

LETTERS

Pressure-induced ordering in $(\text{Ni,Mg})_2\text{SiO}_4$ olivine

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ABSTRACT

An imaging-plate detector interfaced to a large-volume high-pressure device allows quantitative in situ powder X-ray diffraction measurements at the National Synchrotron Light Source (NSLS). High-quality diffraction patterns were recorded from an $(\text{Ni,Mg})_2\text{SiO}_4$ olivine solid-solution sample at 4 GPa and 800 °C as a function of time using 3 min exposures at 40, 63, and 109 min. Refinement of the crystal structure indicated an increase in the ordering of Ni^{2+} and Mg^{2+} cations over the M1 and M2 sites at high pressure. The unit-cell volume was found to decrease with increasing ordering. Kinetic phenomena associated with the cation redistribution were observed on the time scale of tens of minutes. Extrapolation based on an exponential law of ordering relaxation toward equilibrium gave a distribution coefficient (K_D) of 10.7(1) at 4 GPa and 800 °C; the starting sample, which was annealed at 800 °C and room pressure, gave $K_D = 8.3(1)$.

INTRODUCTION

The ordering of cations over available crystallographic sites in minerals can greatly influence their thermodynamic properties. Traditionally, studies of changes in ordering as a function of temperature and pressure have been performed using quench techniques; the presumption is that the quench products represent at least a facsimile of the state existing under the conditions of synthesis. However, in view of difficulties such as variations in quench rates, it is now widely accepted that in situ diffraction experiments provide the most reliable and reproducible means of obtaining information on the state of cation ordering (Navrotsky 1994). Commercially available high-temperature apparatus and widely distributed Rietveld refinement software (Larson and Von Dreele 1986; Rietveld 1969) enable routine in situ study of structural changes accompanying variation of temperature (Zhao et al. 1993a, 1993b). However, studies in which both temperature and pressure are maintained, while data suitable for full structural refinement are collected, are rare (Hazen and Finger 1982).

Recent developments in high-pressure devices, capable of sustained heating over a period of days, interfaced to monochromatic synchrotron X-radiation sources and an imaging plate (IP) detector, have facilitated studies at high temperatures and pressures simultaneously (Chen et al. 1995, 1996). This system produces powder diffraction data suitable for Rietveld refinement (Rietveld 1969). We report here the first in situ study designed to test recent predictions that, in selected systems, pressure can have a

profound effect on cation site ordering (Hazen and Navrotsky 1996 and references therein).

EXPERIMENTAL METHODS AND RESULTS

A sample of olivine of composition $(\text{Ni}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4$ was synthesized from a mixture of dried oxides, NiO, MgO, and SiO_2 gel. The X-ray powder diffraction pattern of this material showed that the oxides had reacted completely to form a pure phase of olivine after 50 h at 1500 °C. This was sintered by hot pressing at 4 GPa and 800 °C to form a stress-free bulk sample for high-pressure diffraction measurements. The sintered pellet was then annealed at room pressure and 800 °C for 24 h and quenched by dropping into liquid nitrogen.

In situ high-pressure diffraction was performed at the superconductor wiggler beamline, X-17B, of the National Synchrotron Light Source (NSLS) with the large-volume multi-anvil press SAM85 (Weidner et al. 1992). A two-dimensional monochromatic diffraction system with an imaging plate was developed for quantitative measurements of intensities (Chen et al. 1996). White radiation was monochromatized using an Si(220) Laue-Bragg focusing monochromator. A movable back stop was used to switch between monochromatic and polychromatic radiation, which thereby allowed two modes of diffraction, angle dispersive and energy dispersive, in one experiment. A solid-state detector was used in the energy-dispersive diffraction mode to collect data rapidly for mapping the geometry of the high-pressure cell (Chen et al. 1996).

