Crystal structure and cation distribution of “cleavable” olivines

Nobuyuki AIKAWA* and Masayasu TOKONAMI**

**Department of Geosciences, Faculty of Science, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka*

***Mineralogical Institute, Faculty of Science, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo*

Abstract

Crystal structure and cation distribution of “cleavable olivines” with distinctive partings on (010), (100), and (001) from two ultrabasic rock masses (Ōeyama and Happo-O'ne) were investigated by X-ray diffraction method. Crystal structure of the cleavable olivine does not possess any peculiarity in contrary to the Kuroda and Shimoda's claim that it has some structural anomaly on the basis of strong 020 diffraction intensity observed by them. Strong 020 reflection in powder X-ray patterns is merely due to the preferred orientation. Cation distribution of Fe and Mg between M1 and M2 sites is random for Happo-O'ne olivine, and Fe atom slightly prefers for the M2 site for Ōeyama olivine, indicating that both of the cleavable olivines are equilibrated at low temperature, which is consistent with petrologic evidences.

Introduction

Olivine with well-developed cleavages on (010), (100) and (001), has been reported to occur at various localities in the world (Hawkes, 1946; Velinsky and Pinus, 1969; Nixon *et al.*, 1963), whereas olivine does not generally show such perfect cleavages. Hawkes (1946) was the first to note such olivine from a dunite in northern California, and named it “cleavable olivine”. Kuroda and collaborators have reported the cleavable olivine from two tectonic regions in Japan (Kuroda and Shimoda, 1967; Matsuhisa, 1968; Kuroda, 1969), and have intensively studied these cleavable olivines mineralogically and geologically. Most distinctive feature of the cleavable olivine (*e.g.* Kuroda, 1969) is abnormally intense 020 reflection in X-ray powder pattern. They gave a model structure to account for the abnormal intensity of 020 reflection, and suggested that it might preserve the structure under high pressure. Although the presence of cleavable olivine called attention of many geologists and mineralogists, it has been quite difficult to check the Kuroda's hypothesis, because large and uniform single crystal samples of cleavable olivine are not available for precise crystallographic study due to parting and alteration along the parting planes closely spaced.

Aikawa (1981) showed that the strong 020 reflection of the cleavable olivine from

Ōeyama was merely due to the preferred orientation by the powder and single crystal X-ray diffraction method and that partings were planes made by dislocation arrays using the oxidation decoration method. Uda (1984) also investigated the dislocation structure in cleavable olivine from Ōeyama by the oxidation decoration method, and made clear that cleavage was due to the formation of antigorite films along dislocation cell walls which were formed through annealing-recovery process during contact metamorphism in a tectonic environment.

In their recent experimental study on the intersite distribution of Mg and Fe in ferromagnesian olivine, Aikawa *et al.* (1985) have shown (1) the rate of cationic exchange reaction is very fast at high temperatures above 600°C, and (2) the cationic ordering (towards the preference of Fe for M1) takes place with the increase of temperature. Further, it is predicted that the cationic distribution will show the reverse ordering (towards the preference of Fe for M2) from the disordering over the M1 and M2 sites at very low temperatures, where the exchange reaction is expected to be very sluggish. Uda (1984) has shown that the typical cleavable olivine from the Ōeyama ultrabasic rock mass occurs in zone II of the metamorphic grade of 350–450°C from the study of mineral assemblages in the thermally metamorphosed dunite. This suggests a possibility that the cation distribution of cleavable olivines has been equilibrated at the very low temperatures below 350–450°C over the geologic time. Therefore, it is an interesting subject to clarify the cation distribution of cleavable olivines in relation to their thermal history. The aim of this study is to carry out the crystal structure analysis of the cleavable olivine, which may be equilibrated at very low temperatures.

