A Spectrographic Interpretation of the Shock-Produced Color Change in Rhodonite (MnSiO₃): The Shock-Induced Reduction of Mn(III) to Mn(II).[1]

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Abstract

Samples of rhodonite (MnSiO₃-pyroxenoid from Franklin, New Jersey) have been shock-loaded to pressures up to 496 kilobars. Optical spectral studies of four recovered samples show a decreasing Mn^{3+} content upon recovery from successively higher shock pressures; after shock-loading to 496 kbar, the Mn^{3+} has essentially disappeared. No corresponding change in the optical spectrum results from heating rhodonite to 1250°C for 3.5 hours in a reducing atmosphere. Rhodonite heated to 1360° under the same conditions melts incongruently to manganese-rich glass and silica with disappearance of the 540 nm Mn^{3+} absorption band. The color change in the shocked rhodonite arises from irreversible reduction of Mn^{3+} during high shock pressures and possible high shock temperatures. It is suggested that Mn^{3+} is reduced to Mn^{2+} by water present in the sample during the shock event.

Introduction

Rhodonite (MnSiO₃, variety fowlerite, from Franklin, New Jersey) has a characteristic pink color. During optical and X-ray studies performed while attempting to characterize shock-induced phase changes in rhodonite, we observed that this color was not present in intensely shocked samples. Absorption spectra of several specimens, both shocked and unshocked, were measured to determine what optically apparent physical or chemical change was occurring as a result of the shock wave experiments. The characteristic color of the variety of rhodonite is caused by a prominent absorption band in the visible region of the rhodonite spectrum at 540 nm due to an electronic transition in Mn^{3+}. This absorption band decreases in intensity with increasing shock pressure and disappears by 496 kbar.

A series of experiments has been performed to determine the shock pressures required to cause this phenomenon, and to obtain spectroscopic information on the effect of the high shock pressure event upon the manganese in the samples.

Experimental

A specimen of coarsely crystalline rhodonite (analysis in Table 1) was sawn into slabs, parallel to (001), from which several discs 4.75 mm in diameter and 0.5 mm thick were cored and prepared for shock recovery experiments. The discs were shock-loaded using the techniques and facilities described by Gibbons and Ahrens (1971). The peak shock pressures reached in the samples were determined graphically by an impedance matching technique, as described by Gibbons and Ahrens (1971). The accuracy of those pressures is ±3 percent at lower shock pressures and ±6 kbar at pressures greater than 200 kbar. Four samples were recovered, ground, and polished to approximately 0.15 mm thickness for spectroscopic studies. Optical absorption spectra were obtained between 300 and 2500 nm on a Cary 17I spectrophotometer, and infrared spectra were obtained with a Perkin Elmer model 180 infrared spectrophotometer.

Optical Spectra

The optical spectrum of an unshocked rhodonite specimen (Fig. 1, spectrum A) shows, within the infrared, a weak band at about 2300 nm, a more intense band at 1530 nm, and the dominant band at 1035 nm. In the visible-ultraviolet prominent bands occur at 540 nm, 408 nm, and 345 nm, with less intense shoulders at 360 nm and 400 nm. A second component at 411 nm appears on the 408 nm band, which in turn is a closely spaced doublet.

TABLE 1. Analysis* of Rhodonite from Franklin, New Jersey

Oxide	Weight Percent	Oxide	Weight Percent
SiO_2	46.94	MgO	1.93
MnO**	37.18	FeO***	1.86
CaO	6.09	Al_2O_3	0.06
ZnO	5.72	K_2O	0.03
			99.81

*Average of analyses made on two fragments by A. Chodos using the California Institute of Technology electron microprobe.
**Total Mn as MnO. The concentration of Mn^{3+} calculated on the basis of sample thickness = 0.075 cm, absorbance of the 540 nm Mn^{3+} band = 0.3, and ε = 20 is 0.3 percent. The ε value was estimated from known ε values of Mn^{3+} absorption in $Mn(H_2O)_6^{3+}$ and Mn (oxalate)$_3$ (Dingle, 1966), and tourmaline (Manning, 1973).
***Total Fe as FeO.

