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Precision Estimates of Interatomic Distances using Site Occupancies, Ionization Potentials and Polarizability in *Pbnm* Silicate Olivines

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Abstract

All interatomic distances $[D(\text{calc.})_j]$ in *Pbnm* silicate olivines are linearly related with $M1$ and $M2$ site occupancy through a relationship of the type: $D(\text{calc.})_j = \Sigma_s \Sigma_i \omega_{ij_s} X_{i_s} + \xi_j$, where ω_{ij_s}, ξ_j are adjustable coefficients, and X_{i_s} are the fractions of ith ion in site s. The precision attained by this relation, based on seven divalent ions (Mg, Fe, Ca, Mn, Co, Ni, Zn), is satisfactory, the mean difference $|D(\text{calc.}) - D(\text{obs.})|$ always being less than 0·005 Å for each distance. Moreover, all ω_{ij_s} coefficients are related to properties of ions through a relation of the type: $\omega_{ij_s} = K1_{j_s}(\Sigma^Z_{m=1} I_m)_i^{-1/2} + K2_{j_s}\alpha_i^{f\,1/4} + K3_{j_s}$, where $\Sigma^Z_{m=1} I_m$ is the sum of the ionization potentials for the ith ion up to its valency state (Z), α_i^f is its polarizability, and $K1_{j_s}$, $K2_{j_s}$ and $K3_{j_s}$ are numerical constants. The existence of this strict dependency is predictable, based on the concept of effective nuclear charge and its relationship with polarizability and ionic potentials. As a consequence, all interatomic distances may be simulated through an equation of the type: $D(\text{calc.})_j = \Sigma_s\{W1_{j_s}\Sigma_i[X_{i_s}(\Sigma^Z_{m=1} I_m)_i^{-1/2}]\} + \Sigma_s[W2_{j_s}\Sigma_i(X_{i_s}\alpha_i^{f\,1/4})] + W3_j$, where $W1_{j_s}$, $W2_{j_s}$ and $W3_j$ are adjustable parameters which directly involve the ionization potentials and polarizabilities of the ions.

Introduction

Olivine is a very common and important rock-forming mineral. Its structure is characterized by hexagonal closest-packed arrays of oxygen anions in which half of the octahedral interstices are occupied by divalent cations in two non-equivalent sites, $M1$ and $M2$. The silicon cation occupies one-eighth of the tetrahedral interstices in natural olivines, while $M1$ and $M2$ are mainly Fe, Mg and subordinately

Mn, Ni, Ca, Co and Zn. Ni and Co show a definite site preference for the smaller $M1$ octahedron, while Ca and Mn prefer $M2$.

An understanding of olivine energetics is of fundamental importance for the geology of the earth's mantle. It has recently been shown that an accurate Born parametrization of lattice energy can lead to satisfactory results in the thermochemical investigation of silicate olivines (Ottonello, 1987). However, the accuracy of the procedure depends to a great extent on the precision attained in the simulation of the structure pertaining to a given state of intracrystalline disorder.

It has long been accepted that the concept of ionic radius is not sufficient alone to describe in adequate detail the interatomic distances observed in crystal structures, but needs to be associated with more or less empirical parameters whose significance remains partly obscure. Donnay (1969), Donnay & Allman (1970), Brown & Shannon (1973) and Brown & Wu (1976) proposed several empirical bond length–bond strength relationships. Clark, Appleman & Papike (1969) describe the interionic distances D_{ij} with a linear relation that explicitly disregards the crystal radius:

$$D_{ij} = a_{ij} + b_{ij}S + c_{ij}S^2 \qquad (1)$$

where a_{ij}, b_{ij} and c_{ij} are adjustable parameters, assuming distinct values for each i–j ion pair, and S is Pauling's bond strength (Pauling, 1929). The concept of bond strength is intimately related to the state of ionization through Pauling's electrostatic valence principle (Pauling, 1929), which states that the summation of the mean bond strength S in the coordination polyhedron approaches the valence of the ion in question. However, Baur (1970) has shown that the electrostatic valence principle has only approximate validity in silicates.

It will be shown here that all interatomic distances in the asymmetric units of *Pbnm* silicate olivines are correctly reproduced by linear proportionality rules involving atomic proportions on sites and multiplicative coefficients related to both ionic potential and polarizability of the intervening ions through the concept of 'effective nuclear charge'. It will also be shown that in this kind of structure, in which cations mix only in sixfold coordinated sites, a single set of individual ion polarizabilities is sufficient to characterize all the bond lengths (*cf.* Tosi, 1964; Mahan, 1980).