Experimental details

Sample

Cleavable olivines from two different localities were used; one is from zone II in the Ōeyama (Kōmori) ultrabasic rock mass (Uda, 1984) and the other from A-type dunite in the Happo-O'ne ultrabasic rock mass (Matsuhisa, 1968). These two ultrabasic rock masses have been thermally metamorphosed by the granitic rocks intruded adjacent to them. Olivines in ultrabasic rock masses near granitic rocks have been recrystallized (Kuroda and Shimoda, 1967; Matsuhisa, 1968; Uda, 1984). The ages of metamorphism due to intrusion of granitic rocks are 50–60 Ma (lowest Tertiary) for Happo-O'ne mass (Kawano and Ueda, 1966; Kato and Sato, 1983) and about 65 Ma (uppermost Cretaceous) for Ōeyama mass (Aldrich *et al.*, 1962; Kawano and Ueda, 1966). The cleavable olivines from both of the ultrabasic rock masses occur at distance of 1–2 km from the boundary of granitic rocks and ultrabasic rock masses. The microscopic observation of thin section shows both the well-developed cleavage,

which is essentially parting (Aikawa, 1981) and dislocation textures (cell structures, see Aikawa, 1981 and Uda, 1984). Parting (cleavage) is filled with serpentine mineral (antigorite; Uda, 1984).

Chemical compositions are about Fo=90 for Ōeyama cleavable olivines (EPMA analysis, Uda, 1984), and about Fo=91 for Happo-O'ne cleavable olivines (X-ray determinative curve of d_{130} by X-ray powder method and bulk chemical analysis, Matsuhisa, 1968). However, cleavable olivine grains from Ōeyama are heterogeneous and contain recrystallized parts which are rich in Mg (maximum 96 percent forsterite; Uda, 1984), indicating an evidence of thermal metamorphism. Cleavable olivine grains from Happo-O'ne may also contain recrystallized parts. Therefore, bulk compositions of single cleavable olivine grains from both of the ultrabasic rock masses may be the average of the primary olivine and the recrystallized olivine and more Mg rich than Fo=90.

X-ray diffraction experiments

Olivine grains were hand-picked under the microscope. The crystallographic orientation of cleavable olivines is easily identified because of the rectangular prism with parting planes corresponding to (100), (010) and (001).

Preliminary X-ray examinations were made by precession method prior to the data collections for crystal structure analysis. All of reflections from the cleavable olivines have never been sharp, but were diffuse on precession photographs, even though grain size was less than 100 μm . Two kinds of diffuse reflections are recognized; (1) a streak along the powder ring (no change of d-spacing) and (2) rounded diffuse spot without streak (non-uniform change of d-spacing). The first represents that the olivine grain consists of subgrains which are misoriented among them, the second reflects large density of dislocations of lattice imperfection in the crystal. The first type of diffuse streaks, in particular, is generally observed on a^*c^* and a^*b^* planes (Aikawa, 1981), indicating that Burger's vectors and slip planes of dislocation in these olivine samples are statistically constrained by crystal structure. Generally the reflections from the cleavable olivine grains show two kinds of diffuse nature at the same time.

Lattice parameters of cleavable olivines are measured on the precession photographs and also by a four-circle diffractometer. Results are given in Table 1. Precise measurements of lattice parameters could not be performed, because of the diffuseness of reflections.

The olivine crystal from Ōeyama selected for the crystal structure analysis shows slightly diffuse streaks on a^*c^* plane but not practically on a^*b^* plane. The selected single crystal from Happo-O'ne does not show diffuse streaks along the powder ring but gives somewhat rounded diffuse spots. The existence of diffuse streaks common to cleavable olivine does not allow us to use the ordinary technique of data collection

TABLE 1. Lattice parameters of cleavable olivines (Å)

		a	b	c
Ōeyema	1)	4.769(6)	10.243(27)	6.003(11)
	2)	4.75 (1)	10.21 (2)	6.00 (1)
Happo-O'ne	1)	4.754(5)	10.209(25)	5.986(10)
	2)	4.76 (1)	10.22 (2)	6.00 (1)

1) Lattice parameters obtained by four-circle diffractometer.

