LETTER

High-temperature Fe-Mg cation partitioning in olivine: In-situ single-crystal neutron diffraction study

G. Artioli
Dipartimento di Scienze della Terra, Università di Milano, I-20133 Milan, Italy

R. Rinaldi
Dipartimento di Scienze della Terra, Università di Perugia, I-06100 Perugia, Italy

C. C. Wilson
DRAL, Rutherford Appleton Laboratory, ISIS Facility, Chilton, Didcot OX11 OQX, U.K.

P. F. Zanazzi
Dipartimento di Scienze della Terra, Università di Perugia, I-06100 Perugia, Italy

Abstract

The intracrystalline partitioning of Fe and Mg in the octahedral sites of olivine is known to be dependent on temperature, pressure, and composition. Interpretations of the temperature effect on the partitioning have been mostly based on heating and quenching experiments, which seem to indicate that Fe^{2+} preferentially orders into the M1 site with increasing temperature. The present single-crystal neutron diffraction experiments yield the first in-situ high-temperature structure refinements above 900 °C and clearly indicate an ordering reversal above this temperature. Three data sets collected at 960, 1030, and 1060 °C show a remarkable progressive decrease in the K_D parameter with temperature, whereas the data at 880 °C are consistent with a slight preference of Fe^{2+} for M1, as reported in the literature. The effect is tentatively interpreted on the basis of competing contributions of configurational and vibrational entropy at high temperature, and it is expected to have profound implications for the thermodynamic modeling of olivine in the Earth's mantle and in planetary processes.

Introduction

In the olivine solid solution (Mg_2SiO_4-Fe_2SiO_4), the Fe-Mg cation partitioning between the two octahedral sites (M1 and M2) as a function of temperature and pressure has implications for the modeling of the physicochemical state and properties of the upper mantle and for the interpretation of the cooling history of meteorites and crustal rocks (Ghose and Ganguly, 1982). The cation partitioning coefficient (K_D) of the intracrystalline exchange reaction $Fe_{M2} + Mg_{M1} \rightleftharpoons Fe_{M1} + Mg_{M2}$ is commonly expressed as the reaction equilibrium constant:

$$K_D = (Fe_{M1} \cdot Mg_{M2})/(Fe_{M2} \cdot Mg_{M1}).$$

Several experimental studies have been performed by single-crystal X-ray diffraction and Mössbauer spectroscopy on olivine samples quenched from high temperature (e.g., Virgo and Hafner, 1972; Ottonello et al., 1990;

Princivalle, 1990). The quenching time is usually on the order of half a second or higher, which is about two orders of magnitude larger than the time constant of diffusion, estimated to be in the range of 10^{-2}–10^{-4} s at 1000 °C (Akamatsu and Kumazawa, 1993) and, therefore, totally insufficient to freeze the Fe-Mg site partitioning at high temperature. However, the partitioning coefficients obtained by quenching from temperatures below 800 °C are in general agreement with the studies performed with rapid cooling rates from temperatures up to 1000 °C (quenching time 0.01 s; Aikawa et al., 1985) and with the few in-situ single-crystal diffraction studies performed on olivine up to 900 °C (Brown and Prewitt, 1973; Smyth and Hazen, 1973; Hazen, 1977; Motoyama and Matsumoto, 1989); most experimental evidence indicates a slight to moderate partitioning of Fe in the smaller M1 octahedron.

Our neutron data include the first diffraction data obtained in situ under nonoxidizing conditions at temper-

TABLE 1. Summary of neutron and X-ray diffraction data collections and structure analyses

