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Structure energy calculations on optimum distance model structures: application to the silicate olivines

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Abstract

In order to understand more quantitatively the causes of ordering in the divalent-cation silicate olivines, we have modeled eight ordered and anti-ordered binary olivine pairs (Fe–Mg, Mg–Ni, Fe–Mn, Mg–Ca, Mg–Co, Mg–Mn, Mn–Ca, and Fe–Ca) using distance least-squares computer modeling. Relative structure energies were calculated for the hypothetical ordered and anti-ordered intermediate olivine structures using an electrostatic model with Coulomb and repulsive terms. Observed and model cell parameters agree very well, and changes in order/anti-order are reflected primarily in variations in the *b* cell parameter. Details of the structures demonstrate that the interatomic distances of any given M1 coordination polyhedron depend not only on its chemical occupancy, but also on the occupancy of the M2 polyhedron; likewise for the M2 polyhedral geometry. The calculated structure energies of the optimum distance models correctly and semi-quantitatively predict the observed site preferences in all eight cases, in contrast to the approximation using linear combinations of end-member site energies. The calculated energies are an approximation to the cation exchange energies to which ligand field stabilization energies and any covalency or polarization contributions may be added.

Introduction

Order–disorder phenomena are commonplace in virtually all silicate mineral groups. Complete characterizations of silicate structures must include, therefore, determinations of cation distributions and related states of long-range ordering (see, for example, Burnham, 1973). Structural rationalizations of observed cation distributions have been based, for the most part, on generalizations and empirically derived relationships. Among these are the so-called aluminum-avoidance principle (Lowenstein, 1954), arguments that relate polyhedral sizes and distortions to ligand field stabilization energies of transition elements (Burns, 1970), and, of course, classical size arguments that base predicted occupancies on ionic radii (Shannon and Prewitt, 1969).

Few attempts have been made to evaluate directly the structure energies associated with actual or potential cation distribution schemes. Although more quantitative and thus potentially of far greater predictive value, such an approach has difficulties associated with it that have been, until recently, quite insurmountable. Assuming that the ionic approximation would be suitable for silicates and that the desired energy is made up essentially entirely of Coulomb electrostatic interactions plus short-range repulsive interactions, one must, in order to carry out the calculation, know the precise atomic positions and appropriate nearest-neighbor repulsive interaction terms in the structure under consideration. Atomic positions are, of course, known with high precision for a wealth of observed cation distributions in many silicates but they are unknown for hypothetical or unobserved distributions. Suitable parameters describing the short-range repulsive interaction are available for certain cation–oxygen bonds, specifically those in the coordination polyhedra of close-packed cation oxides in which bulk compressibility can be directly related to cation–oxygen bond compressibility.

Ohashi and Burnham (1972) examined the energetics of ordered ($MgFeSi_2O_6$) and anti-ordered ($FeMgSi_2O_6$) hypersthene by making simplifying assumptions that sidestepped the above difficulties. They calculated the electrostatic energies for only the M1 and M2 sites in end-member orthoenstatite and orthoferrosilite using observed structures and calculated repulsive energies for these sites using parameters obtained from bulk moduli of periclase and wüstite. Hypothetical ordered and anti-ordered hypersthenes were compared using linear combinations of the end-member site energies. This approximation assumes that the structure energy of the silicate part

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of the pyroxene remains constant irrespective of Fe–Mg distribution and that the geometry, and hence site energy, of the M1 site is not affected by changing the content of the M2 sites and vice versa. Their results are consistent with the observed site preference, that is the combination of $Mg_{M1} + Fe_{M2}$ site energies was computed to be lower than that of $Fe_{M1} + Mg_{M2}$ by 12.1 kcal/mole. Tossell (1980) used the modified electron gas method (Cohen and Gordon, 1976) to obtain Mg–O and Fe–O repulsive energies that he then combined with the Ohashi and Burnham M1 and M2 electrostatic site energies to obtain an energy difference of 7.6 kcal/mole favoring $Mg_{M1} + Fe_{M2}$.

Whittaker (1971) obtained good qualitative agreement between observed site preferences in amphiboles and those predicted by electrostatic calculations using two different sets of amphibole atomic coordinates and a number of different ordered distributions of ionic species of varying charge. In a similar manner, Alberti and Vezzalini (1978) modeled ordering in olivine-type structures. Using observed structures and considering only the electrostatic energy, they calculated energies for various charge distributions on M1 and M2, going from all the cation charge on M1 to all on M2, and they obtained results in agreement with observed distributions. Recently Brown and Fenn (1979) applied structure energy calculations to the problem of alkali-site positional disorder and Al,Si disorder in alkali feldspars. They showed that Al in the T_1O tetrahedron yields a lower electrostatic energy than with Al in any of the other three crystallographically distinct sites, and that the minimum-energy position of Na is, in fact, affected by the arrangement of Al and Si in the tetrahedra immediately surrounding the alkali cavity. In all these studies the electrostatic calculations were based on fixed structures, in other words all interatomic distances were assumed to remain constant throughout substantial changes in both cation species and charge distributions. Repulsive contributions were specifically included only for Na–O and K–O polyhedra using repulsive parameters from alkali fluoride bulk modulus data.

These studies on cation distributions contrast with the empirical linear regression treatment of Lumpkin and Ribbe (1983) who related observed lattice parameters to the effective ionic radii of the cations occupying M1, M2, and the tetrahedral site in olivine. They found that the occupant of M1 exhibited dominant control over the *a* parameter and the M2 cation controlled the *b* parameter. It thus appeared that the *a* and *b* cell dimensions of a silicate olivine might be used to predict the cation distribution in M1 and M2.

We report here two innovations in the technique of calculating ionic structure energies for silicates with varying ordered cation distributions. First, and most important, we employ the method of distance least-squares (DLS), originally described by Meier and Villiger (1969), to obtain atomic coordinates and unit-cell dimensions for structures with assumed yet unobserved ordered cation distributions. These coordinates and cell dimensions constitute what Dollase (1981) has called an optimum distance model structure in that they are optimally consistent with an assumed set of interatomic distances. Second, we use observed force constants for Si–O stretching vibrations to obtain the required terms of the Born exponential approximation for the short-range repulsive potential within a Si tetrahedron, following a method outlined by Lasaga (1980).

Using these new procedures we have calculated structure energies of both ordered and anti-ordered forms for eight intermediate silicate olivine compositions. In all cases optimum distance model structures have been used, and comparison of the calculated energies shows that they successfully account for the observed cation distributions in 100% of the cases. We show also that analysis of these olivines using earlier methods based solely on energies of end-member configurations fails to account for the observed distribution in seven out of eight cases and yields a quantitatively misleading result in the eighth case.

Distance least squares modeling

The technique of distance least-squares has been described by several authors, among them Meier and Villiger (1969), Dempsey and Strens (1976), and Baur (1977). An optimum distance structure model is obtained by varying atomic coordinates and unit-cell dimensions to minimize discrepancies between interatomic distances in the model structure and a prescribed set of expected interatomic distances that comprise the data. The least-squares procedure is an iterative one for non-linear observational equations; our DLS program was originally coded by H. Villiger and has been modified to consider up to 32 prescribed distances.

To model ordered and anti-ordered Fe–Mg, Co–Mg, Ni–Mg, Fe–Mn, Mg–Mn, Mg–Ca, Mn–Ca, and Fe–Ca intermediate olivines, interatomic distances were obtained from the end-member Mg, Mn, Fe, Co, Ni, and Ca olivines (Table 1). Prescribed distances for each intermediate structure were obtained as follows: (1) Si–O and tetrahedral O–O distances were taken as averages of those in the two end-member structures; (2) M1–O, M2–O, and O–O distances were selected from the corresponding distances in the appropriate end members; (3) cation–

Table 1. Olivine structures used for energy calculations and DLS modeling

Mg_2SiO_4	Hazen (1976)
Ca_2SiO_4	Brown (1970)
Mn_2SiO_4	Francis and Ribbe (1980)
Fe_2SiO_4	Smyth (1975); Hazen (1977)
Co_2SiO_4	Brown (1970); Morimoto et al. (1974)
Ni_2SiO_4	Brown (1970); Lager and Meagher (1978)

cation distances were set according to the two cations involved. For each case some 29 distinct distances were prescribed, and 11 atomic coordinates and 3 orthorhombic cell dimensions were varied simultaneously from initial values corresponding to those of forsterite. All refinements converged quickly to the optimum distance models whose energies are reported here.

