The determination of site occupancies in two natural olivines by ALCHEMI method using only Si atoms as the reference atoms

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Abstract

The site occupancies of major and minor elements in two olivines have been determined by ALCHEMI method using only Si atoms as the reference atoms and assuming the homogeneities in the chemical composition. Since Si atoms in many silicate minerals occupy only the tetrahedral sites, they can be used for the reference atoms. Therefore, the analytical technique derived in this study is useful for the determination of the site occupancies not only in olivine in which Mg atoms show ordered distribution but also in other silicate minerals which contain SiO_4 tetrahedra. The determined site occupancies for Mg and Fe show weak preferences in M2 and M1 sites, respectively, which are opposite to those reported previously by ALCHEMI method. However the tendency of the preferences of the major elements (Mg and Fe) in this study is in accordance with those obtained by X-ray diffraction method. The site occupancies for minor elements, Mn and Ni, shows strong preferences in M2 and M1 sites, respectively, which are consistent with previous results by ALCHEMI method.

Introduction

Frequently, cations distribute over the crystallographically non-equivalent cation sites in a mineral. The determination of cation distribution is important for obtaining the conditions of crystallization in the fields of earth sciences and engineering technology. For this purpose, X-ray or neutron diffraction and Mössbauer techniques have been used (Nord, Annersten and Filippidis 1982; Motoyama and Matsumoto 1989; Virgo and Hafner 1972; Shinno, Hayashi and Kuroda 1974). However, these techniques are not always effective for the minerals with more than three major elements over two sites and for the determination of cation distributions of minor elements. Recently, ALCHEMI (Atomic Location by CHanneling Enhanced MLCroanalysis) method on the basis of channeling-enhanced X-ray emission has been used to determine the site occupancies for major and minor elements in various minerals. In particular, this technique has large advantages to determine the site occupancies of minor elements and also those of elements with similar atomic numbers in minerals. Indeed, this technique has been applied to spinel, olivine, K-feldspar and other minerals (e.g., Taftø, 1982; Taftø and Liliental,

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1982; Taftø and Spence, 1982; Smyth and Taftø, 1982; Taftø and Buseck, 1983; McCormick, Smyth and Lofgren 1987; McLaren and Fitz Gerald, 1987; Tabira, Ishizawa and Marumo, 1993).

For olivines Taftø and Spence (1982), Smyth and Taftø (1982) and McCormick *et al.* (1987) determined site occupancies of a major element (Fe) and minor elements (Ni, Mn and Ca etc.) by ALCHEMI method. They assumed the complete disordering of Mg in order to determine the proportions of the other elements on M1 site. However, the preferences of Mg and Fe obtained previously are not in accordance with the results of X-ray diffraction method and the site occupancy of Mg is not always completely disordered (Brown, 1980; Motoyama and Matsumoto, 1989). Matsumoto, Motoyama and Okuno (1989) determined the site occupancies of two major elements (Mg and Fe) and minor elements (Ni and Mn) by ALCHEMI method. They assumed only Mg and Fe atoms for major elements in olivine. After the calculation of the occupancies of these major elements, those of minor elements were calculated. In this paper, we show that the site occupancies of Mg, Fe, Ni and Mn in two natural olivines, whether they are major or minor elements, can be determined using only Si atoms as the reference atoms of ALCHEMI method without the assumption of Mg disordering.

Experimental

For present study, two specimens were selected, Mg-rich olivine in lherzolite from Salt Lake Crater, Hawaii in U.S.A. (Goto and Yokoyama, 1989) (henceforth this olivine is symbolized as SL165) and Fe-rich one in rhyolite from Kagoshima Pref. in Japan (this olivine is symbolized as Hayato). The crystal structures and the cation distributions of Mg and Fe of these specimens have been studied by Motoyama and Matsumoto (1989) using an X-ray single crystal diffraction method. The compositions of these olivines analyzed by an electron microprobe analyzer (Goto and Yokoyama, 1988; Motoyama and Matsumoto, 1989) are shown in Table 1. These microprobe analyses showed no significant chemical inhomogeneities of these olivine crystals.