2) Lattice parameters obtained by precession photographs.

Numbers in parentheses represent estimated errors referring to the last decimal place quoted.

for crystal structure analysis. The intensity measurement of rounded diffuse reflections of Happo-O'ne cleavable olivine was done by the ordinary 2θ - ω scan method using a sufficiently wide receiving slit and a sufficiently wide scanning range, and that of streaked diffuse reflections of Ōeyama cleavable olivine by the ω -scan method (moving crystal and fixed detector), with a sufficiently wide receiving slit and a sufficiently wide scanning range.

The intensity data for crystal structure analysis were acquired by a computer-controlled Rigaku AFC diffractometer with Moka α radiation monochromatized by pyrolytic graphite. The intensities of approximately 450 independent reflections in the range of $2\theta = 3$ –55 deg. were reduced in the standard fashion and converted to structure amplitudes. Because of the small sample size and relatively small linear absorption coefficient ($\mu R < 0.3$), no absorption correction was applied. Using neutral atomic scattering factor (Doyle and Turner, 1968), refinement of the structure was

TABLE 2. X-ray data

Ōeyama	Happo-O'ne
459*	466*
Fo = 90	Fo = 88
R = 3.8%	R = 4.4%
wR = 2.8%	wR = 3.4%
Fo = 92	Fo = 90
R = 3.7%	R = 4.3%
wR = 2.7%	wR = 3.2%
Fo = 94	Fo = 92
R = 3.8%	R = 4.3%
wR = 2.7%	wR = 3.2%

*Number of reflections used for structural refinement ($I_{\text{obs}} > 3\sigma I_{\text{obs}}$).

made with the program RFINE (Finger, 1972) modified by Horiuchi (private communication), starting from positional and thermal parameters of forsterite reported by Birle *et al.* (1968).

Results

Calculations of positional and thermal parameters were done for several compositions around Fo=90 because of the uncertainty of the chemical composition of cleavable olivines. However, the results on the two cleavable olivine crystals agreed within experimental errors and within the presumed compositional range as shown in Table 2. Atomic coordinates and bond distances of olivine with Fo=90 are listed in Tables 3

TABLE 3. Atomic parameters of olivines

		Oeyama ¹⁾	Happo-O'ne ²⁾	Kuraoda's ³⁾ structure	Forsterite ⁴⁾ (40 Kb)	Bergell ⁵⁾ Alps	Assab ⁶⁾ Ethiopia
M(1)	X = 0, Y = 0, Z = 0						
	B*	0.36 (3)	0.43 (3)		0.37 (9)	0.34 (1)	0.40 (1)
M(2)	X	0.9901(4)	0.9900(4)	0.960	0.991(1)	0.98968(8)	0.9900(1)
	Y	0.2775(1)	0.2779(2)	0.300	0.280(1)	0.27772(4)	0.2777(1)
	Z=1/4						
	B	0.44 (3)	0.41 (4)		0.52 (10)	0.37 (1)	0.41 (2)
Si	X	0.4270(3)	0.4268(3)	0.430	0.426(1)	0.42681(7)	0.4269(1)
	Y	0.0944(1)	0.0946(2)	0.060	0.093(1)	0.09443(4)	0.0944(1)
	Z=1/4						
	B	0.33 (3)	0.37 (3)		0.45 (7)	0.20 (1)	0.34 (1)
O(1)	X	0.7665(7)	0.7657(8)	0.740	0.768(2)	0.76589(18)	0.7662(2)
	Y	0.0916(3)	0.0914(4)	0.060	0.097(2)	0.09148(9)	0.0918(1)
	Z=1/4						
	B	0.4 (1)	0.5 (1)		0.1 (2)	0.43 (1)	0.48 (2)
O(2)	X	0.2191(7)	0.2199(9)	0.240	0.228(2)	0.22066(19)	0.2201(2)
	Y	0.4478(3)	0.4477(4)	0.440	0.444(2)	0.44767(8)	0.4478(1)
	Z=1/4						
	B	0.4 (1)	0.5 (1)		0.0 (2)	0.42 (1)	0.50 (2)
O(3)	X	0.2782(5)	0.2791(6)	0.310	0.276(2)	0.27838(13)	0.2784(2)
	Y	0.1637(2)	0.1632(3)	0.140	0.158(2)	0.16333(6)	0.1633(1)
	Z	0.0342(4)	0.0345(4)	0.050	0.035(1)	0.03329(10)	0.0337(1)
	B	0.44 (5)	0.4 (1)		0.4 (1)	0.47 (1)	0.53 (2)