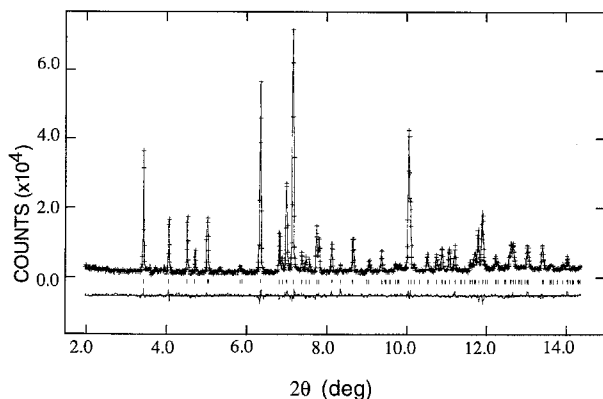


FIGURE 1. Calculated (continuous line) and observed (crosses) synchrotron X-ray diffraction profiles for $(\text{Ni}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4$ olivine at 4 GPa and 800 °C. A difference curve ($I_{\text{obs}} - I_{\text{calc}}$) is plotted at the bottom on the same scale. Allowed reflection positions are indicated by vertical lines.

A cell assembly, including a disk-type heater to eliminate scattering from the furnace, was used in this experiment. The sample was surrounded by pressure medium, a mixture of amorphous boron and epoxy resin in the weight ratio 4:1, and the temperature was determined by a W5%Re/W26%Re thermocouple. Pressure was derived from the measured unit-cell volume of NaCl using the Decker equation of state (Decker 1971). The lattice parameter of NaCl was determined from a diffraction pattern taken in energy-dispersive mode with polychromatic X-rays and with the solid-state detector. At the desired pressure and temperature the incident beam was switched from polychromatic to monochromatic radiation, and diffraction patterns of the sample and the pressure medium were recorded on the imaging plate. The wavelength of the monochromatic X-rays was 0.3051(2) Å, and diffraction patterns were recorded up to 15° 2θ on 200 × 250 mm imaging plates. A double-plate holder was used to determine the IP-to-sample distance with a single exposure. The two-dimensional diffraction patterns were then converted into conventional, one-dimensional diffraction profiles (Fig. 1) by radial integration using techniques developed at the Photon Factory (Shimomura et al. 1992). The diffraction pattern from the sample position contains peaks from both the olivine and the boron-epoxy pressure medium. The latter were eliminated by subtracting the pattern of the pressure medium from that of the sample (Chen et al. 1996). Further experimental details were published elsewhere (Chen et al. 1996).

A diffraction pattern of the starting material in the high-pressure cell was taken at room temperature before pressurizing. The pressure was then increased to 4 GPa, and the temperature was increased to 800 °C. Several diffraction patterns were collected as a function of time under these conditions, with each imaging plate exposed for 3 min. Rietveld refinements were performed using the General Structure Analysis System (GSAS), and Figure 1 shows a typical result with 131 diffraction lines con-

tributing to the pattern. All structural sites were considered to be fully occupied, and the site-occupation fractions for the M1 and M2 sites were constrained by the composition of the starting material. Preliminary refinements suggested the displacement parameters for the M1 and M2 sites were equal within error and were therefore constrained as such in subsequent refinements. The displacement parameters (Table 1) for all atoms were assumed to be isotropic, with those sites occupied by O also constrained to be identical. The results of the final refinements are summarized in Table 1.

DISCUSSION

Quench experiments generally show an increase in disorder in $(\text{Ni,Mg})_2\text{SiO}_4$ olivine with increasing temperature (Bish 1981; Ottonello et al. 1989). The distribution coefficient K_D [$K_D = (X_{\text{Ni}}/X_{\text{Mg}})^{M1}/(X_{\text{Ni}}/X_{\text{Mg}})^{M2}$] of the starting material used in our experiments (Table 1) is 8.3(1). This is smaller than that for $\text{Ni}_{0.51}\text{Mg}_{0.49}$ olivine ($K_D = 11.4$) synthesized at 890 °C (Ottonello et al. 1989), probably because of difficulties in quenching (Boström 1987; Ottonello et al. 1989) the cation distribution achieved at the higher temperatures. For example, a sample of composition $\text{Ni}_{0.3}\text{Mg}_{0.7}$ annealed at 800 °C shows a strong decrease in K_D , from 16.9 to 10.6, in comparison with the same sample synthesized at 900 °C, suggesting the true state of order at the higher temperature was not retained after quenching. The calculation for a minimum Gibbs free energy gave a possible range from 7.61 to 13.30 for the value of K_D in an olivine sample with $\text{Ni}_{0.5}\text{Mg}_{0.5}$ composition (Ottonello 1987; Ottonello et al. 1989).