An Akashi EM-002B transmission electron microscope fitted with EDAX9100 energy dispersive X-ray analysis facilities and a double tilt specimen holder was used for ALCHEMI experiments. Specimens for TEM observations and measurements were prepared by ion-bombardment thinning of thin sections. The accelerating voltage is 180kV. The olivine crystals were oriented to show the (00 l) systematic row of diffraction spots (based on the space group, **Pbnm**), avoiding other low indices diffractions, and the specimen holder was tilted about 10° toward the X-ray detecting device. Three types of spectra were collected from each area. Two were collected on the channeling orientations, one angle with the incident beam slightly smaller than 002 Bragg angle ($\theta < \theta_B$) and the other angle with slightly larger than 002 Bragg angle ($\theta > \theta_B$). The third spectrum was collected on a non-channeling orientation. Diffraction patterns on two channeling conditions are shown in Fig. 1. The beam diameter was roughly

TABLE 1. The chemical compositions of olivines used in this work.

composition(wt%)	SL165 ^a	Hayato ^b
SiO ₂	41.32 wt%	30.40 wt%
FeO*	8.12	59.70
MnO	0.13	3.53
MgO	50.47	5.36
CaO	0.07	0.03
NiO	0.37	0.00
Total	100.48	99.02
numbers of atoms per 4.000 oxygens		
Si	1.001	0.999
Fe	0.165	1.640
Mn	0.003	0.098
Mg	1.823	0.262
Ca	0.002	0.001
Ni	0.007	0.000
Total	3.001	3.000

*: Total Fe as FeO

a: Analysed by Goto and Yokoyama(1988)

b: Analyzed by Motoyama and Matsumoto(1989)

1000Å. Spectra were collected for 300–500 sec. in live time. For two channeling orientations, the wave field is modulated along [001]. For $\theta < \theta_B$, the X-ray emissions from the M2 and Si positions are enhanced, and for $\theta > \theta_B$, the emission from the M1 position is enhanced (Fig. 2). Typical X-ray spectra for these orientations are shown in Fig. 3. Fig. 4 shows the intensity variation of characteristic X-ray emission for Mg, Fe, Mn and Ni in SL165 olivine with respect to observed angles. Using the intensity of the $K\alpha$ line of Mg as reference, the intensity of the $K\alpha$ line of Si is enhanced for $\theta < \theta_B$ and decreased for $\theta > \theta_B$. The intensity of Mn changes in similar manner with that of Si whereas Ni shows an opposite change to Si. The intensity of Fe is almost constant. Si is ordered into the same atomic plane as the position of M2 site (Fig. 1). Therefore Mn is ordered into the M2 site, Ni is ordered into the M1 site and Fe is almost disordered.

Results and discussion

Calculation procedures

In previous work for Mg-rich olivine (Taftø and Spence, 1982; Smyth and Taftø, 1982; McCormick *et al.*, 1987), Mg was assumed to be completely disordered over the M1 and M2 sites for the calculations of the site occupancies for Fe and minor elements. However, Mg is not always completely disordered (Brown, 1980; Motoyama and Matsumoto, 1989). When Mg is ordered more or less, the above assumption is not correct, and calculated occupancies may include systematic errors. Therefore, we do not use the above assumption of Mg disordering but assume homogeneity in chemical composition of the specimen. The results of microanalyses

FIG. 1. Typical diffraction patterns for two channeling orientations of SL165 olivine. (a) $\theta < \theta_B$
(b) $\theta > \theta_B$.

for the specimens support this assumption. In this ALCHEMI study, Mg atom is not used for the reference atom but only Si is used for the reference atom.

The number of X-ray counts, N_X , from element X in olivine with the composition, $(A,B,C, \dots, X, \dots)_2\text{SiO}_4$, is expressed as follows,

FIG. 2. The ideal structure of olivine projected on (100) and electron intensity (I_e) across the unit cell (Bloch waves). (The large open circles are oxygen, the intermediate solid circles are M1 and the open circles are M2 and the small solid circles are Si. The numbers show the heights of atoms.)

$$N_X = C_X \beta_X I \quad (1),$$

where C_X the number of element X per 4 oxygens; β_X is a factor which takes into account differences in X-ray yield, detection efficiency and other scaling factors; I is an electron

FIG. 3. Typical X-ray spectra for SL165 (a, b) and Hayato (c, d) olivines at two channeling orientations. (a) and (c) $\theta < \theta_B$, (b) and (d) $\theta > \theta_B$.

