

Cation Disorder in Shocked Orthopyroxene

R. W. Dundon and S. S. Hafner

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Abstract. *The distribution of magnesium and iron over the M1 and M2 positions in Bamle enstatite shocked at 1 megabar is highly disordered. It corresponds to an equilibrium distribution of at least 1000°C. The distribution in samples shocked at 450 kilobars or less is undisturbed.*

The study of cation distributions over nonequivalent lattice sites in minerals may reveal information on the history of temperature and pressure in rocks. Pyroxenes, chain silicates with compositions close to $(Ca,Mg,Fe)SiO_3$, are typical examples. In pyroxene crystals that have been cooled slowly to temperatures lower than 500°C, the Fe^{2+} ions populate primarily the M2 position whereas the Mg^{2+} ions occur predominately at the M1 position. In crystals that have been rapidly cooled, a more disordered Mg,Fe distribution over the M1 and M2 sites is observed. Although the effect of temperature on the Mg,Fe exchange reaction between M1 and M2 sites in pyroxenes has been investigated in some detail (1-3), little is known about the effect of shock on this reaction. Shocked pyroxenes occur on the earth and on the moon, for example, in ejecta from impact craters and in certain meteorites (4). Shock effects in minerals may be recognized by the presence of regions which show microstructures due to deformation (for example, "shock lamellae"), transitions to high-pressure phases, oxidation, decomposition, vitrification without melting, partial melting, and flow structures. However, DeCarli has pointed out that sometimes shocked minerals have none

of these more obvious traces of their shock history (5); hence it is of interest to find additional physical evidence that will indicate shock.

An earlier investigation of pyroxene separates from the shocked meteorites Farmington, McKinney, and Rose City indicated considerable cation disorder (6). Unfortunately, the analysis of natural materials is frequently complicated by additional factors such as chemically inhomogeneous crystals or zoning, very fine-grained matrices, initial mixtures of ortho- and clinopyroxenes, and sub-microscopic exsolution. We report here some results obtained from chemically homogeneous orthopyroxene specimens that were shocked under well-controlled conditions in the laboratory in order to provide a basis for the interpretation of more complex natural materials. In addition, heating experiments were carried out on the same orthopyroxene in an effort to analyze the effect of temperature, since elevated temperature is an integral part of the shock effect. It should be noted that, if shock does cause cation disordering, it will destroy the preexisting thermal record in the crystal.

Our orthopyroxene specimens consisted of enstatite crystals from Bamle, Norway, which were shocked in De-

Carli's laboratory at intensities of 150 to 250, 400 to 450, and 900 to 1000 kb. The duration of the pressure pulse was less than 1 μ sec. The same materials were also studied in detail by Pollack and DeCarli, who used x-ray diffraction techniques (7). We have determined the occupancy of iron at the M1 and M2 sites by means of Mössbauer absorption spectroscopy. For this measurement absorbers were prepared which consisted of approximately 50 mg of sample mixed with Lucite powder and were pressed into a homogeneous disk. The absorbers were held at 77°K. The density of the absorbers was between 4 and 5 mg of natural iron per square centimeter. A thin section prepared from a specimen shocked at 900 to 1000 kb was examined microscopically with polarized light. Specimens of the natural Bamle material were heated in evacuated quartz tubes at 800°, 1000°, 1100°, and 1200°C for at least 10 hours. This heating time is more than sufficient to attain the equilibrium distribution of the cations at these temperatures (1). After heating, the tubes were quenched to room temperature within seconds. X-ray diffraction patterns of all specimens were taken with a Guinier camera. No decomposition and no change in space group were detected after the heating. Electron microprobe analyses showed that all of our material had the composition $Mg_{0.86}Fe_{0.14}SiO_3$.

The Mössbauer spectra consist of an inner doublet due to Fe^{2+} at the M2 sites and an outer doublet due to Fe^{2+} at the M1 sites. Two typical spectra are shown in Fig. 1. The isomer shifts,

Table 1. Magnesium-iron order-disorder in shocked and heated orthopyroxene. The site occupancy for Fe^{2+} was calculated by means of the relations $X_{M1} = 2cI$ and $X_{M2} = 2c(1 - I)$ where c is the atomic ratio $Fe/(Mg + Fe)$ of the pyroxene and I is the area ratio $M1/(M1 + M2)$ of the doublets. The peak height ratio was used as the area ratio (I); p was obtained from Eq. 1.

