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An attempt to simulate high pressure structures of Mg-silicates by an energy minimization method

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Abstract

A computer program that refines unknown repulsive parameters of ions or structural parameters of a crystal by minimizing the potential energy has been applied to simulating the crystal structures of high pressure minerals. The program (WMIN, Busing, 1981) is written under the assumption of Born–Mayer type repulsive forces. The repulsive parameters, ionic radius A and ionic compressibility B for Mg^{2+}, Si^{4+}, and O^{2-} ions obtained from the structural data of α-Mg_2SiO_4 (forsterite), have been applied to simulating the crystal structures of β-Mg_2SiO_4, γ-Mg_2SiO_4, hypothetical Mg_2SiO_4 with Sr_2PbO_4 and $CaFe_2O_4$ structures, and $MgSiO_3$ with perovskite and ilmenite structures. The results were compared with the observed structures refined by the X-ray diffraction data. We also tried to predict the crystal structures of the minerals *in situ* at high pressure under the constraint that the cell dimensions are fixed at the observed values at high pressure. Our approach appears to be moderately successful in constructing the "frameworks" of relatively complex crystal structures of high pressure minerals.

Introduction

High pressure minerals give us information about the structure and evolution of the Earth's mantle. It is important to study high pressure phase transformations of these minerals on the basis of more detailed crystal structures. Many workers have carried out crystal structure analyses of these minerals under high pressure as well as 1 atm, and given their crystal chemical interpretations (e.g., Hazen, 1976; Hazen and Prewitt, 1977; Hazen and Finger, 1978, 1979; Akimoto et al., 1976; Finger et al., 1979; Levien and Prewitt, 1981). These approaches have the advantage of observing directly the crystal structure changes. However, we have often encountered difficulty in growing large enough single crystals for the structure refinements or in carrying out high pressure experiments. It is necessary to develop a method to predict the crystal structures semi-theoretically in order to supplement the experimental work.

The distance least-squares (DLS) method (Meier und Villiger, 1969) has been successful in simulating crystal structures from ionic radii data and other additional constraints. For example, the crystal structures of nine different polymorphs of Mg_2SiO_4 were simulated with the DLS method by Baur (1972), and Ito and Matsui (1978) predicted the perovskite-type structure of $MgSiO_3$. Thus, the crystal structures of high pressure minerals have been shown to be simulated from the ionic radii data alone.

Carrying this one step further, an attempt has been made to estimate the repulsive parameters of some ions in silicates from their crystal-structure data and to predict the crystal structures of mantle minerals (Miyamoto et al., 1979; Takeda et al., 1979; Miyamoto and Takeda, 1980) by making use of the WMIN program (Busing, 1981). The computer program WMIN was written by Busing (1970) to compute the "potential energy" of a crystal by assuming the Born–Mayer type repulsive energy as modified by Gilbert (1968) (Born and Huang, 1954; Tosi, 1964). This program enabled us to obtain repulsive parameters of ions from the structural parameters of a known structure, or to adjust the structural parameters of a hypothetical structure by employing the refined repulsive parameters thus obtained so that they give a minimum potential energy. We have already shown that the repulsive parameters defined as ionic compressibility and ionic radius can be determined from the structural parameters of a rela-

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tively complex crystal structure such as α-Mg_2SiO_4 (forsterite), and that a complex crystal structure can be predicted by energy minimization using the program WMIN (e.g., Miyamoto and Takeda, 1980; Takeda et al., 1979). In this simulation each ion in the crystal structure occupies the position where the calculated potential energy is minimum.

The repulsive parameters of Mg^{2+}, Si^{4+}, and O^{2-} and some transition metals (Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}) in their olivine structures and those of Ca^{2+} in diopside and Al^{3+} in spinel obtained with the WMIN program have been reported by Miyamoto and Takeda (1980) and Miyamoto et al. (1982).

In this paper, we report an attempt to simulate the crystal structures of high pressure minerals by the WMIN program on the basis of the repulsive parameters of Mg^{2+}, Si^{4+}, and O^{2-} ions obtained from the crystal structure data of α-Mg_2SiO_4 (forsterite). These predicted structures have been compared with those obtained by X-ray crystal structure analyses to examine the differences between the simulated and observed structures and the limit of the ionic model for the mineral structures. Then, the method was applied for prediction of the crystal structure at high pressure by employing the cell dimensions measured *in situ* at high pressure.

Estimation of repulsive parameters

The expression for the potential energy used in this study is

$$W = \frac{1}{2}\sum_i\sum_j\left[\frac{Q_iQ_j}{r_{ij}} + P_{ij}\cdot f_0\cdot(B_i + B_j)\cdot\exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right)\right], \quad (1)$$

where r_{ij} is the distance between the two ions; Q_i is ionic charge (Busing, 1970, 1981). The second term in square brackets represents the repulsive energy. A_i is an ionic radius and B_i is an ionic compressibility (softness parameter). A constant f_0 is a standard force arbitrarily chosen to have a numerical value of one and dimensions kcal/(mol · Å) (Busing, 1970). This expression for the repulsive term is discussed in more detail in Gilbert (1968), Busing (1970, 1981), and Ida (1976). P_{ij} is a Pauling coefficient (Pauling, 1960), which is expressed as,

$$P_{ij} = 1 + \frac{Q_i}{N_i} + \frac{Q_j}{N_j},$$

where N_i is the number of outer electrons contained in the ith ion. When the crystal is a stable phase, $\partial W/\partial X_j = 0$ for all structural parameters X_j's (i.e., X_j's are the cell dimensions and coordinates of ions) is expected. Therefore, we can determine the repulsive parameters by minimizing the following function D by the nonlinear least-squares method

$$D = \sum_j\left\{\frac{\partial W}{\partial X_j}\right\}^2 \quad (2)$$

The details of the procedure are described in Busing (1970, 1981) and Miyamoto and Takeda (1980). We assumed complete ionicity in this study, and thus the ionic charges for Mg, Si, and O are taken as +2, +4, and −2, respectively. We neglected the effect of the thermal and van der Waals energies to simplify the problems for the interpretation of the ionic structures of the minerals because these energies might cause additional sources of ambiguity at the present stage of development (Ida, 1976).