1), this study; 2), this study; 3), structure of "cleavable" olivine (Kuroda, 1969); 4), structure of forsterite under 40 Kbar (Hazen, 1976); 5), metamorphic olivine with Fo $\approx$ 90 (Wenk and Raymond, 1973); 6), volcanic olivine with Fo $\approx$ 90 (Basso *et al.*, 1979).

*Equivalent isotropic thermal factor from anisotropic thermal coefficients.

Numbers in parentheses represent estimated errors referring to the last decimal place quoted.

and 4, and the cation distribution constants ($K_d = X(M1Fe)X(M2Mg)/X(M1Mg)X(M2Fe)$; X is site occupancy number) are listed in Table 5 for two cleavable olivines with the presumed compositions.

In Tables 3 and 4, atomic coordinates and bond distances of cleavable olivine are compared with those of forsterites with nearly the same compositions; metamorphic forsterite ($K_d = 0.97$; Wenk and Raymond, 1973), volcanic forsterite ($K_d =$

TABLE 4. Selected interatomic distances of olivines (Å)

	Oeyama ¹⁾	Happo-O'ne ²⁾	Kuroda's ³⁾ structure	Forsterite ⁴⁾	Bergell ⁵⁾ Alps	Assab ⁶⁾ Ethiopia
Si—O(1)	1.620(8)	1.611(8)	1.473	1.62(1)	1.6150(9)	1.618(2)
O(2)	1.655(4)	1.653(5)	1.465	1.66(2)	1.6572(9)	1.655(2)
O(3)	1.639(3)	1.627(4)	1.556	1.60(1)	1.6382(7)	1.637(1)
Mean	1.638(5)	1.630(5)	1.513	1.62(1)	1.6372(8)	1.637(2)
M(1)—O(1)	2.091(4)	2.086(4)	2.033	2.08(1)	2.0891(6)	2.091(1)
O(2)	2.081(5)	2.073(5)	2.033	2.04(1)	2.0741(6)	2.077(1)
O(3)	2.148(4)	2.140(5)	2.072	2.07(2)	2.1420(6)	2.143(1)
Mean	2.107(4)	2.100(5)	2.046	2.06(2)	2.1017(6)	2.104(1)
M(2)—O(1)	2.183(5)	2.182(5)	2.624	2.12(1)	2.1829(10)	2.181(2)
O(2)	2.058(5)	2.050(5)	1.950	2.00(2)	2.0571(9)	2.057(2)
O(3)	2.072(4)	2.066(5)	2.025	2.07(1)	2.0639(7)	2.067(2)
O(3)	2.220(5)	2.219(5)	2.618	2.22(1)	2.2241(7)	2.223(1)
Mean	2.137(4)	2.133(5)	2.310	2.11(2)	2.1360(7)	2.136(2)

1), 2), 3), 4), 5) and 6) are the same as those of Table 2.

Numbers in parentheses represent estimated errors referring to the last decimal place quoted.