The optical spectrum of a rhodonite recovered from shock-loading to 496 kbar (Fig. 1, spectrum B) displays a relatively-sharp asymmetric band at 418 nm and a weak band at 520 nm. The 540 nm band has disappeared completely. The near-infrared region now has a much broader absorption band with a maximum in the vicinity of 1035 nm; the 1530 nm band has disappeared. Features in the 2230–2450 nm and 1710 nm regions arise from organic materials used in preparation of the recovered sample. All features are superimposed upon a background, steadily rising towards the ultraviolet, which results from scattering from the pervasively
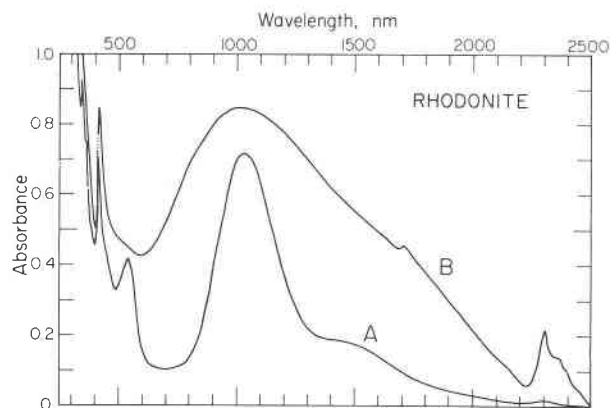

FIG. 1. Absorption spectra of rhodonite. A= spectrum of unshocked sample. B = spectrum of sample shocked to 496 kbar. The Mn^{3+} absorption bands occur at 540 nm and 1530 nm. The intense band at 1035 nm is due to Fe^{2+}; the bands between 340 and 450 nm are due to Mn^{2+}.

internally-shattered specimen recovered from the shock experiment.

The 540 nm band, which we attribute to Mn^{3+} (see below), decreases in intensity at shock pressures above 210 kbar. Thus, in the spectra of samples shocked to 78 (not illustrated) and 210 kbar, the area of the Mn^{3+} band remained essentially unchanged whereas at 390 kbar it was about two-thirds as great as it was at 210 kbar, and by 496 kbar it had disappeared completely revealing the band at 520 nm (Fig. 2).

Other changes in the spectra involve the character and position of the set of sharp bands near 408 nm attributable to Mn^{2+}. In the standard sample and those shocked to 78 (not illustrated) and 210 kbar, the band system remains split, indicating crystalline order in the mineral and distortion of the multiple Mn^{2+} sites away from regular octahedral geometry. This splitting, which appears as a series of well-resolved, closely-spaced bands on the low energy side of the 408 nm band in expanded scale spectra, is too small to be resolved at the scales of Figures 1 and 2. In the 390 kbar and the 496 kbar samples, no appreciable splitting is observed, probably because of disorder and partial vitrification of those specimens produced by the shock process. The shift of the band to 420 nm in the 496 kbar sample may be another indicator of vitrification; in the other samples it stays at 408 nm.