The repulsive parameters A and B for Mg^{2+}, Si^{4+}, and O^{2-} ions have been estimated by employing the structural parameters of α-Mg_2SiO_4 (forsterite) obtained from single-crystal X-ray diffraction data (Smyth and Hazen, 1973). We designate A for Mg and B for Mg as A_{Mg} and B_{Mg}, respectively, and so on. The reported repulsive parameters A and B of Mg, Si, and O ions (Miyamoto and Takeda, 1980) were initially obtained by fixing A_{Mg} and B_{Mg} at the values 0.97 and 0.065, respectively, which were obtained for $MgCl_2$ by Busing (1970) with the WMIN program, and by varying the remaining 4 parameters (A_{Si}, B_{Si}, A_O, and B_O) simultaneously to convergence (Table 1, solution N1).

Using solution N1 as initial values, all 6 repulsive parameters for Mg, Si, and O are varied simultaneously to converge on the basis of the structural data of α-Mg_2SiO_4. The weight matrix calculated from the standard errors of the observed structural parameters (Smyth and Hazen, 1973) is included for the nonlinear least-squares (Busing, 1981). The results for the repulsive parameters are listed in Table 1 for both cases when the Pauling coefficient P_{ij} is included (solution WP) and when P_{ij} is excluded (i.e., $P_{ij} = 1$; solution WN). The damping constant for the parameter change in the nonlinear least-squares method is 1.0 throughout our calculations.

Prediction of crystal structures of high pressure minerals

Once the repulsive parameters in equation (1) are estimated for all kinds of ions contained in the crystal, we can simulate the crystal structure so that potential energy W in equation (1) gives the minimum value by adjusting structural parameters X_j's. The method is described in more detail by Busing (1970, 1981).

Before attempting to simulate the structures of high pressure minerals, we have reconstructed the structure of α-Mg_2SiO_4 (forsterite) with the WMIN method by using the repulsive parameters obtained from the forsterite structure in the preceding section to check our procedures. Table 2a shows the atomic coordinates of the reconstructed structures of α-Mg_2SiO_4 compared with those obtained from the single-crystal X-ray diffraction data (Smyth and Hazen, 1973). The reconstructed structures are calculated for solutions, WN, WP,and N1.

Table 1. Repulsive parameters of Mg^{2+}, Si^{4+}, and O^{2-} for solutions N1, WN, and WP

		N1	WN⁺	WP⁺
Mg^{2+}	A_i	0.97*	0.788	0.749
	B_i	0.065*	0.0218	0.0284
Si^{4+}	A_i	0.608	0.528	0.382
	B_i	0.0172	0.0149	0.0065
O^{2-}	A_i	1.770	1.789	1.848
	B_i	0.105	0.104	0.102
		Without P_{ij}		With P_{ij}

f_0= 1 kcal/(mol·Å)
A_i: Ionic radius (Å); B_i: Ionic compressibility (Å)
\+ Weighted; * Fixed, Busing (1970)
P_{ij}:Pauling coefficient

There are no significant differences in the atomic coordinates between the reconstructed structures by using WN and that by WP. The average value of deviations of the atomic coordinates by N1 from the observed ones is the largest among the three reconstructed structures. Also, the maximum value of the deviations of bond lengths by N1 from the observed values is the largest among the three reconstructed structures. However, the mean value of bond lengths in coordination polyhedra in the N1 structure agrees best with the observed one among the three reconstructed structures (Table 2b).

Table 2a. Calculated positional parameters (× 10^4) of α-Mg_2SiO_4 and comparison with the observed ones

		WN	WP	N1	N1*	Obs.**	120kb⁺
M2	x	9826[-89]	9827[-88]	9814[-101]	9782[-133]	9915(2)	9784
	y	2766[- 8]	2765[- 9]	2800[26]	2819[45]	2774(1)	2754
Si	x	4265[3]	4265[3]	4344[82]	4325[63]	4262(1)	4294
	y	0954[14]	0953[13]	0974[34]	0970[30]	0940(1)	0993
01	x	7602[-55]	7607[-50]	7717[60]	7728[71]	7657(3)	7743
	y	0880[-33]	0879[-34]	0863[- 50]	0868[- 45]	0913(2)	0874
02	x	2143[-72]	2137[-78]	2121[- 94]	2127[- 88]	2215(4)	2134
	y	4485[11]	4486[12]	4492[18]	4492[18]	4474(2)	4444
03	x	2851[74]	2855[78]	2880[103]	2883[106]	2777(2)	2743
	y	1618[-10]	1620[- 8]	1635[7]	1622[- 6]	1628(1)	1652
	z	0332[1]	0332[1]	0278[- 53]	0286[- 45]	0331(2)	0244
Average of deviations (|calc. - obs.|/n)							
		0034	0034	0057	0059		
Cell dimensions (Å)							
	a	4.777[21]	4.776[20]	4.799[43]	4.756*	4.756	4.652⁺
	b	10.199[-8]	10.199[-8]	10.141[-66]	10.207*	10.207	9.781⁺
	c	5.986[6]	5.987[7]	5.911[-69]	5.980*	5.980	5.795⁺
Cell volume ($Å^3$)							
		291.6[13]	291.6[13]	287.7[-26]		290.3	263.7

M1 (0,0,0); M2, Si, 01, 02 with z=1/4; Space group: Pbnm
* Cell dimensions are fixed at observed values.
** Observed value, Smyth and Hazen (1973); ( ): Standard error
\+ Cell dimensions are fixed at values calculated by Kumazawa and Anderson (1969); Repulsive parameters from N1
[ ]: Deviation from the observed value
Deviation and standard error refer to the last digit.