FIG. 4. The intensity variations of characteristic X-ray emission for (a) Mn, (b) Ni, (c) Si, (d) Fe in SL165 olivine with incident beam direction. The intensity ratio of individual position to non-channeling position normalized by the ratio of Mg is shown. Because the cation distribution of Mg is generally almost disordered over the M1 and M2 site in olivine.

intensity of incident beam in the crystal. When the crystal is oriented to the channeling position, the number of X-ray counts is expressed as follows,

$$iN_X = P_X C_X \beta_X iI_1 + (1-P_X) C_X \beta_X iI_2 \quad (2),$$

where P_X is the proportion of element X in the M1 site; I_1 and I_2 the electron intensities on the crystallographic planes including the M1 and M2 sites, respectively; i the position of X-ray spectra measured: $i = -$ is for $\theta < \theta_B$, $i = +$ is for $\theta > \theta_B$, $i = 's'$ is for non-channeling position. Then from three equations ($i = -, +$, and $'s'$) for (2), P_X is obtained as follows,

$$P_X = (-n_X - {}^+n_X)/(I_e^S n_X) = x/I_e \quad (3),$$

where n is N_X/N_{Si} , I_e is $(I_1/I_2 - {}^+I_1/{}^+I_2)$ and x is $(-n_X - {}^+n_X)/S n_X$. Total occupancy of M1 site is 1.0, therefore

$$P_A C_A + P_B C_B + \dots + P_X C_X + \dots = 1.0 \quad (4).$$

From the equations (3) and (4), I_e is expressed as follows;

$$I_e = aC_A + bC_B + \dots + xC_X + \dots \quad (5).$$

Thus by substituting the equation (4) into the equation (2), we can get the following equation;

$$P_X = x/(aC_A + bC_B + \dots + xC_X + \dots) \quad (6).$$

Using this new equation we can easily calculate the proportions of each elements for the M1 and M2 sites without the assumption of disordering of Mg atoms.

Furthermore, this equation is useful for not only the determination of site occupancies in olivine but also in other silicate minerals. Since Si atoms in many silicate minerals occupy only the tetrahedral sites, they can be used for the reference atoms. Proportions of elements on the M1 site for SL165 and Hayato olivines calculated by the present procedure are shown in Table 2 with those calculated by Taftø and Spence's (1982) procedure ($P_{Mg} = 0.5$ for SL165 olivine and $P_{Fe} = 0.5$ for Hayato olivine). The proportions of Mg and Fe on the M1 site in Hayato olivine calculated by Taftø and Spence's procedure deviate systematically from those obtained by the present equation. The small deviations from the results by X-ray diffraction analysis are reported in the ALCHEMI analysis on Mg-rich olivine by McCormick *et al.* (1987).

Ordering of Ni and Mn

The average of the proportion of Ni in the M1 site is 0.94(4) for SL165 and those of Mn

TABLE 2. Proportions of elements on the M1 sites for SL165 and Hayato olivines calculated by the present procedure and Taftø and Spence's (1982) procedure.

SL165 olivine				Taftø and Spence's(1982) procedure*		
Present procedure						
P _{Mg}	P _{Fe}	P _{Mn}	P _{Ni}	P _{Fe}	P _{Mn}	P _{Ni}
0.493	0.572	0.166	0.987	0.581	0.168	1.002
0.494	0.561	0.007	0.938	0.567	0.008	0.949
0.494	0.564	0.134	0.851	0.571	0.136	0.861
0.494	0.562	0.186	0.925	0.569	0.188	0.937
0.494	0.570	0.071	0.862	0.578	0.072	0.873
0.494(2)	0.57(2)	0.11(5)	0.91(4)	0.57	0.11	0.92
* P _{Mg} is assumed 0.5						
Hayato olivine				Taftø and Spence's(1982) procedure**		
Present procedure						
P _{Mg}	P _{Fe}	P _{Mn}		P _{Mg}	P _{Mn}	
0.465	0.528	0.122		0.440	0.115	
0.504	0.525	0.076		0.480	0.073	
0.496	0.528	0.048		0.470	0.045	
0.501	0.522	0.129		0.480	0.123	
0.49(3)	0.526(7)	0.09(3)		0.468	0.089	
** P _{Fe} is assumed 0.5.						

are 0.11(5) for SL165 and 0.09(3) for Hayato (the standard deviations were estimated on the basis of counting statics only). Ni shows a strong preference for the M1 site and Mn shows for the M2 site as well as the results of previous studies by ALCHEMI method for Mg-Fe olivines. Taftø and Spence (1982) reported for the olivine in alkali basalt from San Carlos based on ALCHEMI method that the proportion of Ni and Mn in the M1 site were 0.97(5) and 0.01(5) respectively. The proportions of Ni and Mn in the olivines of present study are more disordered than those of San Carlos olivine. Furthermore, these results are in accordance with those of previous work based on X-ray structure refinement and Mössbauer studies for olivines containing much Ni and Mn as major elements (Rajamani, Brown and Prewitt, 1975; Francis and Ribbe, 1980; Bish, 1981; Nord *et al.*, 1982; Annersten, Ericsson and Filippidis, 1982; Boström, 1987; Akamatsu *et al.*, 1988; Ottenello, Della Giusta and Molin, 1989).

Ordering of Mg and Fe

The averages of the proportions of Mg and Fe in the M1 site are 0.494(2) and 0.57(2) for SL165 and 0.49(3) and 0.562(7) for Hayato respectively. Mg shows a slight preference for the M2 site and Fe shows for the M1 site in these two olivines. These results are in good agreement with the results of Motoyama and Matsumoto (1989) by the X-ray structure refinements. Taftø and Spence (1982) reported the proportion of Fe in the M1 site for San Carlos olivine was 0.496(1), and McCormick *et al.* (1987) also reported that Fe preferred for the M2 site in the

TABLE 3. The site occupancies of elements for SL165 and Hayato olivines.

		SL165 olivine			Hayato olivine		
		X-ray*	ALCHEMI		X-ray*	ALCHEMI	
			present	T & S**		present	T & S**
M1 site	Mg	0.915(2)	0.901	0.912	0.122(4)	0.129	0.123
	Fe	0.085	0.093	0.094	0.878	0.863	0.820
	Mn		0.000	0.000		0.009	0.009
	Ni		0.006	0.006			
	Total	1.000	1.000	1.015	1.000	1.001	0.952
M2 site	Mg	0.919	0.922	0.912	0.140	0.133	0.139
	Fe	0.081	0.072	0.071	0.860	0.777	0.820
	Mn		0.003	0.003		0.089	0.089
	Ni		0.001	0.000			
	Total	1.000	0.998	0.987	1.000	0.999	1.048

* X-ray diffraction analyses by Motoyama and Matsumoto (1989)

** calculated by Taftø and Spence's (1982) procedure

heated olivine. According to the previous results based on the X-ray diffraction data, however, in almost unheated and heated olivines in volcanic and lunar rocks, Fe prefers for the M1 site (Finger, 1970; Finger and Virgo, 1971; Motoyama and Matsumoto, 1989). Therefore, the results obtained in this study are consistent with those by X-ray diffraction analyses.

The site occupancies calculated from the averages of the proportion of cations obtained by the present procedure and Taftø and Spence's procedure for these two olivines are listed in Table 3 together with the data for Mg and Fe reported the Motoyama and Matsumoto (1989) by means of X-ray diffraction analyses. The site occupancies of Mg and Fe obtained in this work are in good agreement with those of Motoyama and Matsumoto (1989). The total of the site occupancies for M1 and M2 sites is quite close to unity. This indicates the present results are considerably reliable. If the calculated proportion of each element is not correct, the total of the site occupancies for both sites differ from unity. Therefore, if the composition at an illuminated area coincides with the bulk composition of a mineral, that is a mineral compositionally homogeneous, the present procedure is very useful for the determination of cation distribution.

