentation.