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β-Mg_2SiO_4: Single-crystal X-ray diffraction study

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Abstract

The crystal structure of β-Mg_2SiO_4 has been refined using a single crystal synthesized at 185 kbar and 2000°C, by means of X-ray diffraction data. Magnesium and silicon atoms are completely ordered on octahedral and tetrahedral sites, respectively. Octahedral distortions are smaller in MgO_6 octahedra and greater in the larger unoccupied octahedra, $\square O_6$. The density increase involved in the $\alpha \rightarrow \beta \rightarrow \gamma$ phase transformations is mainly attributed to the volume decrease of unoccupied octahedra. The distortions from regular octahedra and the octahedral volumes in the β-Mg_2SiO_4 structure are much smaller than those of α-Mg_2SiO_4 and the octahedral distortions and volumes of MO_6 and $\square O_6$ will be further decreased in association with the $\beta \rightarrow \gamma$ phase transformation to the minimum degree observed in β-Mg_2SiO_4.

Introduction

The presence of a complex intermediate phase in the high pressure transformation of olivine(α)$\rightarrow$spinel(γ) was first pointed out for compositions close to nearly iron-free $(Mg,Fe)_2SiO_4$ by Ringwood and Major (1966). This intermediate phase was confirmed to be a stable phase by Akimoto and Sato (1968) and Akimoto (1970) by analogy to new high-pressure polymorphs of Co_2SiO_4 and Mn_2GeO_4 which were subsequently designated as the "β-phase". A number of phase equilibrium studies of Mg_2SiO_4–Fe_2SiO_4 were subsequently initiated, because the phase transformations $\alpha \rightarrow \beta \rightarrow \gamma$ of this system are believed to directly involve the structure and constitution of the transition zone in the earth's mantle. For example, phase equilibria in the system MgO–FeO–SiO_2 and in pure Mg_2SiO_4 up to pressures around 200 kbar were reported by Akimoto (1972) and by Suito and Kawai (1979), respectively, and the post-spinel phases of Mg_2SiO_4 were studied by several investigators such as Kumazawa, Sawamoto, Ohtani and Masaki (1974), Liu (1976), Ito (1977) and others.

The crystal structure of the β-phase was determined by Morimoto, Akimoto, Koto and Tokonami (1969) for a single crystal of Mn_2GeO_4, and almost simultaneously by Moore and Smith (1970) for a powder specimen of $(Mg_{0.9}Ni_{0.1})_2SiO_4$ synthesized by Ringwood and Major (1969). Following the determination of the crystal structures of the aforementioned compounds, those of β–Co_2SiO_4 and $Ni_3Al_2SiO_8$ III(β-phase) were also studied in detail by Morimoto, Tokonami, Watanabe and Koto (1974), and Ma and Sahl (1975), respectively.

Precise studies on the crystal structures of β- and γ-phases of Mg_2SiO_4 have not been carried out because of technical difficulties in obtaining single crystals large enough for single-crystal investigations, although its prime importance has been widely recognized in the investigation of mantle substances.

In this work, the crystal structure of pure β-Mg_2SiO_4 was refined using single crystal X-ray diffraction data. The crystal structure is described in detail in comparison with the α-phase of Mg_2SiO_4.

Experimental

Single crystals of β-Mg_2SiO_4 were synthesized from powdered α-Mg_2SiO_4 crystals at 2000°C and 185 kbar by means of a multi-anvil-type high pressure and high temperature apparatus. The run-time

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was 60 minutes. The crystals obtained are around 100 μm in maximum size, colorless and transparent, and optically biaxial. The specimen studied in this experiment approximates a parallelopiped in shape and is 88 × 75 × 75 μm in size. X-ray photographs indicate systematic absence of reflections with $h+k+l = 2n+1$, and with $h = 2n+1$ for $hk0$, which is consistent with space group *Im2a* or *Imma*. Cell dimensions were determined by the least-squares method using 73 reflections (28 $K\alpha_1$; $\lambda = 0.70930$, 28 $K\alpha_2$; $\lambda = 0.71359$ and 17 $K\beta$; $\lambda = 0.63229$Å reflections) which were measured on a four-circle diffractometer. The crystal data are summarized in Table 1.

Table 1. Crystallographic data of β-Mg_2SiO_4

Space Group <u>Imma</u>

Lattice Constants (Å):

	Present Work	AMS	MS
a =	5.6983(4)	5.694(1)	5.6960(5)
b =	11.4380(7)	11.467(2)	11.444(2)
c =	8.2566(8)	8.248(2)	8.248(1)
V =	538.14 Å^3	538.54	537.65

Z = 8

$D_{calc} = 3.474$ gcm^{-3}

$\mu = 11.10$ cm^{-1}(MoKα)

References: AMS; Akimoto, Matsui and Syono(1976), powder data obtained from pure β-Mg_2SiO_4. MS; Moore and Smith(1970), powder data from β-$(Mg_{0.9}Ni_{0.1})_2SiO_4$.

MoKα radiation monochromatized by pyrolytic graphite was used for intensity measurement. The intensities of 2545 reflections including crystallographically equivalent reflections within the range $0° < 2\theta < 70°$ were obtained by the $2\theta-\theta$ scan technique on a four-circle (RIGAKU AFC-3) diffractometer. All the observed reflections were condensed to 675 unique reflections, of which 237 had high standard deviations ($3\sigma_{hkl}(Fo) > |Fo|$) or zero intensity, where $\sigma_{hkl}(Fo)$ is a standard deviation of each reflection obtained from counting statistics. Conventional polarization and Lorentz corrections were carried out in the process of the data collection. No absorption correction was applied because of the sufficiently small value of $\mu r(<0.05)$.

Refinement of the structure

The β-Mg_2SiO_4 structure refinement was initiated with the atomic coordinates of β-$(Mg_{0.9}Ni_{0.1})_2SiO_4$ reported by Moore and Smith (1970). The space group, *Imma*, was assumed for the structure and was confirmed by structure refinement. The scattering factor curves of Mg, Si and O used for calculations are those of neutral atoms (*International Tables for X-Ray Crystallography,* Vol. IV(1974)). The 438 reflections with $|Fo| > 3\sigma_{hkl}(Fo)$ were used in the structure refinement, applying the weight $1/\sigma_{hkl}^2(Fo)$ for each reflection.

Two modes of refinement were carried out in order to clarify the cation distributions on octahedral and tetrahedral sites. In the first mode, case (1), perfect ordering of cations was assumed (Mg and Si atoms on octahedral and tetrahedral sites, respectively) and only atomic coordinates and anisotropic temperature factors were refined. In the second mode, case (2), the starting distribution of 0.25Si + 0.75Mg and 0.50Si + 0.50Mg was assigned to octahedral and tetrahedral sites, respectively, and the occupancy factors together with coordinates and anisotropic temperature factors were refined.

The value of R, roughly 0.15 for the initial atomic parameters, was reduced to 0.028 for both cases after about 10 cycles of refinement. The final atomic parameters thus obtained are given in Table 2 for both cases together with the initial ones reported by Moore and Smith (1970).

The choice of atomic scattering factors, whether for neutral or charged atoms, does not affect the results because the value of the difference between them, particularly in the range of $\sin\theta/\lambda > 0.2$, is quite small and more than 97% of the reflections used for the structure analysis lie in the above range.

Table 3 show bond distances and angles calculated with the results of case (1). All computations for the least-squares refinement of lattice constants and structure parameters[1], interatomic distances and angles, and crystal structure diagrams, were carried out using the program LCLSQ(Burnham, 1962), RFINE(Finger, 1972), UMBADTEA(Finger, 1968) and ORTEP-II (Johnson, 1971) at the Crystallographic Research Center, Institute for Protein Research, Osaka University (ACOS-700).

Results and Discussion

General features of the β-phase structure

The crystal structure of the β-phase, as shown by β-Mn_2GeO_4(Morimoto *et al.,* 1969), is based on a slightly distorted cubic closest-packing of oxygen atoms. The a-axis of the β-phase is half the diagonal

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[1] To receive a copy of Tables for d(obs) and d(calc), and Fobs and Fcalc, order Document AM-81-159 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Table 2. The refined results of atomic coordinates and thermal parameters of β-Mg_2SiO_4 and the comparison with those reported by Moore and Smith (1970). Anisotropic temperature factors are in the form, $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)]$. Estimated standard errors are given in parentheses.