Database and mathematical treatment

Detailed structural information was available for 61 silicate olivines. Structural data on other components [see Ganguly (1977), Ito (1977), for example] are incomplete or too scanty to allow firm mathematical treatment. Most compositions refer to natural Mg–Fe compositions. Synthetic and natural compositions with high Ca, Co, Ni, Mn contents are included. The cation assignment to $M1$ and $M2$ sites generally rests on both the scattering power and the $M1$ and $M2$ bond distances. Doubts can arise about some of the proposed distributions, but they mainly concern cations present in small amounts. However, the information about these cations – excluding Zn – is supplied by end members, or terms in which they are present in relevant amounts. Our results seem to confirm a sufficient internal consistency for the database. A table giving the cation distributions of the compositions used has been deposited.*

Twenty-four independent interatomic distances were considered, plus Si—O, $M1$—O and $M2$—O mean distances, cell edges and cell volumes. Each distance (hereafter the term 'distance' will also include cell edges and volumes) was treated in the same manner. The treatment basically involved a minimization of the squared reduced residuals:

$$\Sigma\chi_{j,l} = \Sigma\{[D(\text{calc.})_{j,l} - D(\text{obs.})_{j,l}]/D(\text{obs.})_{j,l}\}^2 \quad (2)$$

where j refers to the distances in the asymmetric unit, l to the number of samples, $D(\text{obs.})$ are the experimentally observed distances and $D(\text{calc.})$ are the same distances calculated from site occupancy as follows:

$$D(\text{calc.})_j = \Sigma_s\Sigma_i\omega_{ij_s}X_{i_s} + \xi_j. \quad (3)$$

In (3) X_{i_s} is the atomic fraction of ith species on site s, ω_{ij_s} are adjustable parameters for each ion on each

* Lists of the compositions of the olivines examined and final ω_{ij_s}, ξ_j proportionality coefficients have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52461 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Comparison of cell-parameter simulation of 55 olivines*

Columns (1), (2), (3) show the frequencies within each calc. – obs. interval. (1) Calculated from Lumpkin & Ribbe (1983); (2) calculated from equation (3); (3) calculated from equation (12).

Calc. – obs. (Å × 10³)	a_0			b_0			c_0		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
0–2	17	29	28	9	15	13	2	22	22
2–4	21	13	8	8	7	3	4	10	10
4–6	7	7	7	5	9	4	2	6	9
6–8	5	4	3	2	12	2	2	10	3
8–10	2	2	3	3	4	5	3	2	1
10–15	2	—	3	7	5	6	15	3	5
15–20	1	—	2	4	3	6	10	1	4
20–30	—	—	1	8	—	5	9	—	·
30–40	—	—	—	5	—	6	6	—	—
40–50	—	—	—	1	—	4	2	1	1
>50	—	—	—	3	—	1	—	—	—

site, and ξ_j is the fitting constant for the jth distance. Since all specimens have the tetrahedron completely filled by silicon, this site was not explicitly taken into account, its contribution being included in the fitting constant ξ_j.

Minimization was performed on each distance separately by a computer routine inserted in the function minimization package *MINUIT* of James & Roos (1977). No constraint was imposed on the minimization parameters whose initial values were set to zero for each distance. A preliminary minimization was carried out on each interatomic distance, based on the whole data set. The analysis of the reduced residuals on each sample led to six compositions being discarded: they were apparently affected by large experimental error, the residuals of the cell edges being more than twice the mean value of the residuals of the remaining compositions.

It is noticeable that the cell volume can also be well reproduced by a linear relationship, as already found by Lumpkin & Ribbe (1983). This may be due to the small range of volume variation in our database, which is still satisfactory reproduced by a linear instead of a power relationship. A table containing the final ω_{ij}, ξ_j coefficients of (3) has been deposited.*

Results

The residuals on cell edges and cell volumes are definitely smaller than those obtained through previous generalizations (Lumpkin & Ribbe, 1983; Ottonello, 1987).

Table 1 compares the simulation of cell parameters for the 55 olivines. The results are very similar for all the interatomic distances in the asymmetric unit.

We must point out that the highest $|D(\text{obs.}) - D(\text{calc.})|$ differences are shown by synthetic fayalite, with a maximum value of 0·070 Å for the $M1$—O3A distance. This distance increases quite regularly in

* See deposition footnote.

Table 2. *Comparison between observed and calculated cell edges* (Å) *and atomic coordinates in six olivines*

(1) Observed values; (2) calculated from equation (3); (3) calculated from equation (12). Sample 45, $M1$:Ni 1·0, $M2$:Ni 1·0; sample 59, $M1$:Ca 1·0, $M2$:Ca 1·0; sample 54, $M1$:Mg 1·0, $M2$:Mg 1·0; sample 12, $M1$:Mg 0·028, Fe 0·908, Mn 0·064, $M2$:Mg 0·028, Fe 0·892, Mn 0·057, Ca 0·023; sample 7, $M1$:Mg 0·593, Fe 0·397, Mn 0·006, Ni 0·004, $M2$:Mg 0·610, Fe 0·377, Mn 0·005, Ca 0·008; sample 52, $M1$:Fe 1·0, $M2$:Fe 1·0.

		Sample 45			Sample 59			Sample 54		
		(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
a_0		4·731	4·730	4·766	5·078	5·078	5·084	4·756	4·758	4·758
b_0		10·123	10·122	10·286	11·225	11·224	11·294	10·207	10·206	10·212
c_0		5·914	5·914	5·953	6·760	6·760	6·774	5·980	5·988	5·988
T	x	0·4267	0·4267	0·4296	0·4283	0·4283	0·4281	0·4262	0·4263	0·4263
	y	0·0945	0·0945	0·0962	0·0959	0·0959	0·0963	0·0940	0·0941	0·0942
$M2$	x	0·9925	0·9924	0·9890	0·9904	0·9904	0·9983	0·9915	0·9899	0·9897
	y	0·2737	0·2736	0·2781	0·2809	0·2809	0·2827	0·2774	0·2774	0·2776
O1	x	0·7689	0·7689	0·7691	0·7498	0·7498	0·7493	0·7657	0·7657	0·7658
	y	0·0928	0·0928	0·0919	0·0926	0·0926	0·0927	0·0913	0·0917	0·0916
O2	x	0·2845	0·2845	0·2863	0·2981	0·2981	0·2987	0·2785	0·2784	0·2783
	y	−0·0549	−0·0550	−0·0499	−0·0392	−0·0393	−0·0382	−0·0526	−0·0530	−0·0528
O3	x	0·2742	0·2742	0·2841	0·2954	0·2955	0·2990	0·2778	0·2771	0·2773
	y	0·1630	0·1630	0·1649	0·1620	0·1620	0·1630	0·1628	0·1630	0·1630
	z	0·0331	0·0330	0·0330	0·0567	0·0568	0·0570	0·0331	0·0329	0·0329

		Sample 12			Sample 7			Sample 52		
		(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
a_0		4·826	4·827	4·824	4·786	4·785	4·784	4·818	4·823	4·821
b_0		10·508	10·512	10·473	10·327	10·327	10·314	10·470	10·498	10·456
c_0		6·100	6·099	6·105	6·031	6·030	6·032	6·086	6·084	6·093
T	x	0·4304	0·4307	0·4290	0·4280	0·4282	0·4275	0·4292	0·4314	0·4294
	y	0·0969	0·0967	0·0958	0·0955	0·0952	0·0949	0·0973	0·0972	0·0961
$M2$	x	0·9866	0·9872	0·9888	0·9875	0·9888	0·9894	0·9851	0·9872	0·9890
	y	0·2802	0·2799	0·2788	0·2785	0·2785	0·2780	0·2803	0·2800	0·2789
O1	x	0·7665	0·7673	0·7650	0·7659	0·7666	0·7656	0·7680	0·7685	0·7655
	y	0·0921	0·0916	0·0918	0·0920	0·0917	0·0918	0·0907	0·0918	0·0921
O2	x	0·2896	0·2899	0·2877	0·2834	0·2834	0·2823	0·2921	0·2909	0·2883
	y	−0·0462	−0·0460	−0·0479	−0·0500	−0·0501	−0·0508	−0·0449	−0·0457	−0·0478
O3	x	0·2879	0·2896	0·2863	0·2819	0·2824	0·2810	0·2890	0·2903	0·2866
	y	0·1649	0·1651	0·1640	0·1639	0·1640	0·1635	0·1650	0·1657	0·1644
	z	0·0372	0·0377	0·0379	0·0345	0·0348	0·0348	0·0403	0·0373	0·0375