Specimen No.	Orthopyroxene from Bamle* $Mg_{0.86}Fe_{0.14}SiO_3$	Isomer shift†, ‡ (mm/sec)		Quadrupole splitting† (mm/sec)		Ratio (height × width) $M1/(M1 + M2)$	Peak height ratio $M1/(M1 + M2)$	Disordering parameter p
		M1	M2	M1	M2			
1	Natural	1.28	1.27	3.08	2.15	0.053	0.053	0.041
2	Shocked to 250 kb					.046	.066	.053
3	Shocked to 450 kb					.049	.066	.053
4	Shocked to 1000 kb	1.30	1.26	3.06	2.14	.213	.242	.27
5	Shocked to 1000 kb					.233	.263	.30
6	Heated to 800°C	1.28	1.27	3.07	2.15	.174	.187	.19
7	Heated to 1000°C					.211	.231	.25
8	Heated to 1100°C					.239	.228	.25
9	Heated to 1200°C					.225	.231	.25

* The atomic ratio $Ca/(Mg + Fe + Ca)$ is approximately 0.005; the atomic ratio $Fe/(Mg + Fe)$ is 0.143. † Referred to a metallic iron absorber. ‡ The total errors (including systematic errors) are less than 0.01 mm/sec; absorbers held at 77°K.

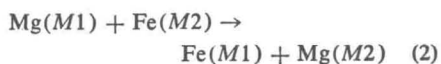
nuclear quadrupole splittings, area ratios of the doublets, and disordering parameters p are reported in Table 1. In Table 1 the degree of cation disorder is expressed in terms of p , where

$$p = \frac{X_1(1-X_2)}{(1-X_1)X_2} \quad (1)$$

and X_1 and X_2 are the site occupancy numbers for Fe^{2+} at the M1 and M2 positions, respectively.

The natural distribution in the Bamle enstatite, which comes from a metamorphic rock of the granulite type, is highly ordered (Fig. 1A). This ordering indicates that this pyroxene was slowly cooled between its crystallization temperature and approximately 480°C (1). No significant increase in disorder occurs in the specimens shocked to 250 and 450 kb. The differences in the p values relative to those of the natural material are not much larger than the experimental error, which is approximately ± 0.01 . However, the specimen shocked to 1000 kb exhibits a marked increase in cation disorder (Fig. 1B), but the isomer shifts and quadrupole splittings are not affected. There is no trace of Fe^{3+} in any of the Mössbauer spectra.

Shocked materials are subjected to subsequent heating as an integral part of the shock effect. Pollack and DeCarli estimated that their specimens shocked to 1000 kb were exposed to a temperature peak of approximately 500° to 1400°C (7). We conclude from our heating experiments that the significant increase in cation disorder observed in the specimens shocked to 1000 kb results primarily from the elevated temperatures associated with the shock. The cation distributions in these specimens correspond to equilibrium temperatures of at least 1000°C . Equilibrium temperatures higher than 1000°C are also possible since the degree of disorder will not substantially increase any more above 1000°C , as the specimens heated to 1100° and 1200°C show (Table 1). This observation is in accord with earlier studies on the equilibrium relationships and kinetics of the Mg,Fe exchange reaction in orthopyroxenes (1). However, the rate constants for the disordering reaction



do suggest temperatures higher than 1000°C . At 500°C this rate constant is approximately 6×10^{-5} per pair of M1,M2 sites per minute (1). At 1000°C it increases to a value of approximately

10^{-2} . Only at temperatures nearer to 1400°C would the rate constant become large enough to account for the observed degree of disorder.

Pollack and DeCarli found considerable stacking disorder of the SiO_3 chains in the specimens shocked to 1000 kb, in contrast to the case for the specimens shocked to 250 and 450 kb, which did not reveal stacking disorder (7). This observation parallels our results on the increase of cation disorder. Specimens shocked to 1000 kb exhibit disordering parameters that are somewhat larger than those obtained merely by heating. This result may be attributed to alterations in the crystal structure caused by the 1000-kb shock as described by Pollack and DeCarli.