As summarized in Table 1, the value of $(X_{\text{Ni}}/X_{\text{Mg}})^{M1}$ increases with pressure and time, indicating that pressure tends to favor ordering in the cation distribution over the octahedral sites of $(\text{Ni,Mg})_2\text{SiO}_4$ olivine (Table 1). The effects of pressure on order-disorder reactions were recently reviewed (Hazen and Navrotsky 1996). These authors introduced a definition for the volume of disordering, $\Delta V_{\text{dis}} = V_{\text{disordered}} - V_{\text{ordered}}$, and derived the following equation from the first and second laws of thermodynamics: $(\partial \Delta G_{\text{dis}} / \partial P)_T = \Delta V_{\text{dis}}$. The sign of ΔV_{dis} determines whether the Gibbs free energy of disordering, ΔG_{dis} ($\Delta G_{\text{dis}} = G_{\text{disordered}} - G_{\text{ordered}}$), increases or decreases with pressure. In our experiment, the unit-cell volume decreases as a function of time at 4 GPa and 800 °C, showing a tendency toward decreasing volume with increased ordering (Table 1). A linear fit to the data with slope -0.03 Å^3 is shown in Figure 2. This results in a positive ΔV_{dis} , which is consistent with the quench experiments at room pressure (Ottonello et al. 1989). The tendency of pressure to favor ordering conforms to the prediction of Hazen and Navrotsky (1996).

Because cation redistribution is relatively slow at 800 °C, this affords an opportunity to study the kinetics of the ordering process at high pressure and temperature. Although there are few studies in which the kinetics of cation distribution in the olivine system have been studied in situ under simultaneously high-temperature and high-

TABLE 1. Crystal-structure data of (Ni_{0.5}Mg_{0.5})₂SiO₄ olivine from Rietveld refinement

		Room pressure, 23 °C (800 °C quenched)	4 GPa and 800 °C		
			40 min	63 min	109 min
<i>a</i>		4.7362(2)	4.7325(2)	4.7330(2)	4.7322(2)
<i>b</i>		10.1682(3)	10.1454(4)	10.1452(4)	10.1453(4)
<i>c</i>		5.9401(2)	5.9313(2)	5.9303(2)	5.9309(2)
<i>V</i>		286.066(15)	284.779(17)	284.753(18)	284.747(18)
<i>R</i> [*]		0.08	0.08	0.08	0.08
M1	<i>U</i> (Å ²)	0.015(3)	0.017(1)	0.017(1)	0.016(1)
	<i>X</i> (Ni)**	0.742(3)	0.754(2)	0.757(2)	0.762(2)
M2	<i>x</i>	0.9898(9)	0.9873(11)	0.9879(11)	0.9892(12)
	<i>y</i>	0.2752(2)	0.2760(3)	0.2757(3)	0.2762(3)
	<i>U</i> (Å ²)	0.015(3)	0.017(1)	0.017(1)	0.016(1)
	<i>X</i> (Ni)**	0.258(2)	0.246(2)	0.243(2)	0.238(2)
Si	<i>x</i>	0.4256(8)	0.4268(9)	0.4269(9)	0.4260(10)
	<i>y</i>	0.0932(4)	0.0940(4)	0.0945(4)	0.0939(4)
	<i>U</i> (Å ²)	0.017(3)	0.011(1)	0.013(2)	0.017(2)
O1	<i>x</i>	0.7719(14)	0.7719(12)	0.7722(13)	0.7687(14)
	<i>y</i>	0.0916(8)	0.0884(9)	0.0885(9)	0.0890(9)
	<i>U</i> (Å ²)	0.009(3)	0.007(1)	0.004(1)	0.010(1)
O2	<i>x</i>	0.2208(12)	0.2254(12)	0.2235(12)	0.2259(13)
	<i>y</i>	0.4447(8)	0.4469(8)	0.4442(9)	0.4450(9)
	<i>U</i> (Å ²)	0.009(3)	0.007(1)	0.004(1)	0.010(1)
O3	<i>x</i>	0.2768(8)	0.2814(8)	0.2796(8)	0.2804(9)
	<i>y</i>	0.1640(6)	0.1613(5)	0.1636(5)	0.1626(5)
	<i>z</i>	0.0319(10)	0.0346(11)	0.0343(12)	0.0326(13)
	<i>U</i> (Å ²)	0.009(3)	0.007(1)	0.004(1)	0.010(1)

Notes: Space group: *Pbnm*, M1 at (0,0,0) and M2, Si, O1, and O2 at (*x*,*y*,¼).