Mg—Fe olivine with increasing iron content, from a minimum of 2·132 Å in synthetic forsterite to 2·232 Å for a natural sample with $Fe(M1) = 0·938$. A further increase of only $0·062 Fe(M1)$ leads to an increase of 0·09 Å in $M1$—$O3A$, which reaches 2·322 Å in synthetic fayalite. Similar inconsistencies between natural and synthetic compounds with high Fe^{2+} content occur in other minerals such as pyroxenes (work in progress). In any case, as a whole, the ω_{ij}, ξ_j coefficients allow all the distances within the investigated chemical range to be reproduced accurately. The DLS76 distance–least-squares program of Baerlocher, Hepp & Meyer (1977) can then be used for further refinement of cell parameters and fractional atomic coordinates, using only the interatomic distances of the asymmetric unit. DLS76 was run with the weighting scheme of Baur (1971, 1972). The agreement between observed and calculated parameters is quite satisfactory. Results for the whole procedure are shown in Table 2 for a few compositions, including synthetic fayalite, which gives the poorest results as previously outlined.

Discussion

The concept of crystal radius is associated with the radial extent of the ion along the line joining it to a nearest neighbour (Tosi, 1964). The experiment map of electron density [see, for olivine, Fujino, Sasaki, Takeuchi & Sadanaga (1981)] shows a minimum along this line, which can be linked with the concept of crystal radius.

The distance corresponding to the minimum density (r_{max}) can be expressed as:

$$r_{max} = \min 4\pi r^2 \rho(r) \qquad (4)$$

where $\rho(r)$ is the electron density at distance r. Equation (4) can be operatively expressed [for example, see Harvey & Porter (1976)] in the form:

$$r_{max} = C_1/Z_{eff} \qquad (5)$$

where C_1 is a constant and Z_{eff} is the effective nuclear charge:

$$Z_{eff} = Z_n S_n. \qquad (6)$$

Here Z_n is the atomic number and S_n a screen constant. In the hydrogen-like approximation, the energy levels of the various orbitals are given by an empirical equation (Harvey & Porter, 1976) in the form:

$$E = (Z_{eff}^2 C_2)/n^2 \qquad (7)$$

where C_2 is a constant. As the ionization potential I is (numerically) equivalent to E in (7), we have

$$r_{max} = [C_1/(C_2^{-1/2}n)]I^{-1/2}. \qquad (8)$$

Equation (8) gives the relation between the 'size' of the ion and the ionization potential. We emphasize that r_{max} [equation (4)], and hence C_1 [equation (5)], may take on different values in different directions of

an irregular coordination polyhedron, like $M1$ and $M2$ in olivine. Moreover, the effective nuclear charge is related to polarizability through the single one-level formula (Van Vleck, 1952; Tosi, 1964):

$$\alpha_i^f = 4n^4 d^3 Z_{\text{eff}}^{-4} \qquad (9)$$

where $d = 0\cdot529$ Å is the Bohr radius for the hydrogen ion. From (8), (9) and (5) we have:

$$r_{\text{max}} = [C_1/(1\cdot4142 n d^{3/4})]\alpha_i^{f 1/4}. \qquad (10)$$

Based on the above discussion, we would expect interionic distances to be related to both ionic potential and polarizability through (8) and (10). Indeed, the usefulness of the concept of 'effective nuclear charge' was largely confirmed by Pauling (1929, 1960). Wasastjerna (1923) based his standard crystal radii on the same concept and on (9). Morever, Ahrens (1952) has already observed a strict dependency between interionic distances in crystal structures and ionization potential. His tabulation of ionic radii is in fact largely based on the 'smooth regularities' observed in logarithmic plots of ionic radii *vs* ionic potential. One of these smooth regularities, shown by dashed lines in Fig. 1 of Ahrens (1952), has a trend that can be closely expressed by (8).*

The regression parameters ω_{ij_s} and ξ_{j_s}, obtained here by least-squares minimization of the experimental D_j distances, bear analogies with the fitting parameters in equation (1) of Clark *et al.* (1969). Moreover, based on the above discussion, we would expect ω_{ij_s} parameters to be directly related to both ionic potential and free-ion polarizability through the concept of effective nuclear charge. Obviously, this can only be expected in structures where all the ions enter only one kind of coordination polyhedron, and consequently, a single value of polarizability can be assigned to each individual ion. [Actually, adopting the empirical rule of Shanker, Kumar & Vermon (1973), and comparing actual ionic radii in $M1$ and $M2$ sites with Pauling's radii one could propose two distinct sets of crystal ion polarizabilities in $M1$ and $M2$; see Tosi (1964), Shanker *et al.* (1973), Mahan (1980) and Vieillard (1982)].

To verify this hypothesis we attempted general regressions in the form:

$$\omega_{ij_s} = K1_{j_s}\left(\sum_{m=1}^{z} I_m \right)_i^{-1/2} + K2_{j_s}\alpha_i^{f 1/4} + K3_{j_s} \qquad (11)$$

* In his regression, Ahrens (1952) used the simple ionization potential pertaining to the 'formal' charge (*i.e.* the second ionization potential for Fe^{2+}). However, as we will see later on, in our case it is more accurate to consider the sum of the ionization potentials up to the formal valence state, instead of the simple ionic potential of the last ionization step. In this way, the reduction in the distance between nucleus and electronic cloud which accompanies ionization is regarded as an additive effect for each ionization step.

Table 3. *Coefficients for equation* (11) *obtained by stepwise regression from BMDP* (*Dixon,* 1980)

R is the correlation coefficient.

	K1	K2	K3	R
O2A—O3A	1·4060	0·0720	1·8584 M1	0·936
M1—O1B	4·9132	0·1563	-0·7328 M1	0·986
M1—O2A	6·1811	0·2281	-0·1680 M1	0·991
M1—O3A	7·6123	0·2705	-0·3521 M1	0·986
Mean M1—O	6·2302	0·2204	-0·8553 M1	0·991
O1B—O2A	8·8115	0·3572	0·3179 M1	0·988
O1B—O3A	6·1686	0·1827	0·9582 M1	0·966
O1B—O3C	11·552	0·4195	0·0752 M1	0·993
O2A—O3C	16·151	0·5740	-0·6596 M1	0·905
O1B—O2B	6·9951	0·1934	1·0069 M1	0·991
M2—O1A	8·4392	0·3092	-1·4253 M2	0·982
M2—O2C	7·3525	0·2576	-0·7356 M2	0·968
M2—O3D	5·6366	0·1738	-0·7300 M2	0·967
M2—O3E	6·4770	0·1854	-1·0222 M2	0·987
Mean M2—O	6·6693	0·2149	-1·0299 M2	0·994
O1A—O3E	16·395	0·5200	-3·6118 M2	0·998
O3D—O3F	11·072	0·3221	-1·7030 M2	0·999
O3E—O3F	10·732	0·3251	-2·3447 M2	0·990
O2C—O3D	11·591	0·4004	-2·4462 M2	0·981
O2C—O3E	6·3085	0·2119	-1·4248 M2	0·964
a_0	7·3633	0·2328	2·1574 M1	0·986
a_0	1·7883	0·0634	0·1920 M2	0·957
b_0	25·462	0·7845	-0·7220 M2	0·994
c_0	11·430	0·2874	1·3087 M1	0·991
c_0	11·322	0·3398	-0·8387 M2	0·997
V	1255·84	38·3462	-3·7834 M1	0·992
V	1466·70	44·3668	-449·44 M2	0·995

where $(\sum_{m=1}^{z} I_m)$ is the sum of the ionization potentials for the ith ion up to its valency state (Z).

For each distance (11) arranges all the ω_{ij_s} coefficients of the various ions, taking account of the polyhedron ($M1$ or $M2$) to which that distance belongs as well as the polarizabilities and ionization potentials, on a common plane defined by appropriate $K1_{j_s}$, $K2_{j_s}$, $K3_{j_s}$ coefficients (Table 3). Only for a_0, c_0 and V does a high correlation exist with the ω_{ij_s} coefficients of both $M1$ and $M2$ sites.

Calculations performed with the *BMDP* package (Dixon, 1980) lead to correlation factors higher than 0·98 for 16 out of 31 distances, as shown in Table 3. We can thus confidently assign a firm statistical meaning to the envisaged relationship. The planes of the set described by (11) are almost parallel to each other, the angles among them very often being less than 6° (with a few exceptions for those angles with low correlation factors, which may reach values up to 20° with respect to the general set). The possible implications of this feature are presently under investigation.

Equation (11) reproduces the ω_{ij_s} coefficients of six out of seven ions considered with sufficient accuracy. The ω_{ij_s} coefficients of zinc relative to both $M1$ and $M2$ are poorly reproduced, because their values obtained through (3) are very inaccurate, owing to scarcity of information on zinc in our database.

Equation (3) shows that all interatomic distances depend on the site population of both $M1$ and $M2$ sites through ω_{ij_s} coefficients; (11) shows that these coefficients are strictly related to the physical properties considered for the intervening ions.