Assignment

The assignment of the spectral features to Mn^{3+}, Mn^{2+}, and Fe^{2+} follows well established assignment schemes for these ions in other systems. Peacor and Niizeki (1963) describe the crystal structure of rhodonite as planes of octahedrally coordinated cations alternating with planes of tetrahedrally coordinated Si-ions between planes of close-packed oxygens. In each unit cell there are four distorted octahedral sites available for the manganese cations, and a fifth site of irregular seven-coordination which calcium preferentially fills. Divalent iron in orthopyroxenes produces two absorption features in the near-infrared, a strong band near 1000 nm in α-polarization and a weaker band near 1900 nm in β-polarization (Bancroft and Burns, 1967). Analogous ferrous iron features appear in the spectra of manganese pyroxenes and pyroxenoids. In the spectrum of pyroxmangite (Figure 1, Manning, 1968) we assign to Fe^{2+} the bands labeled 9800 and 4750 cm^{-1} (1020 and 2105 nm) and, in the case of our rhodonite, the band at
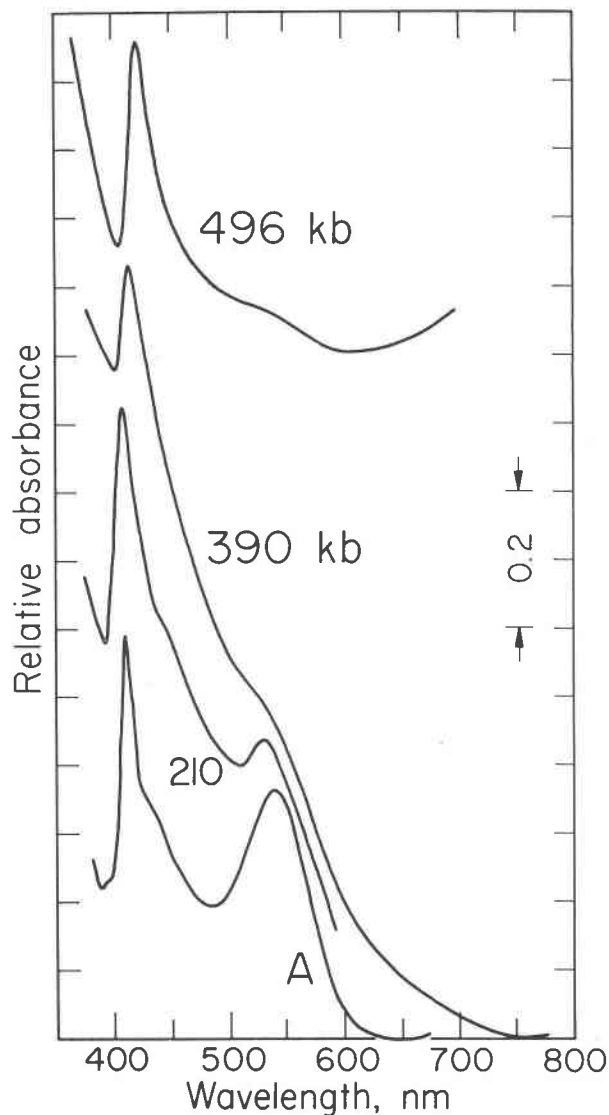
FIG. 2. Rhodonite spectra. The spectra of three samples recovered after being shock-loaded to 210, 390, and 496 kbars are compared with the spectrum of an unshocked rhodonite (A) showing the loss of the Mn^{3+} band at 540 nm in the more intensely shocked samples. These spectra have been normalized to represent the absorbance of a sample of 0.15 mm thickness but have been drawn with vertical displacement in absorbance for purposes of contrast and clarity.

1035 nm. The low energy Fe^{2+} band is not pronounced in the rhodonite orientation shown here. However, in the spectrum of a rhodonite from Broken Hill, New South Wales, Australia, of higher relative iron concentration, low Mn^{3+} concentration, and greater thickness (not illustrated), a feature assignable to the low-energy Fe^{2+} band occurs at 2280 nm. A weak feature can be seen in the New Jersey rhodonite spectrum in the vicinity of 2300 nm. The most intense of the Fe^{2+} spin-forbidden bands occurs at about 500 nm in orthopyroxenes and can be seen at 506 nm in the Broken Hill rhodonite spectrum in both our spectrum and that reported by Keester and White (1966). Its intensity is too low to be important in the New Jersey rhodonite.