	N1	N2	N3	N4	N5	X1	X2
T (°C)	RT	880	960	1030	1060		
a (Å)	4.740(3)	4.76(1)	4.769(5)	4.772(5)	4.77(1)	4.759–4.761(1)	4.760–4.763(1)
b (Å)	10.230(3)	10.33(2)	10.33(1)	10.35(1)	10.38(2)	10.224–10.232(2)	10.222–10.229(2)
c (Å)	5.960(2)	6.05(2)	6.037(7)	6.053(7)	6.07(2)	5.992–5.994(1)	5.991–5.994(1)
Meas. refl.	1040	587	817	790	506		
Ind. refl.	527	319	354	345	238	391–521	477–509
Var.	42	42	42	42	42	45	45
$R(F)$	0.062	0.072	0.062	0.070	0.069	0.019–0.028	0.019–0.035
$R_w(F)$	0.052	0.057	0.059	0.057	0.062	0.018–0.028	0.021–0.030
Fe_{M1}	0.121(11)	0.132(19)	0.098(18)	0.093(18)	0.086(28)	0.115–0.134(2)	0.142–0.148(2)
Fe_{M2}	0.119(11)	0.108(19)	0.142(18)	0.147(18)	0.154(28)	0.122–0.132(2)	0.100–0.121(2)
Fe_{tot}						0.237–0.266	0.242–0.267
K_D	1.02(13)	1.26(29)	0.66(15)	0.60(14)	0.52(19)	0.93–1.08(2)	1.24–1.49(2)
M1 U_{eq} (Å²)	0.0053(8)	0.024(2)	0.024(2)	0.025(2)	0.031(3)	0.0049–0.0060	0.0054–0.0065
M2 U_{eq} (Å²)	0.0061(9)	0.021(2)	0.024(2)	0.025(2)	0.033(3)	0.0046–0.0053	0.0046–0.0066
⟨M1-O⟩ (Å)	2.093(2)	2.114(5)	2.117(3)	2.119(3)	2.122(5)	2.101–2.102(1)	2.099–2.102(1)
⟨M2-O⟩ (Å)	2.131(3)	2.156(6)	2.157(4)	2.165(4)	2.167(6)	2.135–2.136(1)	2.134–2.136(1)
M1 V (Å³)	11.73	12.03	12.09	12.10	12.15		
M2 V (Å³)	12.39	12.82	12.81	12.93	13.01		
M1 Q.E.	1.028	1.032	1.031	1.032	1.032		
M2 Q.E.	1.029	1.030	1.031	1.032	1.030		
M1 A.V.	99.87	111.85	109.36	112.94	114.53		
M2 A.V.	99.34	103.56	107.33	110.76	104.29		

Note: Q.E. = quadratic elongation; A.V. = angle variance. Ranges of X-ray values are given for X1 = four natural crystals before heat treatment and X2 = two fragments of the crystals used for neutron diffraction after heat treatment and one crystal after a complete heating and cooling cycle in quartz capillary. Experiments performed at room temperature.

atures above 900 °C; they were collected on a ferromagnesian olivine of composition $Mg_{1.76}Fe_{0.24}SiO_4$. The partitioning coefficient was checked by single-crystal X-ray diffraction at room temperature before and after the neutron heating cycles. The oxidation state was checked by Mössbauer spectroscopy. All experiments were performed on single crystals, fragments, and powdered specimens extracted from two large natural olivine crystals having a high degree of chemical homogeneity.

EXPERIMENTAL METHODS

Two olivine single crystals of approximately 11 and 18 mm³ from the Brenham pallasitic meteorite (Buseck, 1977) were utilized. Four small fragments from the two crystals were utilized for room-temperature X-ray single-crystal data collection to check the starting Fe-Mg distribution in the two sites. Several smaller fragments were used for electron probe microanalysis and to prepare the polycrystalline mount for Mössbauer spectroscopy. The neutron diffraction data were collected, during two separate experiments, on the time-of-flight Laue diffractometer SXD at the ISIS spallation source (Rutherford Appleton Laboratory, U.K.). The high-temperature furnace consists of an evacuated (10^{-5} mbar) cylindrical vessel lined with a V heating element that is computer controlled to a temperature stability of about ±5 °C in the range 25–1200 °C. The assembly provides an accurate control of the sample environment with negligible absorption and easy access to a large portion of the reciprocal space. Furthermore, the relative scattering lengths of Mg (0.537×10^{-12} cm) and Fe (0.954×10^{-12} cm) for neutrons allow a favorable condition for site population refinements. The other coherent scattering lengths used are Si (0.415×10^{-12} cm) and O (0.581×10^{-12} cm).

In the first experiment, performed in the fall of 1992,

two full neutron data sets were collected on the first crystal at 1060 and then at 880 °C (N2 and N5 in Table 1). As a consequence of the surprising preliminary results (Wilson et al., 1993), a second experiment was performed in the winter of 1994, and three data sets were collected on the other crystal at 25, 1030, and 960 °C (N1, N3, and N4 in Table 1). In this latter experiment a few fragments of the crystal, placed inside a Mo capsule a few millimeters above the large crystal, underwent exactly the same heating cycle and were used for Mössbauer analysis. The small quantity of Fe^{3+} present in the sample, estimated from the ratio to the total resonant absorption area, was found to be 2.01 wt% of the total Fe in both spectra, before and after the heat treatment. This observation testifies to the ideal nonoxidizing conditions maintained during the experiments. Details of the Mössbauer analysis, including the Fe^{2+} isomer shifts and quadrupole splitting values, will be given elsewhere (Artioli et al., in preparation).