* $R = \{\sum [w(I_{\text{obs}} - I_{\text{calc}})]^2 / \sum [w(I_{\text{obs}})]^2\}^{1/2}$.

** $X_{\text{Ni}}^{\text{M1}} + X_{\text{Mg}}^{\text{M1}} = 1$, $X_{\text{Ni}}^{\text{M2}} + X_{\text{Mg}}^{\text{M2}} = 1$.

pressure conditions, theories of ordering and of the kinetics of ordering in alloys (Bragg and Williams 1934; Dienes 1955; Vineyard 1956) can be applied to the present study (Figs. 2 and 3). The relaxation of ordering toward equilibrium follows an exponential law (Vineyard 1956): $X - X_e = A \exp(-Kt)$, where X_e is the occupation fraction at equilibrium, A and K are constants, and t is time. With this relaxation formula, the distribution coefficient K_D at equilibrium was deduced. Before starting to heat at 4 GPa, a diffraction pattern was recorded and Rietveld (1969) analysis showed that the occupation was unchanged from that observed at room pressure for the starting material ($X_{\text{Ni}}^{\text{M1}} = 0.742$ in Table 1, Fig. 3). After pressurization the temperature was increased to 800 °C over a period of 40 min (Fig. 3), and during this time

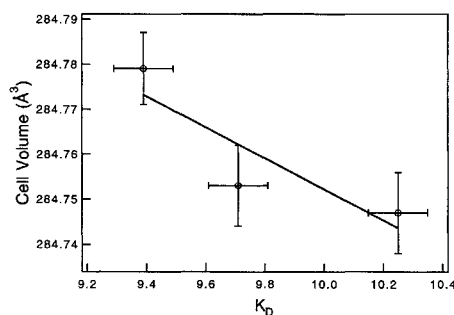


FIGURE 2. Relation of the unit-cell volume to $(X_{\text{Ni}}/X_{\text{Mg}})^{\text{M1}} / (X_{\text{Ni}}/X_{\text{Mg}})^{\text{M2}}$ in (Ni_{0.5}Mg_{0.5})₂SiO₄ olivine at 4 GPa and 800 °C. Bars indicate the experimental errors. A linear fit to the data, with a slope of -0.03 Å^3 , is shown.

several diffraction patterns were collected on the imaging plates. The data taken at 4 GPa and 800 °C (Fig. 3) were fitted to the relaxation formula, and the following parameters were derived: $(X_e)_{\text{Ni}}^{\text{M1}} = 0.766(2)$, $A = -0.024(2)$, and $K = 0.017(3) \text{ min}^{-1}$. Therefore, the distribution coefficient at equilibrium at 4 GPa and 800 °C was extrapolated to $K_D = 10.7(1)$.

These results indicate that an IP system, interfaced to a large-volume high-pressure device capable of sustained and stable heating at 800 °C, can be used to collect reliable monochromatic X-ray powder diffraction data of sufficient quality to allow Rietveld refinement of crystal-structure models. These preliminary experiments also

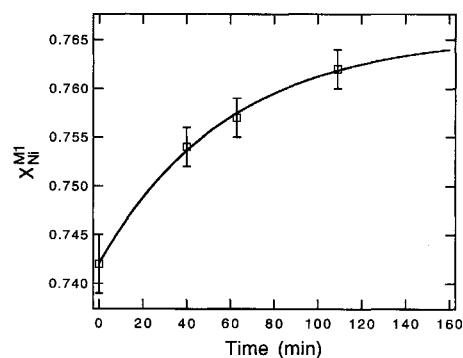


FIGURE 3. Change of the occupation fraction $X_{\text{Ni}}^{\text{M1}}$ as a function of time in (Ni_{0.5}Mg_{0.5})₂SiO₄ olivine at 4 GPa and 800 °C. The line is a fit to the relaxation formula, $X = X_e + A \exp(-Kt)$, which yields fitted parameters $X_e = 0.766(2)$, $A = -0.024(2)$, and $K = 0.017(3) \text{ min}^{-1}$.

demonstrated that the kinetics of ordering processes can be followed using this experimental apparatus.