	Case (1)	Case (2) ·	Moore & Smith		Case (1)	Case (2)	Moore & Smith
Atom	Mg(1)	1.19Mg-0.19Si(0.97Mg)	0.9Mg+0.1Ni	Atom	O(1)	O(1)	O(1)
x	0	0	0	*x*	0	0	0
y	0	0	0	*y*	1/4	1/4	1/4
z	0	0	0	*y*	0.2166(6)	0.2166(6)	0.2202
β11	0.0025(13)	0.0012(12)		β11	0.0029(17)	0.0029(17)	
β22	0.0011(2)	0.0007(2)		β22	0.0007(4)	0.0007(3)	
β33	0.0017(4)	0.0011(4)		β33	0.0014(7)	0.0014(7)	
β12	0	0		β12	0	0	
β13	0	0		β13	0	0	
β23	0	0		β23	0	0	
Atom	Mg(2)	1.02Mg-0.02Si(1.00Mg)	0.9Mg+0.1Ni	Atom	O(2)	O(2)	O(2)
x	0	0	0	*x*	0	0	0
y	1/4	1/4	1/4	*y*	1/4	1/4	1/4
z	0.9701(4)	0.9702(3)	0.9771	*z*	0.7164(6)	0.7164(6)	0.7004
β11	0.0035(12)	0.0034(11)		β11	0.0034(15)	0.0034(17)	
β22	0.0008(2)	0.0008(2)		β22	0.0001(2)	0.0002(3)	
β33	0.0013(3)	0.0012(3)		β33	0.0013(5)	0.0014(7)	
β12	0	0		β12	0	0	
β13	0	0		β13	0	0	
β23	0	0		β23	0	0	
Atom	Mg(3)	1.03Mg-0.03Si(1.00Mg)	0.9Mg+0.1Ni	Atom	O(3)	O(3)	O(3)
x	1/4	1/4	1/4	*x*	0	0	0
y	0.1276(2)	0.1276(2)	0.1175	*y*	0.9900(3)	0.9900(3)	0.9853
z	1/4	1/4	1/4	*z*	0.2558(5)	0.2559(5)	0.2279
β11	0.0030(6)	0.0028(6)		β11	0.0033(15)	0.0034(15)	
β22	0.0008(1)	0.0008(1)		β22	0.0005(2)	0.0005(2)	
β33	0.0017(2)	0.0016(2)		β33	0.0011(5)	0.0011(5)	
β12	0	0		β12	0	0	
β13	-0.0003(2)	-0.0003(2)		β13	0	0	
β23	0	0		β23	-0.0001(3)	-0.0001(3)	
Atom	Si	-0.03Mg+1.03Si(1.00Si)	0.9Mg+0.1Ni	Atom	O(4)	O(4)	O(4)
x	0	0	0	*x*	0.2615(4)	0.2616(4)	0.2745
y	0.1198(2)	0.1198(1)	0.1232	*y*	0.1225(3)	0.1225(3)	0.1257
z	0.6168(2)	0.6168(2)	0.6184	*z*	0.9925(3)	0.9925(3)	0.9950
β11	0.0016(3)	0.0017(3)		β11	0.0026(7)	0.0028(7)	
β22	0.00040(7)	0.00045(7)		β22	0.0006(2)	0.0006(2)	
β33	0.0008(1)	0.0009(1)		β33	0.0013(3)	0.0013(3)	
β12	0	0		β12	-0.0001(7)	-0.0001(7)	
β13	0	0		β13	0.0002(4)	0.0002(4)	
β23	-0.0000(1)	-0.0000(1)		β23	0.0000(2)	0.0000(2)	

of the spinel unit cell, the *b*-axis is associated with the other diagonal, and the *c* axis is in common with the third axis of spinel. There are 64 tetrahedral and 32 octahedral sites per unit cell, and one-eighth of the tetrahedral and one-half of the octahedral sites are occupied by cations in the β-phase as well as in the γ-phase structures. There are four crystallographically non-equivalent cations in the structure, of which one (T atom) is tetrahedrally and the others (M atoms) are octahedrally coordinated by oxygen atoms. The TO_4 tetrahedron shares a vertex with a neighboring tetrahedron to form the T_2O_7 group. The $M(1)O_6$ octahedron shares edges with adjacent $M(2)O_6$ octahedra and together they form a single octahedral chain, –M(1)–M(2)–M(1)–M(2)–, which runs parallel to the *b*-axis. The M(3) octahedron shares an edge with the adjacent crystallographically equivalent M(3) octahedron to form a double chain running along the *a*-axis. The double chain of M(3) octahedra is crossed by –M(1)–M(2)– single chains, and octahedra of these two chains share vertices. The perspective view of the structure of β-Mg_2SiO_4 is illustrated in Figure 1, in which Mg and Si correspond to M and T atoms in the above explanation.