The DLS procedure requires that each prescribed distance be weighted according to some measure of its compliance. Distances with high weights will vary little during refinement, whereas those with low weights may vary substantially. Our weighting scheme is similar to that employed by Baur (1977) for olivine. Weights of cation–anion distances are proportional to the Pauling bond strengths, namely, $w_{(Si-O)} = 1.0$ and $w_{(M-O)} = 0.33$. The weights for O–O distances are somewhat arbitrary. Examination of a large number of divalent cation olivine structures reveals that the edge-sharing O–O distances, specifically O(2)–O(3) and O(3)–O(3) between an octahedron and a tetrahedron and O(1)–O(3) and O(1)–O(2) between two octahedra (nomenclature after Hazen, 1976) are remarkably constant. These distances were given weights of 0.14. Weights for the remaining O–O distances were set to 0.07 or 0.04 depending on whether the distance is less than or greater than 3.2Å. All cation–cation distances were assigned weights of 0.04.

It has been noted (Baur, 1977; G. V. Gibbs, pers. comm.) that more realistic weights might be obtained from bending and stretching force constants. If we use the Mg–O and Si–O stretching force constants reported by Iishi (1978), 0.46 and 3.47 mdyn/Å respectively, we obtain a weight of 0.13 for Mg–O with $w_{(Si-O)} = 1.0$. Weights for O–O distances obtained from bending force constants calculated using *ab initio* molecular orbital methods (Gibbs, 1981) are comparable to the 0.07 to 0.14 range we used.

Energy calculations

Numerous authors (Tosi, 1964; Ohashi and Burnham, 1972; Brown and Fenn, 1979; Lasaga, 1980) have discussed the details of electrostatic structure energy calculations; we will therefore not describe the methods at length. To calculate electrostatic energies both for individual sites and entire structures we used the program ELEN coded by Y. Ohashi, and calculations were performed on an Interdata 8/32 computer using double precision arithmetic. The computational method is described by Ohashi and Burnham (1972); the program employs the Bertaut (1952) Fourier method as modified by Templeton (1955), Jones and Templeton (1956), and Templeton and Johnson (1961) to achieve more rapid convergence and correct for series termination effects. We assumed a fully ionized model and commonly computed the summation to $h = 3\pi$, which was sufficient to achieve convergence.

We have used the Born exponential form (Kittel, 1971) to calculate the M–O repulsive energies: $U_r(j) = \Sigma_i \lambda_{ij} \exp(-r_{ij}/\rho_{ij})$, where λ_{ij} is the repulsive energy parameter for a bond between the ith and jth ions and ρ_{ij} is the repulsive range parameter. These parameters describe the shape of the short-range repulsive potential as a function of distance r_{ij}; the summation includes only first-neighbor interactions. From bulk modulus data for cubic oxides (Table 2), λ and ρ may be calculated using formulae given by Kittel (1971). The bulk moduli have not been extrapolated to the static lattice. NiO has been included in our calculations although it occurs in a rhombohedrally deformed structure below 270°C (Naray-Szabo, 1969).

The repulsive potential between Si and O has been calculated using a method outlined by Lasaga (1980). The total potential describing the Si–O bond is written as the sum of a Coulomb electrostatic component and a repulsive component. Appropriate constants describing the repulsive potential, λ and ρ, may be determined if the first and second derivatives of the total potential with respect to r are known. The first derivative is 0.0 at $r = r_{(Si-O)}$ and the second derivative is the Si–O stretching force constant. Iishi (1978) has reported that the Si–O stretching force constant for forsterite that best reproduces optical frequencies and macroscopic elastic constants is 3.460 mdyn/Å. This value yields 0.579Å for ρ_{Si-O} and 6.72×10^{-10} ergs for λ_{Si-O}.