TABLE 5. Intersite distribution of Mg and Fe in "cleavable" olivine

Oeyama	Happo-O'ne
Fo = 90	Fo = 88
$K_d^* = 0.84(6)$	$K_d^* = 1.01(7)$
$Mg/M1 = 0.9076(30)$	$Mg/M1 = 0.8793(35)$
Fo = 92	Fo = 90
$K_d = 0.81(6)$	$K_d = 1.00(7)$
$Mg/M1 = 0.9277(28)$	$Mg/mM1 = 0.8999(33)$
Fo = 94	Fo = 92
$K_d = 0.76(6)$	$K_d = 0.99(7)$
$Mg/M1 = 0.9479(28)$	$Mg/M1 = 0.9205(32)$

* $K_d = (Fe/Mg)_{M1} / (Fe/Mg)_{M2}$

Numbers in parentheses represent estimated errors referring to the last decimal place quoted.

1.15; Basso *et al.*, 1979), cleavable olivine (Kuroda, 1969), synthetic forsterite (Fo=100) under high pressure (Hazen, 1976). As seen in Tables 3 and 4, the atomic structures of cleavable olivine in this study are the same as those of metamorphic and volcanic olivines within experimental errors, whereas the model structure proposed by Kuroda does not show any similarity to any of the structures determined by X-ray structure analysis.

Discussion

The present structural analysis shows that Fe atom is slightly ordered in M2 site in Ōeyama cleavable olivine, and the value of $K_d(0.80 \pm 0.06)$ is the least one ever reported for ferromagnesian olivine. The K_d of the Happon-O'ne cleavable olivine is 1.00 ± 0.07 , showing that Fe and Mg atoms are randomly distributed between the two cationic sites. This large negative deviation from $K_d=1$ for Ōeyama cleavable olivine is in significant contrast to most of olivine samples studied so far.

Recent reliable analyses of cation distribution in Fe–Mg olivine indicate that Fe show a slight ordering on M1. Although the temperature dependency of cation distribution has been studied by several authors (*e.g.* Shinno, 1974 and 1980; Brown and Prewitt, 1973; Brown, 1980), it has been a little controversial; (1) the cationic distribution appeared to increase the ordering of Fe on M1 with temperature, contradicting the common sense (Brown and Prewitt, 1973; Symth and Hazen, 1973; Shinno, 1974), and (2) the intersite exchange reaction of cations appeared to be sluggish, because K_d does not change with the temperature of experimental equilibration (Bush *et al.*, 1970; Virgo and Hafner, 1972). In their experimental study using a very fast quenching technique, Aikawa *et al.* (1985) have resolved the above problems and showed that the K_d of olivine equilibrated at high temperature is larger than unity; Fe shows slight but significant preference for the M1 site ($K_d > 1.0$) with temperature, whereas K_d of olivine cooled slowly or equilibrated at low temperature is almost 1.0 or less. The rough estimation for natural olivine samples is; $K_d = 1.20 - 1.05$ for volcanic olivine and $K_d = 1.05 - 0.90$ for plutonic or metamorphic olivine (*e.g.* Aikawa *et al.*, 1985).

The distribution constant of cleavable olivines from Happon-O'ne ultrabasic rock mass ($K_d = 1.00 \pm 0.07$) suggests the metamorphic origin, indicating that cleavable olivines have experienced slow cooling history or the cationic distribution has been equilibrated at relatively low temperatures. This result is consistent with the petrologic and geologic evidences for Happon-O'ne ultrabasic rock mass. The value of K_d (1.00) for the cleavable olivine from Happon-O'ne probably represents the equilibration temperature less than 500°C, when referred to Aikawa *et al.* (1985). The value of K_d (0.80) of the cleavable olivine from Ōeyama may corresponds to the distribu-

tion constant of the lower temperature than that for Happo-O'ne. Uda's estimation of annealing temperature of cleavable olivine in the Ōeyama ultrabasic rock mass is 350–450°C. Therefore, the value of K_d for Ōeyama olivine may represent the effective equilibration temperature below 400°C, if the slow cooling history after the annealing due to metamorphism is taken into account.

In conclusion, cleavable olivine is not the one with specific anomaly in atomic structure, but the ordinary one with such cationic distribution that is equilibrated at very low temperatures, probably below 400°C. The difference of K_d values between cleavable olivines from two ultrabasic rock masses may reflect the difference of the cooling rate.

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