Table 4. *Coefficients for equation* (12)

Using the listed values, interatomic distances and cell parameters may be derived directly from ionization potentials and polarizability of ions. $\Delta = (\sum \cdot D(\text{obs.}) - D(\text{calc.})|)/55$.

| | M1 | | M2 | | | |
	W1	W2	W1	W2	W3	$\Delta \times 10^3$
T—O1A	0·350 (1)	0·032 (2)	0·097 (2)	−0·010 (2)	1·509 (1)	2
T—O2A	0·061 (2)	−0·017 (3)	0·022 (3)	0·001 (3)	1·648 (2)	4
T—O3A	0·479 (2)	−0·004 (2)	−0·060 (2)	−0·011 (2)	1·559 (1)	3
Mean T—O	0·333 (1)	0·002 (2)	0·002 (2)	−0·008 (2)	1·570 (1)	2
O1A—O2A	−1·287 (2)	−0·041 (3)	1·192 (3)	−0·025 (3)	2·803 (2)	5
O1A—O3A	0·902 (2)	0·009 (3)	−0·800 (2)	−0·023 (3)	2·747 (2)	3
O2A—O3A	1·330 (2)	0·053 (3)	0·283 (3)	−0·008 (3)	2·197 (2)	4
O3A—O3B	0·667 (3)	−0·034 (4)	0·079 (4)	0·021 (4)	2·450 (2)	6
M1—O1B	4·967 (2)	0·126 (3)	2·915 (2)	0·103 (3)	0·311 (3)	4
M1—O2A	5·741 (3)	0·209 (3)	0·806 (2)	0·027 (3)	0·570 (2)	3
M1—O3A	8·120 (4)	0·249 (6)	−1·167 (5)	0·088 (5)	0·495 (5)	10
Mean M1—O	6·618 (2)	0·197 (3)	0·732 (2)	0·066 (3)	0·415 (2)	4
O1B—O2A	8·347 (2)	0·325 (3)	−0·042 (3)	−0·021 (3)	0·945 (3)	4
O1B—O3A	6·344 (4)	0·116 (5)	2·562 (4)	0·202 (4)	0·817 (4)	7
O1B—O3C	12·305 (5)	0·393 (4)	−0·219 (4)	0·058 (4)	0·336 (5)	8
O2A—O3C	15·846 (6)	0·503 (7)	−0·774 (6)	0·145 (7)	−0·168 (7)	14
O1B—O2B	7·170 (3)	0·159 (3)	4·806 (2)	0·200 (3)	0·324 (3)	4
M2—O1A	0·294 (4)	−0·146 (4)	7·594 (3)	0·408 (5)	0·383 (5)	7
M2—O2C	−0·182 (3)	−0·041 (3)	6·548 (4)	0·276 (5)	0·594 (4)	5
M2—O3D	1·406 (5)	−0·028 (6)	4·779 (5)	0·265 (6)	0·797 (6)	9
M2—O3E	2·343 (4)	0·052 (5)	6·833 (4)	0·169 (4)	0·020 (4)	7
Mean M2—O	1·254 (1)	−0·023 (3)	6·215 (2)	0·258 (2)	0·441 (1)	3
O1A—O3E	−3·296 (3)	−0·209 (4)	15·636 (4)	0·584 (3)	0·237 (2)	6
O3D—O3F	−1·761 (2)	−0·090 (3)	10·668 (3)	0·347 (2)	0·989 (2)	4
O3E—O3F	10·809 (3)	0·245 (4)	11·114 (5)	0·405 (3)	−1·556 (2)	8
O2C—O3D	1·868 (4)	−0·010 (3)	10·304 (5)	0·474 (3)	0·391 (2)	8
O2C—O3E	3·209 (2)	−0·015 (3)	5·791 (3)	0·230 (2)	0·930 (2)	5
a_0	7·680 (2)	0·193 (3)	1·393 (2)	0·117 (3)	2·690 (2)	5
b_0	4·739 (7)	0·069 (5)	23·568 (6)	0·992 (6)	3·713 (7)	19
c_0	11·476 (4)	0·210 (3)	11·194 (4)	0·427 (3)	0·893 (4)	8
V	1305·4 (5)	28·9 (4)	1405·9 (6)	56·4 (5)	−323·1 (5)	1012