Table 2b. Comparison of bond lengths between calculated and observed structures of α-Mg_2SiO_4

	WN	N1	N1*	Obs.**	120kb(N1)⁺
Si-01	1.595[-20]	1.623[8]	1.622[7]	1.615	1.608
-03[x2]	1.612[-23]	1.634[- 1]	1.633[- 2]	1.635	1.626
-02	1.643[-10]	1.660[7]	1.659[6]	1.653	1.655
Mean	1.616[-19]	1.638[3]	1.637[2]	1.635	1.629{- 6}
02-03[x2]	2.534[-19]	2.539[- 14]	2.545[- 8]	2.553	2.526
03-03	2.595[1]	2.627[33]	2.648[54]	2.594	2.614
01-02	2.676[-67]	2.707[36]	2.702[- 41]	2.743	2.665
01-03[x2]	2.720[-37]	2.780[23]	2.767[10]	2.757	2.775
Mean	2.630[-30]	2.662[2]	2.662[2]	2.660	2.647{- 13}
		Octahedron M1			
M1-01[x2]	2.087[2]	2.037[- 48]	2.046[- 39]	2.085	1.983
-02[x2]	2.093[25]	2.088[20]	2.091[23]	2.068	2.043
-03[x2]	2.149[17]	2.165[33]	2.156[24]	2.132	2.064
Mean	2.110[15]	2.097[2]	2.098[3]	2.095	2.030{- 65}
02-03[x2]s	2.534[-19]	2.539[- 14]	2.545[- 8]	2.553	2.526
01-02[x2]s	2.886[39]	2.841[- 6]	2.821[- 26]	2.847	2.764
01-03[x2]s	2.922[68]	2.780[- 74]	2.890[36]	2.854	2.775
01-02[x2]	3.024[1]	2.991[- 32]	3.026[3]	3.023	2.928
01-03[x2]	3.068[-36]	3.032[- 72]	3.052[- 52]	3.104	2.947
02-03[x2]	3.402[66]	3.412[76]	3.400[64]	3.336	3.238
Mean	2.973[20]	2.933[- 20]	2.956[3]	2.953	2.863{- 90}
		Octahedron M2			
M2-03[x2]	2.039[-28]	1.971[- 96]	1.979[- 88]	2.067	1.941
-02	2.073[22]	2.042[- 9]	2.040[- 11]	2.051	1.981
-01	2.197[15]	2.207[25]	2.218[36]	2.182	2.069
-03[x2]	2.267[53]	2.299[85]	2.328[114]	2.214	2.183
Mean	2.147[14]	2.132[- 1]	2.145[12]	2.133	2.050{- 83}
03-03 s	2.595[1]	2.627[33]	2.648[54]	2.594	2.614
01-03[x2]s	2.922[68]	2.912[58]	2.890[36]	2.854	2.775
02-03[x2]	2.888[-42]	2.854[- 76]	2.854[- 76]	2.930	2.802
03-03[x2]	3.016[19]	2.991[- 6]	2.998[1]	2.997	2.871
01-03[x2]	3.066[38]	3.032[4]	3.057[29]	3.028	2.895
02-03[x2]	3.216[23]	3.202[9]	3.235[42]	3.193	3.040
03-03	3.391[5]	3.284[-102]	3.332[- 54]	3.386	3.181
Mean	3.017[18]	2.991[- 8]	3.004[5]	2.999	2.880{-119}

* Cell dimensions are fixed at observed values.
** Smyth and Hazen (1973)
\+ Cell dimensions are fixed at values calculated by Kumazawa and Anderson (1969)
s Shared
[ ]: Deviation from the observed value
{ }: Deviation from the observed value (at 1 atm)
Deviations refer to the last digit.

Table 3a shows the simulated structures (calculated structure or W-structure) for β-Mg_2SiO_4 (modified spinel structure) with WMIN using the repulsive parameters of Mg, Si, and O ions obtained from the α-Mg_2SiO_4 structure. In these refinements except for the N1* procedure, the cell dimensions have been varied simultaneously with the atomic coordinates. The W-structures are obtained for solutions of repulsive parameters, WN and N1, and are compared with the structure (X-structure) obtained from the single-crystal X-ray diffraction data (Horiuchi and Sawamoto, 1981). The initial values of atomic coordinates for β-Mg_2SiO_4 were taken from those for β-Co_2SiO_4 (Morimoto et al., 1974). Table 3b shows the comparison of bond lengths of coordination polyhedra between the W-structures and X-structure. Although the maximum deviation of bond lengths in the W-structure for N1 from those in X-structure is larger than that for WN, the mean bond-lengths of coordination polyhedra for N1 are closer to those of the X-structure than those for WN (Table 4). No significant difference was noted in the calculated structures and bond lengths between WN and WP. We will use repulsive parameter N1 for calculating W-structures hereafter, because the mean bond-lengths of coordination polyhedra agree best with those of the X-structure