The Mössbauer absorption lines of all specimens except one of the speci-

mens shocked to 1000 kb (Table 1, specimen 5) show typically small widths of 0.27 to 0.30 mm/sec. Such widths are characteristic for well-crystallized solids. They indicate that the shock left the short-range periodicity of the lattice relatively undisturbed. This conclusion is confirmed by the absence of any anomalous optical effects. No optically isotropic regions, microstructures, or any other features indicative of shock were found in a thin section made from one of the specimens shocked to 1000 kb. Specimen 5 exhibits somewhat broadened lines of 0.30 to 0.33 mm/sec as well as the maximum cation disorder observed in our samples. This sample was taken from the rim of the shocked disk, where it may have been quenched more rapidly than other portions of the disk. The increase in line width may indicate the onset of short-range lattice disorder. The increase in line width is much too small to be interpreted in terms of partial vitrification (8).

The x-ray diffraction patterns of the specimens shocked to 1000 kb reveal considerable loss of long-range periodicity in the lattice as indicated by the diffuseness of the lines, whereas the lines of the specimens shocked at lower intensities are not markedly diffuse. Detailed x-ray diffraction studies of these samples have been reported by Pollack, who compared them with patterns of meteoritic pyroxenes (9). In contrast, our Mössbauer spectra have narrow line widths and nearly invariant isomer shifts and quadrupole splittings (Table 1). These parameters are primarily determined by the local environment of the Fe atoms within the unit cell and are not critically affected by lattice disorder as long as the undisturbed single-crystal domains comprise dimensions of a few unit cells. The effect of stacking disorder on the quadrupole splittings is small.

On the basis of the results presented here, we conclude that the shock intensity barrier above which the cation distribution in pyroxenes will be affected is somewhere between 450 and 1000 kb. Pyroxenes from intensely shocked meteorites or lunar basalts are therefore expected to be disordered, and, as a result, the thermal record prior to the event will have been erased.

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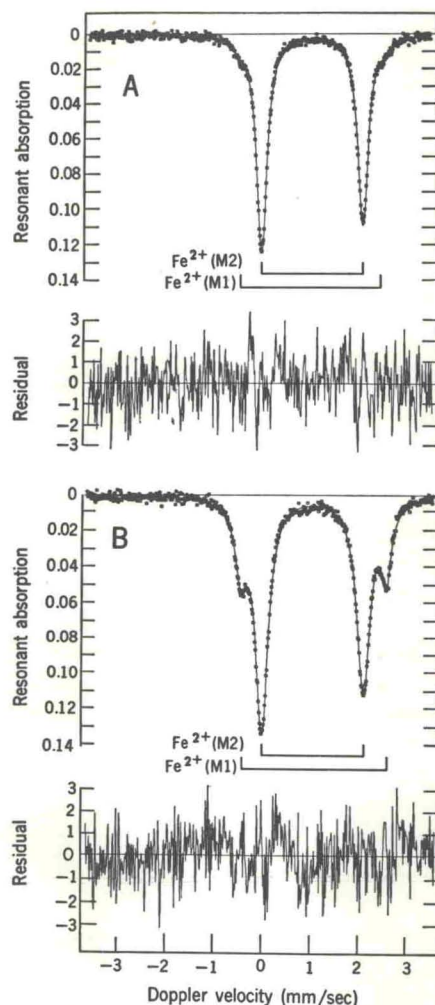


Fig. 1. Mössbauer spectra (^{57}Fe) of natural (A) and shocked (B) Bamle enstatite. The solid line is a least-squares fit to the data on the assumption of four Lorentzian lines. The count rate per data point is $\sim 1 \times 10^5$ (500 points). The deviations are shown as "residuals" below the spectra. Typical average χ^2 values per data point are between 1.0 and 1.5 units.

References and Notes

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10. We thank Dr. S. S. Pollack, Mellon Institute, Pittsburgh, for the materials. Work supported by NSF grant GA-14811 and NASA grant NAS9-8080 (to S.S.H.).

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