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REFERENCES CITED

- Bish, D.L. (1981) Cation ordering in synthetic and natural Ni-Mg olivine. *American Mineralogist*, 66, 770–776.
- Boström, D. (1987) Single-crystal X-ray diffraction studies of synthetic Ni-Mg olivine solid solutions. *American Mineralogist*, 72, 965–972.
- Bragg, W.L., and Williams, E.J. (1934) The effect of thermal agitation on atomic arrangement in alloy. *Proceeding of the Royal Society*, A145, 699–730.
- Chen, J., Weidner, D.J., Vaughan, M.T., Parise, J.B., and Li, R. (1995) Quantitative X-ray diffraction at high pressure and temperature, 157 p. EOS, Transactions, American Geophysical Union, Baltimore.
- Chen, J., Parise, J.B., Li, R., Weidner, D.J., and Vaughan, M.T. (1996) The imaging plate system interfaced to the large-volume press at beamline X17B1 of the National Synchrotron Light Source. In M.H. Manghnani and Y. Yaghi, Eds., US-Japan meeting on high pressure in geological sciences, in press. American Geophysical Union, Hawaii.
- Decker, D.L. (1971) High-pressure equation of state for NaCl, KCl and CsCl. *Journal of Applied Physics*, 42, 3239–3244.
- Dienes, G.J. (1955) Kinetics of order-disorder transformations. *Acta Metallurgica*, 3, 549–557.
- Hazen, R.M., and Finger, L.W. (1982) *Comparative crystal chemistry*, 57–76. Wiley, New York.
- Hazen, R.M., and Navrotsky, A. (1996) Effects of pressure on ordering-disordering reactions. *American Mineralogist*, 81, 1021–1035.
- Larson, A.C., and Von Dreele, R.B. (1986) GSAS, General Structure Analysis System. Report LAUR 86-748, Los Alamos National Laboratory.
- Navrotsky, A. (1994) Repeating patterns in mineral energetics. *American Mineralogist*, 79, 589–605.
- Otonello, G. (1987) Energies and interactions in binary (*Pbnm*) orthosilicates: A Born parametrization. *Geochemica et Cosmochimica Acta*, 51, 3119–3135.
- Otonello, G., Della Giusta, A., and Molin, G.M. (1989) Cation ordering in Ni-Mg olivines. *American Mineralogist*, 74, 411–421.
- Rietveld, H.M. (1969) A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2, 65–71.
- Shimomura, O., Takemura, K., Fujihisa, H., Fujii, Y., Ohishi, Y., Kikegawa, T., Amemiya, Y., and Matsushita, T. (1992) Application of an imaging plate to high pressure X-ray study with a diamond anvil cell. *Review of Scientific Instruments*, 63, 967–703.
- Vineyard, G.H. (1956) Theory of order-disorder kinetics. *Physical Review*, 102(4), 981–992.
- Weidner, D.J., Vaughan, M.T., Ko, J., Wang, Y., Liu, X., Yeganeh-Haeri, A., Pacalo, R.E., and Zhao, Y. (1992) Characterization of stress, pressure, and temperature in SAM85, a DIA type high pressure apparatus. In Y. Syono and M.H. Manghnani, Eds., *High-pressure research: Application to Earth and planetary sciences*, p. 13–17. Terra Scientific Publishing Company, Tokyo, and American Geophysical Union, Washington, D.C.
- Zhao, Y., Weidner, D.J., Parise, J.B., and Cox, D.E. (1993a) Thermal expansion and structural distortion of perovskite—Data for NaMgF₃ perovskite. Part I. *Physics of the Earth and Planetary Interiors*, 76, 1–16.
- (1993b) Thermal expansion and structural distortion of perovskite—Data for NaMgF₃ perovskite. Part II. *Physics of the Earth and Planetary Interiors*, 76, 17–34.

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