Table 3a. Calculated positional parameters (× 10^4) of β-Mg_2SiO_4 and comparison with the observed ones

		WN	N1	N1*	Obs.**	120kb$^+$	180kb$^+$
Mg2	z	9841[140]	9906[205]	9912[211]	9701(4)	9910	9918
Mg3	y	1257[- 19]	1282[6]	1280[4]	1276(2)	1281	1281
Si	y	1220[22]	1207[9]	1206[8]	1198(2)	1200	1198
	z	6185[17]	6196[28]	6191[23]	6168(2)	6212	6218
01	z	2285[119]	2296[130]	2283[117]	2166(6)	2329	2353
02	z	7149[- 15]	7155[- 9]	7140[- 24]	7164(6)	7231	7270
03	y	9879[- 21]	9919[19]	9918[18]	9900(3)	9949	9959
	z	2586[28]	2573[15]	2579[21]	2558(5)	2544	2526
04	x	2651[36]	2602[- 13]	2606[- 9]	2615(4)	2585	2576
	y	1229[4]	1228[3]	1226[1]	1225(3)	1232	1235
	z	9912[- 13]	9921[- 4]	9919[- 6]	9925(3)	9924	9933
Average of deviations (|calc. - obs.|/n)							
		0039	0040	0040			
Cell dimensions (Å)							
	a	5.728[30]	5.686[-12]	5.6983*	5.6983(4)	5.5684$^+$	5.5034$^+$
	b	11.484[46]	11.452[14]	11.4380*	11.4380(7)	11.0949$^+$	10.9233$^+$
	c	8.212[-45]	8.182[-75]	8.2566*	8.2566(8)	8.0882$^+$	8.0039$^+$
Cell volume (Å^3)							
		540.2[21]	532.8[-53]		538.14	499.70	481.16

Mg1 (0,0,0); Mg2, 01, 02 with x=0 and y=1/4; Si, 03 with x=0;
Mg3 with x=z=1/4; Space group: Imma
* Cell dimensions are fixed at observed values.
** Observed value, Horiuchi & Sawamoto (1981); ( ): Standard error
\+ Cell dimensions are fixed at values estimated from Mizukami et al. (1975); Repulsive parameters from N1
[ ]: Deviation from the observed value
Deviation and standard error refer to the last digit.

among the three solutions of repulsive parameters. Table 5 shows the results of the W-structure refinements of γ-Mg_2SiO_4 (spinel structure) (Matsui et al., 1979).

Table 6 shows the data of the W-structure of a hypothetical structure which is isostructural with Sr_2PbO_4. This high pressure polymorph of Mg_2SiO_4 is proposed to be isomorphous with δ-Mn_2GeO_4 (Morimoto et al., 1972). The initial values of atomic coordinates for this W-structure were taken from those of δ-Mn_2GeO_4 (Morimoto et al., 1972). Table 6 also shows the data for another hypothetical structure isomorphous with $CaFe_2O_4$. The initial values of atomic coordinates were taken from Prof. Y. Matsui (pers. comm., 1980).

We tried to simulate the structures of high pressure phases of $MgSiO_3$ on the basis of the repulsive parameters of Mg, Si, and O ions obtained from the forsterite structure. Table 7 shows the data of the W-structure of $MgSiO_3$-ilmenite. The results are compared with those obtained by the single-crystal X-ray diffraction method (Horiuchi et al., 1982). As initial values for $MgSiO_3$-ilmenite ideal atomic coordinates of $FeTiO_3$ were employed. Table 8 shows the data of the W-structure of $MgSiO_3$-perovskite compared with those obtained from the X-ray powder diffraction data (Ito and Matsui, 1978; Matsui, 1982). The initial values of atomic coordinates for $MgSiO_3$-perovskite were the same as those obtained by Ito and Matsui (1978).

Table 3b. Comparison of bond lengths between calculated and observed structures of β-Mg_2SiO_4