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References

- AKAMATSU, T., FUJINO, K., KUMAZAWA, M., FUJIMURA, A., KATO, M., SAWAMOTO, H. and YAMANAKA, T. (1988) Pressure and temperature dependence of cation distribution in Mg-Mn olivine. *Phys. Chem. Minerals*, **16**, 105-113.
- ANNERSTEN, H., ERICSSON, T. and FILIPPIDIS, A. (1982) Cation ordering in Ni-Fe olivines. *Am. Mineral.*, **67**, 1212-1217.
- BISH, D.L. (1981) Cation ordering in synthetic and natural Ni-Mg olivine. *Am. Mineral.*, **66**, 770-776.
- BOSTRÖM, D. (1987) Single-crystal X-ray diffraction studies of synthetic Ni-Mg olivine solid solutions. *Am. Mineral.*, **72**, 965-972.
- BROWN, G.E. (1980) Olivines and silicate spinels. *Reviews in mineralogy*, **5**, 275-381.
- FINGER, L.W. (1970) Fe/Mg ordering in olivines. *Carnegie Inst. Washington Year book*, **69**, 302-305.
- FINGER, L.W. and VIRGO, D. (1971) Confirmation of Fe/Mg ordering in olivines. *Carnegie Inst. Washington Year book*, **70**, 221-225.
- FRANCIS, C.A. and RIBBE, P.H. (1980) The forsterite-tephroite series. I. Crystal structure refinements. *Am. Mineral.*, **65**, 1263-1269.
- GOTO, A. and YOKOYAMA, K. (1988) Lherzolite inclusion in olivine nephelinite tuff from Salt Lake Crater, Hawaii. *Lithos*, **21**, 67-80.
- MATSUMOTO, T., MOTOYAMA, T. and OKUNO, M. (1989) The determination of M1 and M2 site occupancies of minor elements in a olivine crystal by ALCHEMI method. *J. Min. Petr. Econ. Geol.* Special Issue (in Japanese), **4**, 101-104.
- MCCORMICK, T.C., SMYTH, J.R. and LOFGREN, G.E. (1987) Site occupancies of minor elements in synthetic olivines as determined by channeling-enhanced X-ray emission. *Phys. Chem. Minerals*, **14**, 368-372.
- MCLAREN, A.C. and FITZGERALD, J.D. (1987) CBED and ALCHEMI investigation of local symmetry and Al, Si ordering in K-feldspars. *Phys. Chem. Minerals*, **14**, 281-292.
- MOTOYAMA, T. and MATSUMOTO, T. (1989) The crystal structures and the cation distributions of Mg and Fe of natural olivines. *Mineral. J.*, **14**, 338-350.
- NORD, A.G., ANNERSTEN, H. and FILIPPIDIS, A. (1982) The cation distribution in synthetic Mg-Fe-Ni olivines. *Am. Mineral.*, **67**, 1206-1211.
- OTTENELLO, G., DELLA GIUSTA, A. and MOLIN, G.M. (1989) Cation ordering in Ni-Mg olivines. *Am. Mineral.*, **74**, 411-421.
- RAJAMANI, V., BROWN, G.E. and PREWITT, C.T. (1975) Cation ordering in Ni-Mg olivine. *Am. Mineral.*, **60**, 292-299.
- SHINNO, I., HAYASHI, M. and KURODA, Y. (1974) Mössbauer studies of natural olivines. *Mineral. J.*, **7**, 344-358.
- SMYTH, J.R. and TAFTØ, J. (1982) Major and minor element site occupancies in heated natural forsterite. *Geophys. Res. Lett.*, **9**, 1113-1116.
- TABIRA, Y., ISHIZAWA, N. and MARUMO, F. (1993) Cobalt atoms at M(2) site in C2/c clinopyroxenes of the system $\text{CaMgSi}_2\text{O}_6(\text{Di})$ - $\text{CaCoSi}_2\text{O}_6(\text{CaCoPx})$. *Mineral. J.*, **16**, 225-245.
- TAFTØ, J. (1982) The cation-atom distribution in a $(\text{Cr,Fe,Al,Mg})_3\text{O}_4$ spinel as revealed from the channeling effect in electron-induced X-ray emission. *J. Appl. Cryst.*, **15**, 378-381.
- TAFTØ, J. and BUSECK, P.R. (1983) Quantitative study of Al-Si ordering in an orthoclase feldspar using an analytical transmission electron microscopy. *Am. Mineral.*, **68**, 944-950.
- TAFTØ, J. and LILIENTAL, Z. (1982) Studies of the cation atom distribution in $\text{ZnCr}_x\text{Fe}_{2-x}\text{O}_4$ spinels using the channeling effect in electron-induced X-ray emission. *J. Appl. Cryst.*, **15**, 260-265.
- TAFTØ, J. and SPENCE, J.C.H. (1982) Crystal site location of iron and trace elements in a magnesium-iron olivine by a new crystallographic technique. *Science*, **218**, 49-51.
- VIRGO, D. and HAFNER, S.S. (1972) Temperature-dependent Mg, Fe distributions in a lunar olivine. *Earth. Planet. Sci. Lett.*, **14**, 305-312.

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