The Mn^{2+} spectrum in rhodonite has been reported previously by Keester and White (1966) and Manning (1968). We agree with their choice of an octahedral symmetry to assign the spectra and with their assignment of the 408 nm system to the $^6A_1 \rightarrow$ ($^4A_1$, ^4E) transition and the 440 nm band to the $^6A_1 \rightarrow {}^4T_2$ transition of Mn^{2+}. However, we do not agree with the assignment of the 540 nm band to the $^6A_1 \rightarrow {}^4T_1$ transition, but instead will show below that the 540 nm band is properly assigned to Mn^{3+}. The remaining Mn^{2+} transition, $^6A_1 \rightarrow {}^4T_1$, which is expected to have an intensity comparable to the $^6A_1 \rightarrow {}^4T_2$ 440 nm band, is instead assigned to the band at 520 nm which appears in the shocked samples. This band is analogous to the 514 nm band in rhodonite from which Mn^{3+} has been removed thermally. The same band is observed as a shoulder on the 540 nm band in Keester and White's (1966) spectrum.

The remaining two important bands at 540 and 1530 nm are attributed to Mn^{3+}. In Jahn-Teller distorted octahedral oxygen environments, Mn^{3+} has a prominent absorption band in the 470–560 nm region (Dingle, 1966; Burns, 1970; Burns and Strens, 1967; and Davis, Fackler, and Weeks, 1968), with which we associate the 540 nm rhodonite band. The low energy absorption feature arising from the transition between the components of the Jahn-Teller split ^5E_g state can appear over the range of 5000 to 20,000 cm^{-1} (Davis *et al*, 1968). We assign the 1530 nm rhodonite band to this transition because (1) its intensity is not correlated with the intensity of the 1035 nm Fe^{2+} band, (2) it is qualitatively correlated with the Mn^{3+} band (in low Mn^{3+} material, the intensity of the 1530 nm band is too low to provide meaningful quantitative data), and (3) it disappears with the 540 nm Mn^{3+} band upon shock-loading.

Discussion

Trivalent manganese is lost in rhodonite after shock-loading to high pressures. Burns (1970), in an outline of crystal field theory, briefly describes

the Jahn-Teller effect on certain transition metal ions. In summary, if the distribution of electrons in the *d*-orbitals of a transition metal ion is such that the ground state is degenerate, the coordination polyhedra will distort spontaneously to remove the degeneracy and make one energy level more stable (Jahn and Teller, 1937). High spin Mn^{3+} with d^4 electronic configuration is susceptible to such distortion, and the Mn^{3+} ion is stabilized in distorted octahedra. Conversely, Mn^{3+} is less stable in a regular octahedral site and in this environment will have a tendency to oxidize or reduce to the more stable electronic configurations of Mn^{4+} or Mn^{2+}. From the crystal structure of rhodonite it is known that all cation sites are distorted from octahedral symmetry so that Mn^{3+} could be stabilized in all five sites. Pressures and temperatures produced by shock-loading to more than 210 kbar are probably sufficient to affect the regularity of the manganese octahedra. Any destruction of crystalline order probably increases the regularity of the octahedra and decreases the stability of the Mn^{3+} ions. Hence, Mn^{3+} could be reduced to Mn^{2+} as a result of shock-loading to very high pressures. The alternative of oxidation to Mn^{4+} is not considered further since, concurrent with the loss of the Mn^{3+} spectrum, there is not the growth of a Mn^{4+} (d^3) spectrum whose (spin-allowed) intensity would be expected to be comparable to that of the Mn^{3+} being lost.

The effect of temperature alone must be considered since appreciable increases in sample temperature accompany the shock-loading. In order to determine this effect, two samples were heated to 1250° C and 1360°C respectively; this is just below and above the peritectic melting point of 1291°C. Each sample was held for 3.5 hours in a reducing atmosphere of 99 percent argon and 1 percent H_2 at atmospheric pressure. The 1250°C sample was cooled to room temperature in about 1 hour; the other was quenched more rapidly in about 15 minutes.

The spectra of the standard and the 1250°C sample are compared in Figure 3. There is only a small change in the relative intensities of the Mn^{2+} and Mn^{3+} bands and essentially no color change in the sample. Heating to 1250°C for 3.5 hours does not appreciably affect the oxidation state of the manganese in rhodonite.