	N1	N1*	Obs.**	120kb(N1)$^+$	180kb(N1)$^+$
Si -04[x2]	1.642[11]	1.643[12]	1.631(2)	1.629	1.621
-03	1.637[- 1]	1.638[0]	1.638(4)	1.624	1.615
-02	1.676[- 26]	1.675[- 27]	1.702(3)	1.661	1.653
Mean	1.649[- 2]	1.650[- 1]	1.651	1.636{- 15}	1.628{- 23}
02 -04[x2]	2.620[- 16]	2.622[- 14]	2.636(4)	2.612	2.607
03 -04[x2]	2.697[- 9]	2.703[- 3]	2.706(4)	2.689	2.681
04 -04	2.727[9]	2.728[10]	2.718(4)	2.690	2.668
02 -03	2.779[25]	2.775[21]	2.754(3)	2.723	2.691
Mean	2.690[- 3]	2.692[- 1]	2.693	2.669{- 24}	2.656{- 37}
		Octahedron	Mg1		
Mg1-04[x4]	2.042[- 4]	2.044[- 2]	2.046(3)	1.986	1.958
-03[x2]	2.108[- 7]	2.131[16]	2.115(4)	2.058	2.023
Mean	2.064[- 5]	2.073[4]	2.069	2.010{- 59}	1.980{- 89}
04 -04[x2]	2.816[11]	2.808[3]	2.805(6)	2.737	2.700
03 -04[x4]	2.843[1]	2.859[17]	2.842(4)	2.788	2.754
04 -04[x2]e	2.959[- 22]	2.970[- 11]	2.981(4)	2.878	2.836
03 -04[x4]e	3.024[- 16]	3.045[5]	3.040(4)	2.931	2.874
Mean	2.918[- 7]	2.931[6]	2.925	2.842{- 83}	2.799{-126}
		Octahedron	Mg2		
Mg2-01	1.955[- 80]	1.958[- 77]	2.035(6)	1.956	1.949
-04[x4]	2.076[- 17]	2.081[- 12]	2.093(3)	2.012	1.980
-02	2.251[156]	2.289[194]	2.095(6)	2.167	2.119
Mean	2.085[1]	2.095[11]	2.084	2.029{- 55}	1.998{- 86}
01 -04[x4]e	2.844[56]	2.853[65]	2.788(4)	2.799	2.770
04 -04[x2]	2.913[- 4]	2.914[- 3]	2.917(6)	2.813	2.764
04 -04[x2]e	2.959[- 22]	2.970[- 11]	2.981(4)	2.878	2.836
02 -04[x4]	3.071[- 18]	3.097[8]	3.089(4)	2.965	2.909
Mean	2.950[8]	2.964[22]	2.942	2.870{- 72}	2.826{-116}
		Octahedron	Mg3		
Mg3-01[x2]	1.999[- 18]	2.002[- 15]	2.017(2)	1.946	1.919
-03[x2]	2.112[- 11]	2.112[- 11]	2.123(3)	2.030	1.994
-04[x2]	2.112[- 17]	2.133[4]	2.129(2)	2.085	2.056
Mean	2.074[- 16]	2.082[- 8]	2.090	2.020{- 70}	1.990{-100}
01 -04[x2]e	2.844[56]	2.853[65]	2.788(4)	2.799	2.770
03 -03	2.846[- 5]	2.852[1]	2.851(1)	2.785	2.752
01 -01 e	2.863[- 39]	2.872[- 30]	2.902(2)	2.798	2.762
03 -04[x2]	2.883[- 26]	2.893[- 16]	2.909(4)	2.834	2.803
01 -03[x2]e	2.965[- 27]	2.964[- 28]	2.992(3)	2.836	2.779
03 -04[x2]e	3.024[- 16]	3.045[5]	3.040(4)	2.931	2.874
01 -04[x2]	3.028[- 93]	3.053[- 68]	3.121(5)	2.954	2.900
Mean	2.933[- 21]	2.945[- 9]	2.954	2.858{- 96}	2.814{-140}

* Cell dimensions are fixed at observed values.
\+ Cell dimensions are fixed at values estimated from Mizukami et al. (1975); { }: Deviation from the observed value (at 1 atm)
** Horiuchi & Sawamoto (1981); ( ): Standard error
[ ]: Deviation from the observed value; e: Edge shared
Deviation and standard error refer to the last digit.

In order to examine the crystal structure change with pressure, we tried to simulate the structures at high pressure. Because the cell dimensions are easier to measure *in situ* at high pressure than the single-crystal X-ray diffraction intensities, the compressibility of cell dimen-

Table 4. Maximum values of deviations between calculated and observed structures

	α-Mg_2SiO_4		β-Mg_2SiO_4	
	WN	N1	WN	N1
Fractional coordinate	0.0089	0.0103	0.0140	0.0205
Cell dimensions (Å)	0.021 (0.44)	0.069 (1.2)	0.046 (0.40)	0.075 (0.91)
Bond length of polyhedron (Å)				
Si-0	0.023 (1.4)	0.008 (0.50)	0.032 (1.9)	0.026 (1.5)
Mg-0	0.053 (2.4)	0.096 (4.6)	0.116* (5.5)	0.156* (7.4)
0 -0	0.068 (2.4)	0.102 (3.0)	0.082 (2.6)	0.093 (3.0)
Mean	0.030 (1.1)	0.020 (0.68)	0.039 (1.3)	0.021 (0.71)

* Mg2-02
( ): The ratio in percent to the corresponding observed value

Table 5. Calculated crystal data and bond lengths for γ-Mg_2SiO_4 and comparison with their observed values

	N1	N1*	Obs.**	180kb(N1)+	240kb(N1)+
u	0.3687[2]	0.3685[0]	0.3685(6)	0.3705	0.3711
a (Å)	8.042[-23]	8.0649*	8.0649(1)	7.8396+	7.7645+
V (Å^3)	520.1[45]	524.56	524.56	481.82	468.10
Bond length (Å)					
Si-O[x2]	1.653[- 2]	1.655[0]	1.655(4)	1.636{- 19}	1.628{- 27}
O -O[x6]	2.700[- 3]	2.703[0]	2.703	2.671{- 32}	2.659{- 44}
Mg-O[x6]	2.063[- 7]	2.070[0]	2.070(4)	1.996{- 74}	1.972{- 98}
O -O[x6]s	2.845[- 8]	2.853[0]	2.853	2.773{- 80}	2.746{-107}
O -O[x6]	2.987[-13]	3.000[0]	3.000	2.872{-128}	2.832{-168}

Space group: Fd3m
* Cell dimensions are fixed at observed values.
Previously reported by Miyamoto and Takeda (1980)
\+ Cell dimensions are fixed at values estimated from Mizukami et al. (1975); { }: Deviation from the observed value (at 1 atm)
** Observed value, Sasaki et al.(1982); ( ): Standard error
[ ]: Deviation from the observed value; s: Shared
Deviation and standard error refer to the last digit.

sions is often available. We predicted the crystal structures *in situ* at high pressure by the WMIN method under the constraint that the cell dimensions are fixed at the observed values at high pressure. The estimated fractional coordinates and bond lengths are shown in Tables 2, 3, 5, 7, and 8. The cell dimensions of α-Mg_2SiO_4 at high pressure were calculated from the elastic constants obtained by Kumazawa and Anderson (1969). The cell dimensions of β- and γ-Mg_2SiO_4 at high pressure were estimated by extrapolating the values obtained *in situ* at about 90 kbar by Mizukami et al. (1975). By a similar extrapolation of the values after Yagi et al. (1982), the cell dimensions of $MgSiO_3$-perovskite were estimated. The cell dimensions of $MgSiO_3$-ilmenite were estimated by extrapolating the values obtained for $ZnSiO_3$-ilmenite *in situ* at high pressure by Sato et al. (1977).