Electron probe microanalysis on two small chips of the crystals used in the neutron experiments verified that the crystals were unaffected in their chemical composition and homogeneity. The actual crystal used in the first neutron experiment was cut, polished, and carefully analyzed. Analytical profiles for Fe through the crystal and images from backscattered electrons showed no changes of stoichiometry or texture caused by the heating process for the bulk of the crystal.

Single-crystal X-ray diffraction structure refinements yielded the partitioning coefficients resulting from the heating and cooling cycles in the neutron experiments on two crystals. One more crystal underwent a similar heating and cooling cycle in a sealed capillary with controlled f_{O_2} (Fe-FeO buffer in Ar atmosphere) and showed analogous behavior (Table 1).

The structure analyses from the X-ray and neutron data were carried out with the SHELX (Sheldrick, 1976) and GSAS (Larson and Von Dreele, 1994) computer programs, respectively. All atomic parameters were freely refined, including the Fe and Mg site occupancy factors (constrained to total full occupancy). The Fe site contents from the neutron refinements yield an underestimate of the total Fe content because of parameter correlation, and they were fixed to fit the analytical stoichiometry (Fe_{tot} = 0.24 atoms pfu). The Fe site contents resulting from the X-ray refinements are in good agreement with the estimated formula unit from the chemical analysis. Table 1 summarizes the neutron and X-ray diffraction experimental conditions and structure analyses, together with the relevant atomic and geometric parameters resulting from the least-squares refinements. The unit-cell dimensions derived from neutron data are affected by some uncertainty in the x-y plane of the detector, and, although all data underwent the same treatment, the slightly different arrangements in the two experiments, two years apart, could be responsible for the low accuracy. High-resolution high-temperature X-ray powder diffraction experiments are planned to obtain better accuracy in unit-cell determination. Atomic coordinates and anisotropic displacement parameters from the neutron refinements are reported in Table 2.[1]

RESULTS AND DISCUSSION

The X-ray refinements and the neutron refinement at 25 °C (Table 1) show that the starting olivine sample has an essentially random Fe-Mg distribution, with K_D coefficients (0.93–1.08) well in the range (0.9–1.2) reported for natural olivines of similar compositions. The neutron refinement at 880 °C shows a K_D value of 1.26, indicating some Fe segregation into M1, whereas data at 960, 1030, and 1060 °C yield K_D values substantially lower than unity, indicating an increasing partitioning of Fe into M2 with increasing temperature. The response of K_D to temperature is shown in Figure 1, which also shows that the X-ray refinements of all crystals cooled after the heating cycles yielded larger values of K_D.

Conflicting crystallochemical factors have been invoked to explain the Fe-Mg ordering in the two sites. These include the geometrical size effect due to the difference of ion radius between Fe^{2+} and Mg^{2+}, the M2 site electrostatic potential, which should favor a more covalent character of the M-O bond, the larger distortion of the M1 octahedron, which should allow for a larger crystal-field stabilization energy (Ganguly, 1977; Ghose and Ganguly, 1982; Aikawa et al., 1985; Burns, 1985; Ottonello et al., 1990). Most of the terrestrial, lunar, and meteoritic olivines investigated at room temperature show a slight preference of Fe^{2+} for M1, although some samples
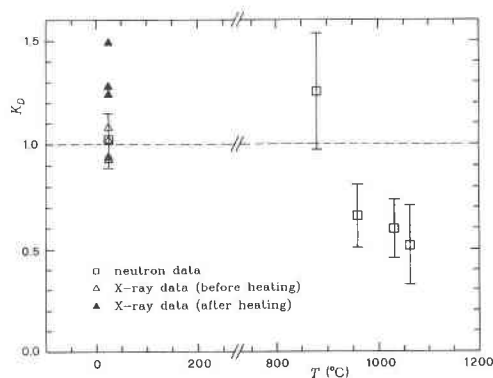

Fig. 1. Measured K_D value vs. temperature for the diffraction data. Error bars represent $\pm 1\sigma$ for neutron experiments. Standard deviations for the X-ray experiments are less than the size of the plotted symbol.

have shown a preference of Fe^{2+} for M2 (Wenk and Raymond, 1973; Ghose and Ganguly, 1982; Brown, 1982; Khisina et al., 1985). The large change in the Fe-Mg ordering pattern we observed at temperatures above 900 °C was totally unexpected from published results, although it is in agreement with earlier predictions (Ghose, 1962; Birle et al., 1968) that Fe^{2+} in olivine should order into M2 because of its larger size with respect to Mg^{2+}.