Cation distributions in β-Mg_2SiO_4

Although the occupancy factors for Mg atoms on the octahedral sites exceed unity, this is in accord with negative values for the factors for Si atoms as shown in Table 2. Therefore the distributions of Mg atoms on their sites, c_M's, may be numerically adjusted to 0.97Mg on M(1), 1.00Mg on M(2) and

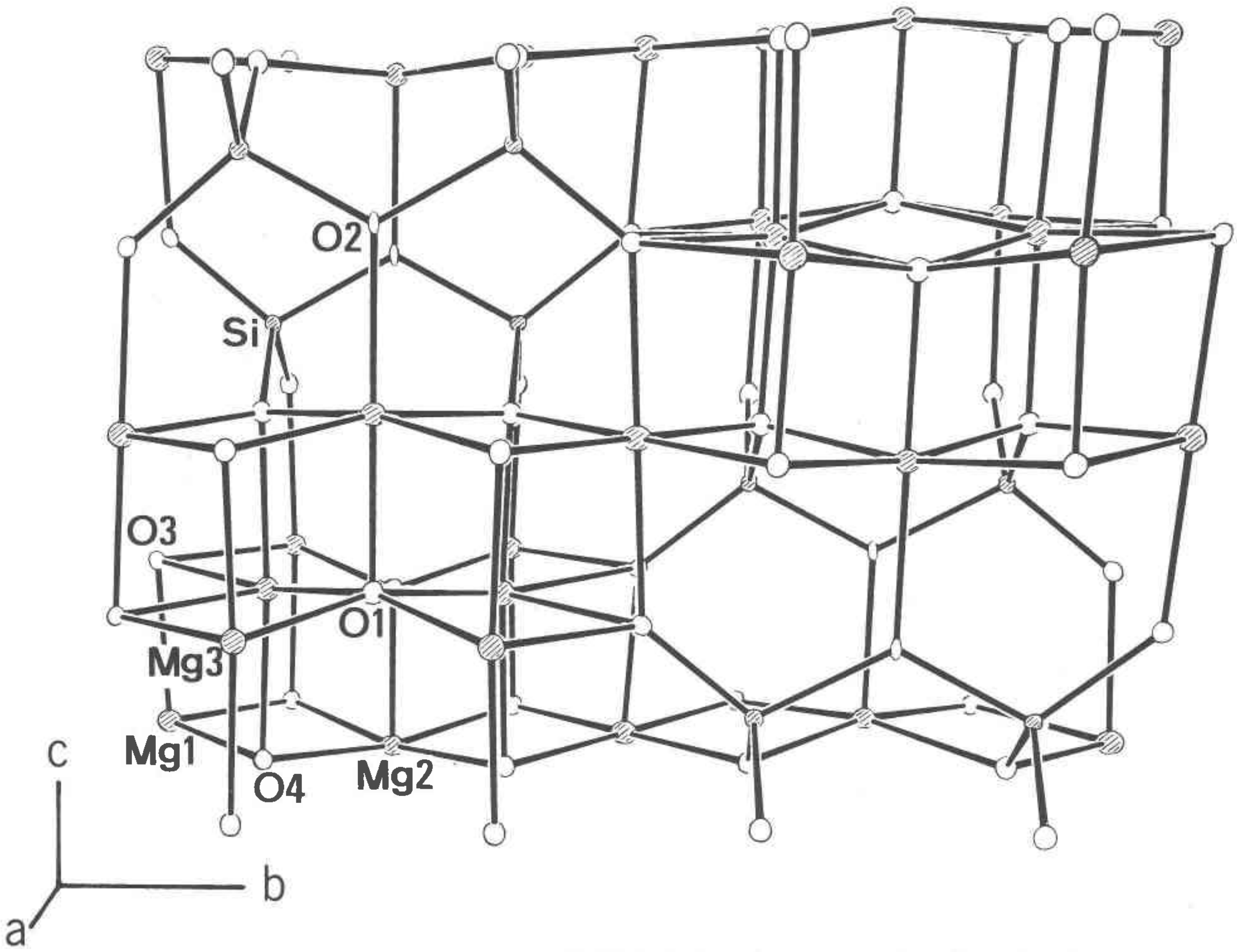

Fig. 1. A perspective view of the structure of β-Mg_2SiO_4 drawn by the ORTEP plot (Johnson, 1971).