Table 6. Calculated crystal data of two hypothetical polymorphs of Mg_2SiO_4

	Sr$_2$PbO$_4$-type		
	x	y	z
Mg	0.0225 (0.0819)	0.2978 (0.3329)	1/2
O1	0.2061 (0.2164)	0.0756 (0.0448)	1/2
O2	0.2990 (0.3925)	0.3384 (0.3087)	0
Cell dimensions (Å)	a	b	c
	4.862 (4.98)	9.241 (8.85)	2.806 (2.75)
Cell volume (Å^3)	126.1 (121.2)		
Space group	Pbam, z=2; Si at (0,0,0)		
	CaFe$_2$O$_4$-type		
	x	y	z
Mg(VIII)	0.5709	0.7619	3/4
Mg(VI)	0.4274	0.5757	1/4
Si	0.8379	0.5931	1/4
O1	0.4127	0.7506	3/4
O2	0.1045	0.5805	3/4
O3	0.2188	0.3966	1/4
O4	0.4304	0.4107	3/4
Cell dimensions (Å)	a	b	c
	13.785	8.196	2.894
Cell volume (Å^3)	327.0		
Space group	Pbnm, z=4		

By using repulsive parameter N1
( ): DLS method by Baur (1972)

Table 7. Calculated crystal data and bond lengths for $MgSiO_3$-ilmenite and comparison with observed values

		N1	N1*	Obs.**	180kb(N1)+	240kb(N1)+
Mg	z	3555[- 42]	3547[- 50]	3597(1)	3534	3531
Si	z	1460[-117]	1495[- 82]	1577(1)	1523	1530
O	x	3331[117]	3305[91]	3214(5)	3279	3274
	y	0313[- 48]	0286[- 75]	0361(4)	0246	0234
	z	2413[5]	2415[7]	2408(1)	2428	2433
Average of deviations (|calc. - obs.|/n)						
		0066	0061			
Cell dimensions (Å)						
	a	4.797[69]	4.7284*	4.7284(4)	4.6382+	4.6081+
	b	4.797[69]	4.7284*	4.7284(4)	4.6382+	4.6081+
	c	13.735[186]	13.5591*	13.5591(16)	13.0441+	12.8725+
	V	273.7[112]		262.54	240.02	236.72
Bond length (Å)			SiO$_6$ octahedron			
Si-O[x3]		2.012[182]	1.950[120]	1.830(2)	1.883	1.864
-O[x3]		1.700[- 68]	1.710[- 58]	1.768(2)	1.708	1.705
Mean		1.856[57]	1.830[31]	1.799	1.796{- 3}	1.785{- 14}
O -O[x3]e		2.427[96]	2.405[74]	2.331(4)	2.370	2.359
-O[x3]f		2.647[150]	2.598[101]	2.497(4)	2.541	2.525
-O[x3]		2.650[- 3]	2.634[- 19]	2.653(3)	2.597	2.576
-O[x3]		2.696[14]	2.658[- 24]	2.682(3)	2.609	2.598
Mean		2.605[64]	2.574[33]	2.541	2.529{- 12}	2.515{- 26}
			MgO$_6$ octahedron			
Mg-O[x3]		2.190[27]	2.146[- 17]	2.163(2)	2.058	2.031
-O[x3]		1.995[5]	1.966[- 24]	1.990(2)	1.909	1.888
Mean		2.093[16]	2.056[- 21]	2.077	1.984{- 93}	1.960{-117}
O -O[x3]f		2.647[150]	2.598[101]	2.497(4)	2.541	2.525
-O[x3]		2.954[13]	2.919[- 22]	2.941(3)	2.801	2.762
-O[x3]e		3.030[- 22]	2.976[- 76]	3.052(3)	2.883	2.836
-O[x3]		3.084[8]	3.026[- 50]	3.076(4)	2.898	2.871
Mean		2.929[37]	2.880[- 12]	2.892	2.781{-111}	2.749{-143}

Mg, Si with x=y=0; Space group: R$\bar{3}$; Positional parameter: x 10^4
* Cell dimensions are fixed at observed values.
\+ Cell dimensions are fixed at values estimated from Sato et al.(1977).
** Observed value, Horiuchi et al.(1982); e:Edge shared; f:Face shared
[ ]: Deviation from the observed value; ( ): Standard error
{ }: Deviation from the observed value (at 1 atm)
Deviation and standard error refer to the last digit.

Discussion

The main purpose of this paper is not to predict the "precise" crystal structures of high pressure minerals by the WMIN method. The precise structures should be determined by experimental studies (e.g., single-crystal X-ray diffraction). The purposes are: (1) to simulate the "framework" of the crystal structure of a relatively complex crystal by the WMIN method where each ion is located at the position which gives the minimum value of "potential energy" W in equation (1), (2) to find the mean deviations of the atomic coordinates thus obtained from those observed, (3) to reveal the limitations of this simple classical ionic model for the silicate minerals, and (4) to predict the structure *in situ* at high pressure, for cases in which the cell dimensions measured at high pressure are known.