The spectra of the standard and the 1360°C sample are contrasted in Figure 4. The 540 nm Mn^{3+} band is not present. Since the melting was done in a reducing atmosphere, the Mn^{3+} was probably re-
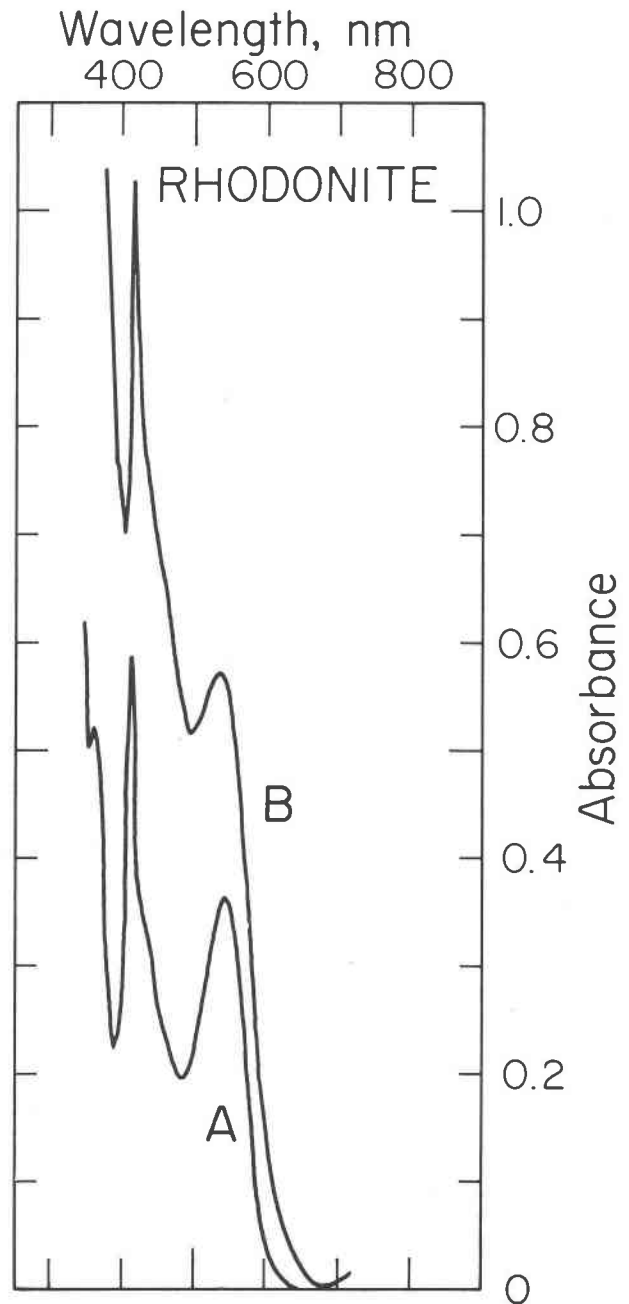

FIG. 3. Rhodonite spectra. A = spectrum of unshocked sample shown in Figure 1. B = spectrum of unshocked rhodonite specimen which was held at 1250°C for 3.5 hours showing that the Mn^{2+} band at 408 nanometers and the Mn^{3+} band at 540 nm are present in both spectra. (The incongruent melting point of rhodonite is 1291°C.)