1.00Mg on M(3) by introducing the relation $c_M = c_{Mg} + (14/12)c_{Si}$, where c_{Mg} and c_{Si} are the refined values of distribution of Mg and Si atoms on each site, and the numbers, 12 and 14, are the atomic numbers for Mg and Si. In the same manner, the distribution of the Si atom on the tetrahedral site numerically results in 1.00Si by introducing the relation $c_T = (12/14)c_{Mg} + c_{Si}$. Thus, the results of the refinement (case (2)) concerning the distribution of Mg and Si atoms, essentially demonstrated an ordered arrangement within the experimental error; that is, Mg and Si atoms are located on octahedral and tetrahedral sites, respectively. This conclusion is also supported by the fact that the refined atomic coordinates of the two cases (1) and (2) are completely consistent as shown in Table 2.

Interatomic distances

The increased density of Mg_2SiO_4 resulting from the $\alpha \rightarrow \beta$ phase transformation must be reflected in the change of the interatomic distances in the structure, since the oxygen coordination numbers around cations do not change before and after the phase transformation although the oxygen arrangement changes from hexagonal to cubic close-packing. Therefore, it is of interest to compare the interatomic distances of β-Mg_2SiO_4 with those of α-Mg_2SiO_4. The interatomic distances for α-Mg_2SiO_4 employed here for comparison were those determined at one atmosphere (Hazen, 1976) after the phase had been subjected to 50 kbar pressure.

The mean interatomic distances of the largest octahedron (Mg–O 2.090 and O–O 2.954Å) of three MgO_6 octahedra in β-Mg_2SiO_4 are comparable to those of the smaller one (mean Mg–O 2.091 and O–O 2.947Å) of two MgO_6 octahedra in α-Mg_2SiO_4. On the average, MgO_6 octahedra are roughly 1 percent compressed in β-Mg_2SiO_4 in comparison with those of α-Mg_2SiO_4. On the other hand, the SiO_4 tetrahedron is about 1.5 percent expanded in β-Mg_2SiO_4 in

Table 3. Bond lengths and angles of coordinated polyhedra, and O–O lengths of unoccupied $\square O_6$ octahedra

Bond Lengths(Å)			Bond Lengths(Å)			Bond Angles(°)
			Octahedron Mg(1)			
Mg(1)-O(4)	2.046(3)	[4]	O(4)-O(4)	2.805(6)	[2]	86.5(2)
-O(3)	2.115(4)	[2]	O(3)-O(4)	2.842(4)	[4]	86.1(1)
Mean	2.069		O(4)-O(4)	2.981(4)	[2]e	93.5(2)
			O(3)-O(4)	3.040(4)	[4]e	93.9(1)
			Octahedron Mg(2)			
Mg(2)-O(1)	2.035(6)		O(1)-O(4)	2.788(4)	[4]e	84.9(1)
-O(4)	2.093(3)	[4]	O(4)-O(4)	2.917(6)	[2]	88.3(2)
-O(2)	2.095(6)		O(4)-O(4)	2.981(4)	[2]e	90.8(2)
Mean	2.084		O(2)-O(4)	3.089(4)	[4]	95.1(1)
			Octahedron Mg(3)			
Mg(3)-O(1)	2.017(2)	[2]	O(1)-O(4)	2.787(4)	[2]e	84.3(2)
-O(3)	2.123(3)	[2]	O(3)-O(3)	2.851(1)		84.3(2)
-O(4)	2.129(2)	[2]	O(1)-O(1)	2.902(2)	e	92.0(1)
Mean	2.090		O(3)-O(4)	2.909(4)	[2]	86.4(1)
			O(1)-O(3)	2.992(3)	[2]e	92.5(2)
			O(3)-O(4)	3.040(4)	[2]e	91.3(1)
			O(1)-O(4)	3.121(5)	[2]	97.7(2)
			Tetrahedron Si			
Si -O(4)	1.631(2)	[2]	O(2)-O(4)	2.636(4)	[2]	104.5(2)
-O(3)	1.638(4)		O(3)-O(4)	2.706(4)	[2]	111.7(1)
-O(2)	1.702(3)		O(4)-O(4)	2.718(4)		112.8(2)
Mean	1.651		O(2)-O(3)	2.754(3)		111.1(2)
Octahedron □(1)			Octahedron □(2)			
O(3)-O(4)	2.706(4)	[4]	O(2)-O(4)	2.636(4)	[2]	
O(4)-O(4)	2.718(4)	[2]	O(3)-O(4)	2.706(4)	[2]	
O(4)-O(4)	2.805(6)	[2]	O(2)-O(3)	2.754(3)	[2]	
O(3)-O(4)	2.909(4)	[4]	O(3)-O(4)	2.842(4)	[2]	
			O(3)-O(3)	2.851(1)		
Octahedron □(3)			O(2)-O(2)	2.903(2)		
			O(2)-O(4)	3.089(4)	[2]	
O(2)-O(4)	2.636(4)	[4]				
O(4)-O(4)	2.718(4)	[2]				
O(4)-O(4)	2.917(6)	[2]				
O(1)-O(4)	3.121(5)	[4]				