On the above evidence, appropriate interatomic distances can be derived from ionization potentials and polarizabilities of ions entering M1, M2 sites through an equation of the type:

$$D(\text{calc.})_j = \sum_s \{W1_{j,}\sum_i [X_{i,}(\sum_{m=1}^z I_m)_i^{-1/2}]\}$$

$$+ \sum_s [W2_{j,}\sum_i (X_{i,}\alpha_i^{f\,1/4})] + W3_j. \quad (12)$$

Equation (12) only requires five adjustable parameters, instead of the 15 required by (3). A further advantage of (12) is that W_j coefficients should also hold for cations not considered in the present paper, since they are related to the total ionization potential and polarizability of the site, in contrast to the ω_{ij_s} coefficients of (3), which are related to single cations. Table 4 gives W_j coefficients resulting from a minimization procedure on the 55 selected olivines. The W_j coefficients fully confirm the results of Lumpkin & Ribbe (1983) concerning the dependence of cell dimensions on M1, M2 and Si sites. The a_0 cell dimension is highly correlated with M1 and Si (the last is included in the $W3_j$ term). In contrast, b_0 is most highly dependent on the W_j parameters relative to M2, while c_0 is equally ruled by both M1 and M2 sites. As expected, all the tetrahedron distances have very low dependence on M1 and M2 sites, the main contribution arising from the $W3_j$ term.

Table 4 also reports the mean reduced residuals computed for each distance with (12). Values are obviously higher than those relative to (3), depending on the reduced number of adjustable parameters and also on the accuracy of polarizability data.

Table 5 reports the ionization potentials and polarizability of ions of interest available in the literature. As regards ionization potentials, most of these data were obtained by ultraviolet spectroscopy. This method is quite accurate and the significant digit would be the first decimal on an eV scale.

Concerning polarizability, we can distinguish free-ion polarizabilities [α^f values in Table 5, from Vieillard, (1982)] and polarizability in a static field [α^t values in the same table, from Lasaga & Cygan (1982)]. According to Lasaga (1980) and Lasaga & Cygan (1982), the latter term better accounts for the effect of surrounding charges on ion size in a crystalline medium [the induced electric field is static and displacement terms are added, so that the 'total' polarizability is slightly higher with respect to an oscillating field, cf. discussion in Lasaga (1980)]. Indeed it has been shown by Lasaga (1980) that 'total' polarizabilities allow precise evaluation of polarizability effects owing to the removal of charges in orthosilicates. However, it should be recalled that the empirical correlation of Shanker et al. (1973) establishes a simple proportionality between α^f and α^t factors:

$$\alpha_i^t = \alpha_i^f (r_i/r_i^f)^3 \quad (13)$$

where r_i^f is the radius of the free ion i, and r_i is the radius of ion i in the structure. The data in Tables 1

Table 5. *Physico-chemical properties of interacting ions*

*I*1 and *I*2 are first and second ionization potentials, respectively, (in eV) from Weast (1980). α^f and α^t are 'free-ion' (Vieillard, 1982) and 'total' polarizabilities, respectively (Lasaga & Cygan, 1982).

	Ionic potentials (eV)		Polarizability (Å^3)	
	*I*1	*I*2	α^f	α^t
Mg	7·646	15·035	0·0750	0·940
Fe	7·870	16·180	0·6875	1·520
Ni	7·635	18·168	0·7710	1·040
Mn	7·435	15·640	0·7172	2·080
Ca	6·113	11·871	0·5110	2·830
Co	7·860	17·060	0·6600	
Zn	9·394	17·964	0·7260	2·100

and 3 were obtained using α^f. Table 2, column 3, gives examples of the application of (12).

Concluding remarks

All interionic distances in silicate olivines are conveniently reproduced by simple proportionality rules involving site occupancy of the different ions in $M1$, $M2$ sites and ω_{ij}, ξ_j proportionality factors. Calculating interionic distances from site occupancies with ω_{ij}, ξ_j factors faithfully reproduces the actual structure, the accuracy of the proportionality rule being of the same order of magnitude as the experimental error. A further optimization of the distances generated by the *DLS* procedure allows precise reconstruction of all the structure parameters needed in structure–energy calculations (Table 2, columns 1 and 2). This allows satisfactory simulations of energetics, mixing properties and order–disorder in silicate olivine mixtures (Ottonello, Della Giusta & Molin, 1989). ω_{ij_s} proportionality factors for the $M1$ site (for distances of the $M1$ polyhedron) and, separately, for the $M2$ site (for distances of the $M2$ polyhedron) are linearly related to Shannon's (1976) 'ionic radii' in sixfold coordination with oxygen, the *R* factors being higher than 0·98 for most distances, excluding Zn. However, ω_{ij_s} factors are more strictly related to the polarizability and the sum of ionic potentials up to the valency state of ions, through expressions like (8) and (10). Based on this evidence, interionic distances may be directly derived from proportionality rules involving the above physico-chemical parameters (12). Results of such simulations are less precise than those involving ω_{ij}, ξ_j factors (3), but are still superior to the regressions hitherto proposed for this class of solids (Lumpkin & Ribbe, 1983; Ottonello, 1987; *cf.* Table 1). We believe that this is not simply an artifact of the fitting procedure but rests on the physical relevance of the adopted magnitudes.