duced to Mn^{2+}. The feature at 514 nm in the spectrum of the heated sample is assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ transition in Mn^{2+}. Since the melted sample, which is a quenched multicrystalline assemblage, will
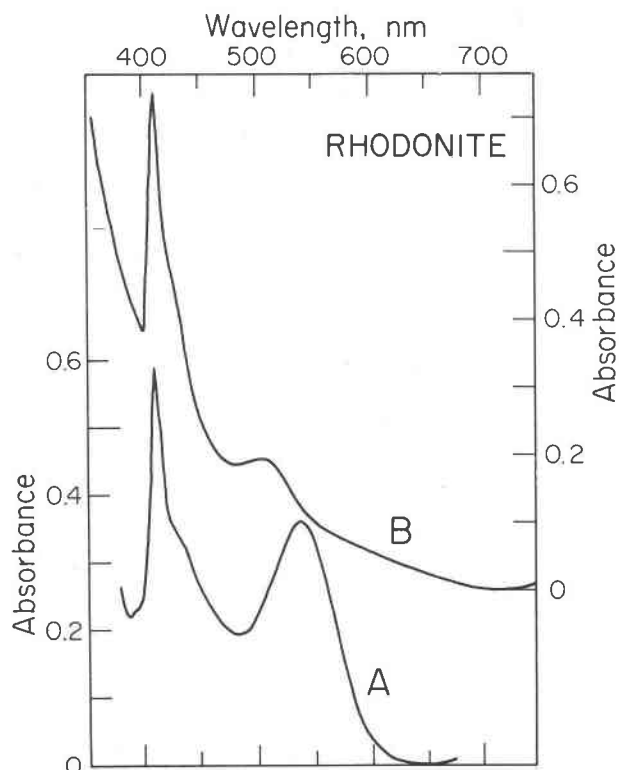
Fig. 4. Rhodonite spectra. A = spectrum of the unshocked sample shown in Figure 1. B = spectrum of an unshocked rhodonite specimen which was held at 1360°C for 3.5 hours showing the disappearance of the Mn^{3+} band at 540 nm and the presence of a band at 514 nanometers which is assigned to the $^6A_{1g} \rightarrow \, ^4T_{1g}$ electronic transition in Mn^{2+}.

not retain the exact same environment about the manganese ions as exists in rhodonite, the positions and intensities of the spectroscopic bands are expected to differ from those of rhodonite. The spectrum of the melted sample in the 400–470 nm region nevertheless bears considerable similarity to the rhodonite spectrum and suggests that there should be a Mn^{2+} band in the vicinity of 510–520 nm in rhodonite. In fact, a weak shoulder at 520 nm has been observed on the 540 nm Mn^{3+} band in the spectra of shocked and unshocked rhodonites.

Reduction of transition metal ions with increasing pressure has been observed in at least two other instances. Drickamer *et al* (1970) and Drickamer and Frank (1973) have observed a reversible reduction of Fe^{3+} to Fe^{2+} in a variety of compounds and Burns, Tossell, and Vaughan (1972) have reported similar $Fe^{3+} \rightarrow Fe^{2+}$ reduction in a synthetic ferric amphibole, using static compression apparatus. Production of Mn^{2+} from Mn^{3+} in $CaCO_3$ by high

temperatures has been observed by Low and Zeira (1972) in ESR spectral studies by heat-treating aragonite and transforming it to calcite. Mn^{3+} is stabilized in the aragonite but unstable in the more regular calcite structure.

Drickamer proposes that Fe^{3+} is reduced to Fe^{2+} by transfer of electrons from nonbonding ligand orbitals to metal $3d$ antibonding orbitals. Low and Zeira believe that the electrons required for the Mn^{3+} to Mn^{2+} reduction in $CaCO_3$ may originate from a charge compensating cation or by release from structural vacancies as a result of higher temperatures.

In analogy to Drickamer's (1970) proposal, a possible source of electrons would be the oxygen ligands of the Mn^{3+}. One is then faced with the difficulty of accounting for the fate of the electron-deficient oxide which tends to be highly unstable. A more reasonable source of electrons would be the charge-compensating cations, in particular Fe^{2+}. The reaction $Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}$ is feasible since divalent iron is present at greater concentrations than the trivalent manganese. We prefer another hypothesis, however, discussed below. We also rule out the possibility that electrons trapped in crystal defects could be present in anywhere near the quantity needed to reduce the estimated 0.3 percent Mn^{3+} (see Table 1).