Estimated standard errors are given in parentheses and refer to last decimal place.
e; Edge shared between two MO_6 octahedra.
Numbers in square brackets are multiplicity factors.
Mean values of O-O bond lengths are given in Table 4.

comparison with that of α-Mg_2SiO_4 (mean values are Si–O 1.651 and O–O 2.693Å for β-Mg_2SiO_4, and Si–O 1.628 and O–O 2.649Å for α-Mg_2SiO_4). The values of the Si–O(2) distance and Si–O(2)–Si angle which are affected by strong Si–Si repulsive force are 1.706Å and 122.2° (109.45° in an ideal closest packed structure), and they are comparable to those in β-Co_2SiO_4.

The calculated density increase for the α → β structural change of Mg_2SiO_4 is approximately 7 percent. Therefore, the compression of unoccupied octahedra $\square O_6$ must be responsible for the density increase of the phase change in Mg_2SiO_4. There are three crystallographically independent $\square O_6$ sites in the β-phase structure, and all of the mean values of O–O distances of $\square O_6$ are much smaller than those of the MgO_6 octahedra. There are two $\square O_6$ in the α-Mg_2SiO_4 structure and their mean values are larger than those of $\square O_6$ in β-Mg_2SiO_4 (see Table 4). For each polyhedron, the deviation of each cation–oxygen or oxygen–oxygen distance from the mean value is greater in α-Mg_2SiO_4 than in the β-Mg_2SiO_4 structure. The magnitude of the above deviation serves as a measure of the distortion from the ideal close-packed structure. The relationship between the sizes and distortions of MO_6 and $\square O_6$ octahedra in the α, β and γ-phase structures is discussed in detail in the next section.

Comparison between Mg_2SiO_4 and Co_2SiO_4

Co_2SiO_4 (Akimoto and Sato, 1968, Morimoto *et al.*, 1974) also shows the α → β → γ phase transformations. The increase and/or decrease of the polyhedral interatomic distances in Mg_2SiO_4, before and after the α → β phase transformation, bear close resemblance to those in Co_2SiO_4; *i.e.*, MO_6 octahedra are compressed and SiO_4 tetrahedron expanded in the β-phase in comparison with the α-phase.

Small structural differences between β-Mg_2SiO_4 and β-Co_2SiO_4 noted here are (1) the mean values of

Table 4. Mean values of O–O lengths and distortion factors, s_{oo}, of octahedra

		polyhedra for O-O and s_{oo}	Co_2SiO_4	Mg_2SiO_4
α-phase	O-O	$M(1)O_6$	2.993Å	2.947Å
		$M(2)O_6$	3.015	2.998
		$\square(1)O_6$	2.855	2.844
		$\square(2)O_6$	3.078	3.053
		SiO_4	2.648	2.649
	s_{oo}	$M(1)O_6$	88.7×10^{-4}	77.6×10^{-4}
		$M(2)O_6$	50.7	47.5
		$\square(1)O_6$	56.7	48.9
		$\square(2)O_6$	86.5	71.6
		SiO_4	13.2	16.6
β-phase	O-O	$M(1)O_6$	2.977Å	2.925Å
		$M(2)O_6$	2.988	2.942
		$M(3)O_6$	3.000	2.954
		$\square(1)O_6$	2.804	2.792
		$\square(2)O_6$	2.827	2.817
		$\square(3)O_6$	2.882	2.858
		SiO_4	2.688	2.693
	s_{oo}	$M(1)O_6$	18.2×10^{-4}	12.3×10^{-4}
		$M(2)O_6$	20.0	19.5
		$M(3)O_6$	15.2	15.3
		$\square(1)O_6$	19.0	11.2
		$\square(2)O_6$	37.8	29.3
		$\square(3)O_6$	70.4	57.9
		SiO_4	2.3	3.1
γ-phase	O-O	MO_6	2.973Å	-
		$\square O_6$	2.784	-
		SiO_4	2.688	-
	s_{oo}	MO_6	10.7×10^{-4}	-
		$\square O_6$	13.0	-
		SiO_4	0.0	-

