Spectra of Shock-Affected Rhodonite: A Reply

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Introduction
The Gaussian resolution procedure of Faye (1975) leading to the conclusion that the spectral changes in a shock-loaded rhodonite are the result of a broadening or intensification of the ultraviolet charge-transfer absorption and that the 540 nm band is present with comparable intensity in both pre- and post-shock samples is not physically meaningful because it has ignored the dominant process which gives rise to the rising baseline "absorption" throughout the near-infrared and visible spectral regions. That process is wavelength-dependent scattering.

Scattering
After recovery from the shock apparatus, the intensely shocked samples were impregnated with metal particles and organic matter and pervasively fractured. Before optical spectroscopic examination, the surfaces of the specimen were ground away to remove much of the imbedded metal leaving a highly fractured slab which was strikingly less intensely colored than rhodonite specimens of comparable thickness after only mild shock. The extent of fracturing was so great that less than 4 percent of of the incident light was transmitted through the specimen. The pervasive fracturing of the sample is important to re-emphasize because it gives rise to extensive scattering of light by the sample during the spectroscopic experiment.

The spectrum of rhodonite shock-loaded to 496 kbar has been redetermined (Fig. 1). The spectrum was obtained on the same specimen reported in Gibbons, Ahrens, and Rossman (1974). It represents a smaller portion of the specimen which was masked off to isolate the clearest region free of extraneous matter. The spectral features are similar to the rhodonite spectrum previously reported, although the quality of the spectrum is noticeably improved in the near infrared region. The 540 nm band appears to be greatly reduced in intensity compared to the spectra of pre-shock samples previously reported.

Several scattering curves were determined by obtaining the absorption spectra of abraded and sandblasted fused silica and glass plates run against clear plates and of pressed KBr pellets of various degrees of clarity run against air. Scattering by these translucent materials is strongly wavelength dependent and varies with the size distribution of the scattering centers. A typical scattering curve is shown in Figure 1 below the rhodonite spectrum. It was chosen as one which provided a reasonable match to the baseline in the low energy region. Although it is impossible to determine the exact scattering baseline of any particular sample, it is felt that the scattering curve in Figure 1 correctly illustrates that for badly fractured samples scattering is a major contributor to the baseline nonlinearity. The contribution of scattering can be as important as that of charge transfer tails in the visible and the most important factor in the near-infrared.

When the contribution of scattering is considered in addition to the contribution from the ultra-violet tail, it is evident from Figure 1 that little intensity remains in the 540 nm region and that a Gaussian analysis which does not consider scattering overestimates the contribution of the 540 nm feature. Direct comparison of the pre-and post-shock spectra is not possible because the two rhodonite samples will differ greatly in their scattering properties.

Fe$^{2+}$ Absorption
From our own studies and the data presented by Faye (1975) and Marshall and Runciman (1975) it is
spectra of post-shock samples obtained at ambient pressure unless a hysteresis effect occurs. In post-shock crystalline samples there was insignificant to no change in the measured interplanar spacings $d_{hkl}$ compared to unshocked samples, although with samples subjected to higher pressures there was loss of back-reflection X-ray lines. The lack of change in $d_{hkl}$ implies lack of significant hysteresis and change in the $M$–$O$ bond length. Changes in the ultraviolet absorption by permanent physical or chemical changes brought about by shock loading, of course, are possible.

Marshall and Runciman (1975) assigned a band at 18500 cm$^{-1}$ (540 nm) in the spectrum of a high-iron rhodonite to the $e_{g}A_{1g}$ transition of Mn$^{3+}$. At 18 K in the $\beta$-spectrum, this band had an absorbance of $0.37$/mm. However, in the spectrum of a nearly gem-quality, low-iron, light pink rhodonite from Franklin, New Jersey, we observed an absorption band at 522 nm in the $\beta$-spectrum which we assign to $e_{g}A_{1g}$ transition. This band can be seen in Figure 3 of Faye (1975). It would be expected that for the low-iron rhodonite sample used in the shock-recovery studies, the $e_{g}A_{1g}$ transition of Mn$^{2+}$ would also occur at 522 nm. In the rhodonite used for shock studies, an absorption band instead occurs at 540 nm with a greater intensity ($1.9$/mm) in an unpolarized spectrum. These differences and the change which occurs during the shock event suggest that the 540 nm band has an origin different from the 522 nm band.

**References**


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