Infrared spectroscopic studies (Fig. 5) show that the unshocked rhodonite contains both a trace of isolated hydroxyl groups and a greater amount of molecular water. The hydroxide stretching bands are a pair of sharp absorption features at 3680 and 3663 cm^{-1}. The more intense 3680 cm^{-1} band has an absorption coefficient of 2.7 cm^{-1}. In the specimen shocked to 496 kbar, the hydroxide band occurs at 3665 cm^{-1} and has been reduced in intensity to 0.3 cm^{-1}. Water present in the unshocked specimen produces an absorption band with maximum absorption at about 3400 cm^{-1} with an absorption coefficient of 7.6 cm^{-1} whereas the 496 kbar shocked specimen shows a considerably reduced absorption intensity of 1.4 cm^{-1}. Since the rhodonite used in these experiments is internally fractured, much of the water present need not be in the crystal structure but, instead, could reside within the fractures. For comparison, a gem-quality rhodonite from Franklin, New Jersey, free of fractures and low in Mn^{3+}, has only a weak water band at 3423 cm^{-1} with an absorption coefficient of 0.96 cm^{-1}, somewhat lower than the shocked sample.

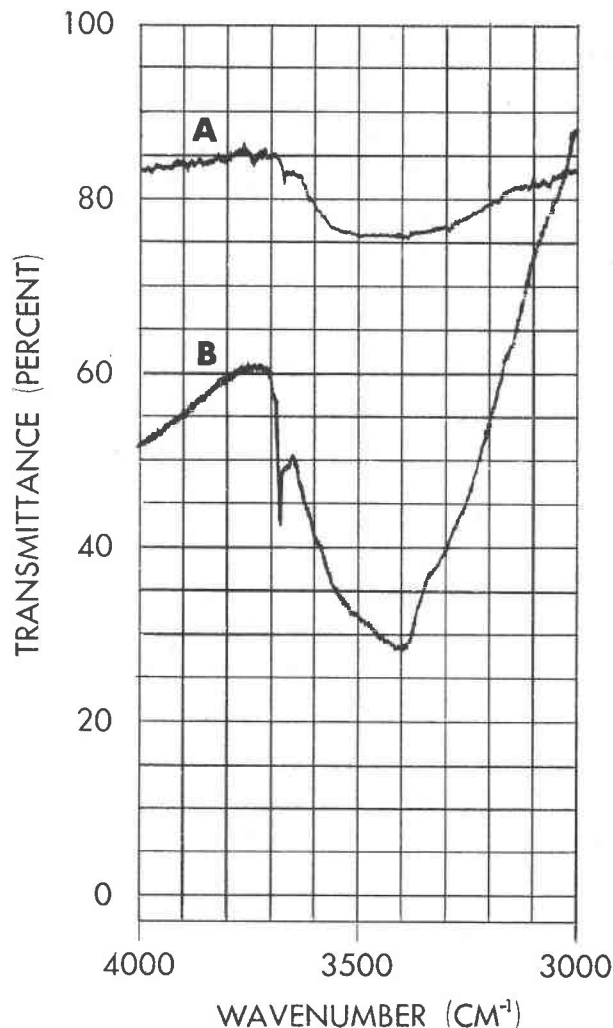The presence of water in the rhodonite samples, wherever its location, is important since it provides

a species with which Mn^{3+} could react. From a comparison of the intensity of the water absorption in the unshocked specimen to that in materials of known water content, we estimate that the initial sample contains about 5.5 mg H_2O cm^{-3}, or 3.1 mmole H_2O cm^{-3}. The Mn^{3+} concentration which was estimated to be 0.3 percent corresponds to 0.2 mmole Mn^{3+} cm^{-3}. Water is thus present in a large stoichiometric excess. At room temperature most manganese(III) compounds are unstable in aqueous solution with respect to disproportionation to Mn(II) and Mn(IV) compounds. We propose that under the conditions of the shock, the Mn^{3+} ions are reduced to divalent manganese by water or its decomposition products. Similarly, in ferric amphibole, Burns *et al* (1972)

postulate that Fe^{3+} to Fe^{2+} reduction is facilitated by the oxidation of OH^- ions to OH free radicals in the $M1$ and $M3$ sites of the amphibole structure.

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