Our WMIN studies appear to be successful in constructing the "framework" of the crystal structure, and show that each ion is located at the position which gives the minimum value of W in equation (1), even in a relatively complex crystal structure. As was shown in Miyamoto et al. (1982), repulsive parameter A is related to the traditional ionic radius (Shannon and Prewitt, 1969; Shannon, 1976).

Because the Si–O bond in silicate minerals is considered to show covalency (e.g., Matsui and Matsumoto, 1982), the fully ionized model used in this study may be unreasonable. Matsui and Matsumoto (1982) have proposed a model for olivine structures where the SiO_4 ion is treated as a rigid body by a similar potential energy calculation. The deviations of the bond lengths in the simulated structure from those in the observed structure are almost the same in our model and that of Matsui and Matsumoto (1982). Our model may be able to simulate the length of the Si–O bond regardless of the specific nature of the bond. The structures of $MgSiO_3$-ilmenite and $MgSiO_3$-perovskite, where the Si atom is octahedrally coordinated are simulated approximately on the basis of the repulsive parameters of Si obtained from the olivine structure, where the Si atom is tetrahedrally coordinated.

Table 8. Calculated crystal data and bond lengths for $MgSiO_3$-perovskite and comparison with observed values

		N1	N1*	Obs.**	240kb(N1)$^+$	300kb(N1)$^+$
Mg	x	5094[- 86]	5101[- 79]	5180(40)	5168	5186
	y	5253[-337]	5441[-149]	5590(30)	5599	5632
01	x	1053[123]	1087[157]	0930(40)	1178	1200
	y	4727[37]	4668[- 22]	4690(70)	4621	4612
02	x	1983[- 7]	1917[- 73]	1990(40)	1871	1860
	y	2021[11]	1968[- 42]	2010(40)	1935	1928
	z	5522[- 58]	5550[- 30]	5580(30)	5591	5600
Average of deviations (|calc. - obs.|/n)						
		0094	0079			
Cell dimensions (Å)						
	a	4.848[73]	4.7754*	4.7754(3)	4.6195$^+$	4.5806$^+$
	b	5.032[103]	4.9292*	4.9292(4)	4.8074$^+$	4.7769$^+$
	c	7.097[200]	6.8969*	6.8969(5)	6.7512$^+$	6.7148$^+$
	V	173.1[108]		162.35	149.93	146.93
Bond length (Å)				SiO_6 octahedron		
Si-01[x2]		1.851[64]	1.808[21]	1.787	1.783	1.776
-02[x2]		1.820[29]	1.803[12]	1.791	1.765	1.755
-02[x2]		1.819[20]	1.793[- 6]	1.799	1.754	1.744
Mean		1.830[38]	1.801[9]	1.792	1.767{- 25}	1.758{- 34}
02-01[x2]s		2.576[127]	2.535[86]	2.449	2.486	2.474
02-01[x2]s		2.581[29]	2.520[- 32]	2.552	2.475	2.463
02-02[x2]s		2.580[16]	2.559[- 5]	2.564	2.503	2.489
Mean		2.579[57]	2.538[16]	2.522	2.488{- 34}	2.475{- 47}
02-02[x2]		2.565[53]	2.527[15]	2.512	2.473	2.459
02-01[x2]		2.611[92]	2.572[53]	2.519	2.527	2.515
02-01[x2]		2.615[6]	2.573[- 36]	2.609	2.531	2.519
Mean		2.597[50]	2.557[10]	2.547	2.510{- 37}	2.498{- 49}
				MgO_8 square antiprism		
Mg-01		1.977[-100]	1.955[-122]	2.077	1.902	1.890
-01		2.319[230]	2.159[70]	2.089	2.031	2.004
-02[x2]		2.030[- 5]	1.993[- 42]	2.035	1.940	1.926
Mean		2.089[30]	2.025[- 34]	2.059	1.953{-106}	1.937{-122}
Mg-02[x2]		2.421[190]	2.338[107]	2.231	2.222	2.195
-02[x2]		2.531[66]	2.433[- 32]	2.465	2.378	2.365
Mean for 8		2.283[79]	2.205[1]	2.204	2.127{- 77}	2.108{- 96}
02-02[x2]		2.565[53]	2.527[15]	2.512	2.473	2.459
02-02		2.807[159]	2.691[43]	2.648	2.578	2.552
02-02		2.807[159]	2.691[43]	2.648	2.578	2.552
02-02[x2]		2.896[36]	2.774[- 86]	2.860	2.662	2.635
01-02[x2]		3.318[27]	3.196[- 95]	3.291	3.023	2.982
01-02[x2]		2.615[6]	2.573[- 36]	2.609	2.531	2.519

Si (1/2,0,1/2); Mg, 01 with z=1/4; Space group: Pbnm
* Cell dimensions are fixed at observed values.
\+ Cell dimensions are fixed at values estimated from Yagi et al.(1982)
** Observed value, Powder X-ray data, Matsui (1982); s: Shared
( ): Standard error; Positional parameter: x 10^4
Standard errors of bond lengths are estimated to be less than 0.05Å
[ ]: Deviation from the observed value
{ }: Deviation from the observed value (at 1 atm)
Deviation and standard error refer to the last digit.