References: α, β and γ-Co_2SiO_4; Morimoto et al.(1974)
α-Mg_2SiO_4; Hazen(1976)

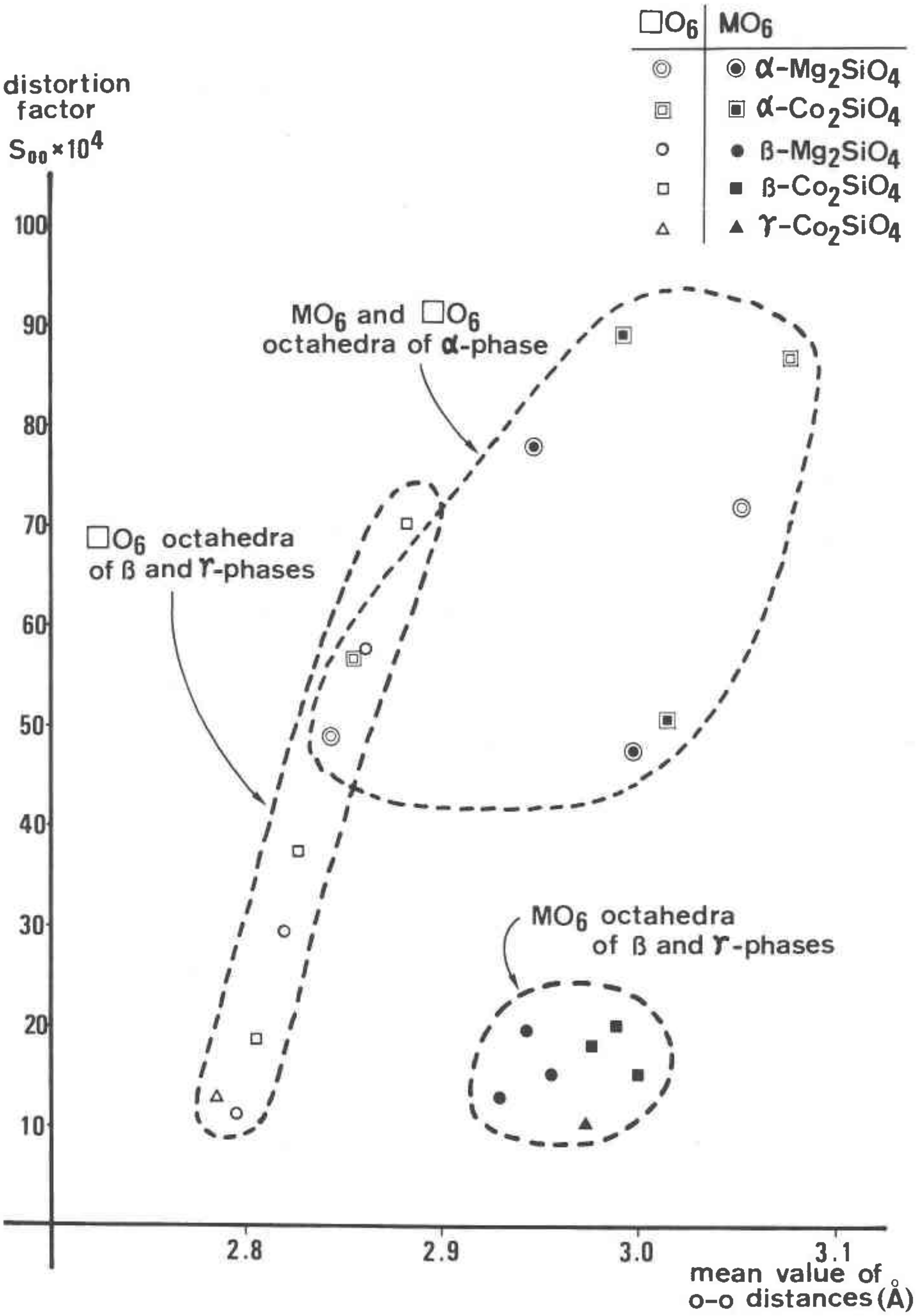

Fig. 2. The relationship between distortion and volume of octahedra MO_6 and $□O_6$ in α-, β-, γ-Co_2SiO_4 and α-, β-Mg_2SiO_4.

Si–O of SiO_4 tetrahedra are slightly larger in β-Mg_2SiO_4 which is stable at higher pressure than β-Co_2SiO_4, and (2) M–O distances of β-Mg_2SiO_4 are slightly smaller than those of β-Co_2SiO_4, in accord with the difference between the ionic radii of Mg^{2+} and Co^{2+}. As a result, the difference between O–O distances of SiO_4 tetrahedra and those of MO_6 octahedra is smaller in β-Mg_2SiO_4 than in β-Co_2SiO_4. This means that the distortion from the regular oxygen close-packing is less in β-Mg_2SiO_4 than in β-Co_2SiO_4.

Configurations of MO_6, $□O_6$ and SiO_4 polyhedra

The polyhedral configurations of oxygen atoms of the β-phases are distinctly different in MO_6 (octahedra occupied by Mg or Co) and $□O_6$ (octahedra unoccupied by cations). The degree of distortion from the regular polyhedron of oxygen atoms can be represented by the distortion factor defined by $s_{oo} = (\sigma/\bar{x})^2$ where σ^2 is the polyhedral O–O distance variance which is given by

$$\sigma^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1).$$

The x_i is the length of the i-th O–O edge of each polyhedron and is the mean value of *n* edge lengths. A greater value of s_{oo} implies a larger distortion of the polyhedron. The value of s_{oo} of each polyhedron is listed in Table 4, and it is plotted against the mean value of the O–O distance, $\bar{x}$ (Fig. 2).

The volume of the octahedron may be proportional to $\bar{x}^3$. In the β-phase, the MO_6 octahedra are greater in volume and less distorted than $\square O_6$ octahedra, and both their volumes and distortion factors are distributed within a narrow range. On the other hand, the distortion factor of the $\square O_6$ octahedron systematically varies depending on the octahedral volume. The larger octahedron