

## **Cation Disorder in Shocked Orthopyroxene**

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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  $(\text{Ca}, \text{Mg}, \text{Fe})\text{SiO}_3$ , are typical examples. In pyroxene crystals that have been cooled slowly to temperatures lower than 500°C, the  $\text{Fe}^{2+}$  ions populate primarily the M2 position whereas the  $\text{Mg}^{2+}$  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  $\mu\text{sec}$ . 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  $\text{Mg}_{0.86}\text{Fe}_{0.14}\text{SiO}_3$ .

The Mössbauer spectra consist of an inner doublet due to  $\text{Fe}^{2+}$  at the M2 sites and an outer doublet due to  $\text{Fe}^{2+}$  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  $\text{Fe}^{2+}$  was calculated by means of the relations  $X_{M1} = 2cI$  and  $X_{M2} = 2c(1 - I)$  where  $c$  is the atomic ratio  $\text{Fe}/(\text{Mg} + \text{Fe})$  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* $\text{Mg}_{0.86}\text{Fe}_{0.14}\text{SiO}_3$	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  $\text{Ca}/(\text{Mg} + \text{Fe} + \text{Ca})$  is approximately 0.005; the atomic ratio  $\text{Fe}/(\text{Mg} + \text{Fe})$  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.