The lack of order in olivine is consistent with an ideal behavior of the forsterite-fayalite solid solution at low temperature, although claims for nonideality have been made to account for the effects of pressure on the cation distribution (Akamatsu et al., 1988, 1993). Pressure has been reported to induce Fe partitioning in the smaller M1 site (Aikawa et al., 1985; Akamatsu et al., 1988, 1993); therefore, temperature should contrast the volume packing effect by an ordering reversal of Fe in the larger M2 site, in keeping with our observations.

At high temperature the entropy contribution to the minimization of Gibbs free energy is larger, and this can be interpreted either in terms of electronic configurational entropy, due to the CFSE contribution (Ottonello et al., 1990), or in terms of a large increase in the thermal vibrational entropy, in analogy with the interpretation of the temperature dependence of cation ordering in the Mn- and Mg-containing olivines, in which CFSE effects are absent (Akamatsu et al., 1988). Two results of the present experiments favor the latter interpretation: first, at the higher temperatures Fe is partitioned into M2, where CFSE splitting of the Fe^{2+} t_{2g} orbitals is smaller because of the smaller distortion of the M2 octahedron, and second, the neutron refinement at 1060 °C shows that the equivalent nuclear displacement parameter of the M2 cations is slightly larger than that of M1, whereas it is the opposite at 880 °C (Table 1). Indeed all refinements and theoretical studies on olivine at room or lower temperatures (Hazen, 1977; Gramaccioli and Pilati, 1992, and literature therein) clearly indicate that the atomic displacement parameters of the M1 site are larger than those of the M2 site. Our high-temperature data are consistent with a large increase of the vibrational contribution to

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[1] A copy of Table 2 may be obtained by ordering Document AM-95-585 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

entropy with temperature, which overrides the decrease of the configurational contribution above about 900 °C, although these observations are to be taken with caution, given the uncertainty in the displacement parameters resulting from the high-temperature structure refinements.

The correlations proposed in the literature between the intracrystalline Fe-Mg ordering in natural olivines and the intensive thermodynamic variables associated with crystallization (temperature, pressure, composition, and f_{O_2}, in particular) are still controversial. Most authors assume that a disordered distribution of Fe and Mg in the octahedral sites of olivine is related to slow cooling of the crystal and the host rock (Basso et al., 1979; Khisina et al., 1985; Motoyama and Matsumoto, 1989; Princivalle, 1990), mainly because the K_D values observed in olivines from volcanic rocks are consistently higher than those observed in olivines extracted from metamorphic rocks and ultramafic nodules. This is in agreement with all experimental observations, including our results, which indicate that Fe invariably partitions into M1 after laboratory heating and cooling cycles, with cooling times from high temperatures (1000–1200 °C) longer than 10^{-2} s (Aikawa et al., 1985; Motoyama and Matsumoto, 1989; Ottonello et al., 1990; and the present work). No proper theoretical explanation for such a partitioning effect upon cooling has been proposed to date, although it might involve a subtle crystallochemical interaction between the size of the cation and distortion of the site and possibly a buildup in strain energy due to the difference between the kinetics of intracrystalline diffusion and structural distortion.

The present in-situ experiments show the shortcomings of quenching experiments aimed at determining the closure temperature of intracrystalline Fe-Mg diffusion at high temperature in olivine from room-temperature measurements of K_D. The high-temperature equilibrium site distribution of the octahedral cations is effectively nonquenchable.

The theoretical models predicting a preference of Fe in M1 at high temperature, because of CFSE considerations or because of the competing roles of ionic size and thermal vibration, will need revision to account for these new high-temperature data. The described partitioning behavior will have profound implications for the thermodynamic modeling of olivine in the Earth's mantle and in planetary processes.

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