shows the greater distortion, resulting in a wide distribution of distortion factors. In particular, the $\square O_6$ octahedra which involve O(2) (*i.e.,* the bridging oxygen of O_3–Si–O–Si–O_3) are more distorted than the others. However, the distortion factors of most of the octahedra in the β-phases are still smaller than those in the α-phase. Volumes and distortion factors of octahedra in the α-phase are arrayed to show expanded volumes and greater distortions without distinction between MO_6 and $\square O_6$ octahedra. On the other hand, those of the octahedra in the γ-gamma phase are comparable to the minimum values of volumes and distortion factors of octahedra in the β-phase.

The distortion of the SiO_4 tetrahedron becomes less in the higher-pressure phase in accordance with the volume expansion.

Conclusion

Mg and Si atoms are completely ordered in the β-Mg_2SiO_4 structure. Mg atoms occupy octahedral sites and Si the tetrahedral site. The degree of distortion of MO_6 octahedra in the β-phase is much less than in the α-phase, and the volumes are slightly compressed in the β-phase. On the other hand, the degree of distortion of $\square O_6$ octahedra, which are unoccupied by cations, systematically decreases in accordance with the decrease in O–O distance. The increase of density through the $\alpha \rightarrow \beta$ phase transformation is mainly attributed to the volume decrease of $\square O_6$ octahedra. The volumes of $\square O_6$ octahedra in the γ-phase will be smaller than those in the β-phase and will approach the minimum limit of $\square O_6$ volumes in the β-phase structure. Therefore, we conclude that the compression of unoccupied oxygen polyhedra plays an important role in the density increase of pressure-induced phase transformations without changes of coordination numbers. In particular, such a phenomenon takes place in association with the $\alpha \rightarrow \beta \rightarrow \gamma$ phase transformations in M_2SiO_4.

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