The relative simplicity of the simulation method rests on the fact that a single set of free-ion polarizabilities is applied to ions entering two distinct sites ($M1$ and $M2$) which are differently distorted, but have the same coordination number. Application of

the method to other structures where the same ion enters different polyhedra, would require an analysis of the effect of the coordination number on the individual ion polarizabilities, just as is done with ionic radii (Tosi, 1964; Shanker *et al.*, 1973; Mahan, 1980, Vieillard, 1982).

References

AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, 2, 155–169.
BAERLOCHER, CH., HEPP, A. & MEYER, W. M. (1977). *DLS76. A Program for the Simulation of Crystal Structures by Geometric Refinement*. ETH-Zentrum, Zurich, Switzerland.
BAUR, W. H. (1970). *Trans. Am. Crystallogr. Assoc.* 6, 129–155.
BAUR, W. H. (1971). *Am. Mineral.* 56, 1573–1599.
BAUR, W. H. (1972). *Am. Mineral.* 57, 709–731.
BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A29, 266–282.
BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* B32, 1957–1959.
CLARK, J. R., APPLEMAN, D. & PAPIKE, J. (1969). *Mineral. Soc. Am. Spec. Pap.* 2, 31–50.
DIXON, W. J. (1980). *BMDP Statistical Software*. Berkeley: Univ of California Press.
DONNAY, G. (1969). *Carnegie Inst. Washington Yearb.* 68, 292–295.
DONNAY, G. & ALLMAN, R. (1970). *Am. Mineral.* 55, 1003–1015.
FUJINO, K., SASAKI, S., TAKEUCHI, Y. & SADANAGA, R. (1981). *Acta Cryst.* A37, 513–518.
GANGULY, D. (1977). *Neues Jahrb. Mineral. Abh.* 130, 303–318.
HARVEY, K. B. & PORTER, G. B. (1976) *Introduzione alla Chimica Fisica Inorganica*. Padova: Piccin.
ITO, J. (1977). *Am. Mineral.* 62, 356–361.
JAMES, F. & ROOS, M. (1977) *MINUIT. A System for Function Minimization and Analysis of the Parameter Errors and Correlations*. CERN Computer Center, Geneva, Switzerland.
LASAGA, A. C. (1980). *Am. Mineral.* 65, 1237–1248.
LASAGA, A. C. & CYGAN, R. T. (1982). *Am. Mineral.* 67, 328–334.
LUMPKIN, G. R. & RIBBE, P. H. (1983). *Am. Mineral.* 68, 169–176.
MAHAN, H. (1980). *Solid State Ion.* 1, 29–45.
OTTONELLO, G. (1987). *Geochim. Cosmochim. Acta*, 51, 3119–3135.
OTTONELLO, G., DELLA GIUSTA, A. & MOLIN, G. (1989). *Am. Mineral.* 74, 411–421.
PAULING, L. (1929). *J. Am. Chem. Soc.* 51, 1010–1026.
PAULING, L. (1960). *The Nature of Chemical Bond*. Ithaca: Cornell Univ. Press.
SHANKER, J., KUMAR, N. & VERMON, M. P. (1973). *Indian J. Pure Appl. Phys.* 2, 644–647.
SHANNON, R. D. (1976). *Acta Cryst.* A32, 751–777.
TOSI, M. (1964). *Solid State Phys.* 16, 1–120.
VAN VLECK, J. H. (1952). *The Theory of Electric and Magnetic Susceptibilities*. London, New York: Oxford Univ. Press.
VIEILLARD, P. (1982). *Modele de Calcule des Energies de Formation des Mineraux, bati sur la Connaissance Affinee des Structures Crystallines*, Memoire No. 69, 206 pp. Univ. Louis Pasteur, Strasbourg, France.
WASASTJERNA, J. A. (1923). *Soc. Sci. Fenn. Comm. Phys. Nat.* 38, 1–25.
WEAST. R. C. (1980). *Handbook of Chemistry and Physics*. Cleveland: Chemical Rubber Company.