The reasons why we use the expression of the repulsive parameters defined as in equation (1) are that (1) the repulsive parameters obtained in the WMIN program are directly applicable to the molecular dynamics (MD) calculations for the silicate structures (e.g., Matsui and Kawamura, 1980), and that (2) it may be possible to examine the change of the coordination number (of the Si atom from 4 to 6) in high pressure phase. This is because the repulsive parameters are defined as those proper to an individual ion. After we have examined in detail the limitations of the simple fully ionized model and of the formula of the repulsive force used in this study, further studies based on more precise models for minerals are required in the future.

There are some differences between the repulsive parameters which are calculated including the Pauling coefficient P_{ij} (WP) and those excluding P_{ij} (WN) (Table 1). The calculated coordinates from repulsive parameter WP are, however, almost identical with those from WN (Table 2).

The differences (maximum values) in α- and β-Mg_2SiO_4 between the W-structures (WN and N1) and the observed structures are summarized in Table 4. The deviation of bond-length Mg2–O2 in β-Mg_2SiO_4 for two W-structures in extraordinarily large, but the difference from the observed value is 5.5% (WN) or 7.4% (N1). Thus, the calculated structures may be reproducible within an error of about 5 percent. The maximum value of the deviations of atomic coordinates from the observed ones is about 0.02 for all W-structures (in Table 4).

The sequence of the bond-lengths in the coordination polyhedra is almost always reproduced in the W-structures (Table 2b and 3b). Only the four pairs: M1–O1 and M1–O2, M2–O3 and M2–O2, and O1–O3 and O2–O3 in α-Mg_2SiO_4, and Si-O4 and Si–O3 in β-Mg_2SiO_4, are in the reverse order in W-structures from the corresponding sequence in the observed structure.

Since Tokonami et al. (1972) have discussed the stability relations between the α, β, and γ polymorphs of Co_2SiO_4 on the basis of their refined crystal structures at 1 atm and experimental results of phase equilibria, we will not discuss the stability relations of the three polymorphs of Mg_2SiO_4 until the precise crystal structures *in situ* at high pressure have been obtained by single-crystal X-ray diffraction methods.

Table 9. The trend of shortening of interionic distances of Mg-silicates with pressure

	α-Mg_2SiO_4	β-Mg_2SiO_4	γ-Mg_2SiO_4	$MgSiO_3$ ilmenite	$MgSiO_3$ perovskite
Si-O**	0.031	0.082	0.082	0.10*	0.085*
Mg-O**	0.29	0.25	0.20	0.20	0.15^+

Values (1/Mb) are in the pressure range of approximate stability-field.
* Six-fold coordination; + Eight-fold coordination
** Mean

On the basis of the results of simulated structures by WMIN, Matsui (1982) has discussed the stability relation of a hypothetical Mg_2SiO_4 with the Sr_2PbO_4 structure under high pressure and has also shown that the W-structure of $MgSiO_3$-perovskite is consistent with his powder X-ray diffraction data. The cell volumes of the W-structures for $MgSiO_3$-ilmenite and -perovskite at 1 atm have a tendency to show larger values than for the observed ones.

The changes of bond lengths with increase of pressure are summarized as follows (e.g., Hazen and Prewitt, 1977): (1) In general, degrees of shortening of larger bonds are larger than those of shorter bonds. More specifically, (2) in Mg-silicates, the Mg–O polyhedron shrinks more than the Si–O polyhedron in a structure; (3) Unshared edges become shorter at a higher rate than shared edges; and (4) The shape of a polyhedron becomes regular, because unshared edges of cation polyhedra tend to approach the lengths of the shared edges. In some cases, the shortest shared edge remains almost constant (Takeda et al., 1979).

One of the notable exceptions to the above principle is the longest tetrahedral lateral edge (O1–O3) in the olivine structure (Table 2b). Although this is the largest among the tetrahedral O–O edges, this length does not shorten as do the others.

Although it is well understood that the transformation of Mg_2SiO_4 or $MgSiO_3$ from the α-phase to the γ-phase and to the ilmenite and perovskite structures achieves more densely packed structures, we view the change of the structures with pressure in terms of bond distances, which are the subjects of crystal-chemical interest. According to the general principles of structural change or bond distance variation with pressure, the rates of shortening of the Mg–O distances with high pressure become small from the α-phase to the perovskite-type structure but not for that of the ilmenite-type (Table 9). At each transition, the mean length of the Si–O tetrahedral bond shows a discontinous increase in going from a lower pressure phase to a higher pressure phase (Tables 2, 3, and 5). However, for each of the phases this bond length decreases at increasing pressure until the next transition. Furthermore, the rate at which the bond length decreases with pressure is significantly higher for the high pressure γ-phase compared to the low pressure α-phase (Table 9). Finally at lower mantle pressure, the rates of shortening of both the Mg–O and Si–O distances tend to approach each other (Table 9).

In conclusion, the WMIN methods enables us to simulate the "framework" of the crystal structures of minerals, and may give us some useful pieces of information about the crystal chemistry of high pressure minerals at high pressure, until the refinements of crystal structures *in situ* at high pressure are available. For example, this method may be useful in predicting the crystal structures of these minerals on the basis of the cell dimensions obtained from the powder diffraction data *in situ* at high pressure, because it is, at present, difficult to carry out single-crystal diffraction experiments *in situ* at pressures higher than 100 kbar. However, any detailed discussion of the crystal structure should be based on the results of the refinement *in situ* at high pressure by single-crystal X-ray structure analyses, since the ionic model for the crystal structure used in this study is a very simple one.

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