To determine the effects of O–O repulsion on our results, we used the Watson modified electron gas short-range potential for O^{2-}–O^{2-} (Cohen and Gordon, 1976); this potential described the binding energies, elastic properties, and high-pressure behavior of MgO and CaO very well. The contribution of O–O repulsion to the calculated structure energies of ordered and anti-ordered monticellite were almost identical. Since these two structures are likely to be the least similar of any of the ordered and anti-ordered pairs we examined because of the large difference between Mg and Ca radii, we neglected O–O repulsions in further calculations.

Structure energies were calculated for the observed structures of end-member olivines listed in Table 1 and for both ordered and anti-ordered optimum distance model structures of the eight intermediate olivine compositions previously mentioned. These energies include Coulomb electrostatic terms assuming fully ionized models and repulsive terms for M–O and Si–O polyhedra. The

Table 2. Repulsive parameters for metal–oxygen bonds

	M-O in oxide (Å)	Bulk Modulus (Mb)	ρ(Å)	λ($\times 10^{-10}$ ergs)
MgO	2.106	1.61^{++}	0.3805	5.84
CaO	2.405	1.12*	0.389	8.75
MnO	2.22	1.54**	0.359	9.42
FeO	2.145	1.82^{+}	0.34	10.83
CoO	2.13	1.85**	0.341	10.46
NiO	2.10	1.90**	0.343	9.55

* Chang and Graham (1977) ** Davies (1976) $^{+}$ Jackson et al. (1978)
$^{++}$ Spetzler (1970)

calculations do not include van der Waals (dipole–dipole and dipole–quadrupole) terms, covalency or polarization effects, ligand-field stabilization energies, or vibrational energies.

Since we are comparing structure energies of ordered and anti-ordered model structures, and since these are, in fact, similar structures in all cases, we anticipate that errors from neglect of van der Waals and vibrational terms will be minimal, except possibly for olivines with large differences in Ml and M2 cation size as noted later. Covalency and ligand-field stabilization terms are, however, strongly site dependent and may contribute significantly relative to the ordered versus anti-ordered energy differences; their potential contributions to certain of the intermediate structures are discussed later.

Results and discussion

An informative test of our modeling procedure can be obtained by comparing cell parameters for model ordered and anti-ordered structures with those experimentally observed for intermediate compositions (Table 3). The good agreement between observed and model cell parameters supports our modeling technique, and trends in the model cell parameters with changes in order/anti-order suggest that our results may lend insight into observed variations of cell dimensions in intermediate partially ordered olivines. Discrepancies between observed and model cell parameters probably reflect incomplete order in the observed samples and errors introduced using end-member bond distances in our DLS modeling. From the model cell dimensions of olivines containing cations of similar size, it is apparent that changes in order/anti-order are primarily reflected in variations in the *b* cell parameter; the *a* and *c* parameters are remarkably constant. In fact, the *a* and *c* cell parameters for observed intermediate composition olivines agree very well with the model *a* and *c* cell dimensions, whereas the *b* parameters show considerable variation. Rajamani et al. (1975) noted that the *b* parameter for their Ni–Mg olivine was significantly smaller than that reported by Matsui and Syono (1968) for material of similar composition. Bish (1981) also found significant deviations in cell parameters of Ni–Mg olivines from the values given by Matsui and Syono (1968). Our DLS results show that the *b* cell parameter in $NiMgSiO_4$ is significantly smaller in anti-ordered olivine ($Mg_{M1}Ni_{M2}$) than in ordered olivine ($Ni_{M1}Mg_{M2}$); it is apparent that variations in degree of cation order cause significant changes in unit cell size.

Most of the intermediate compositions we examined have not been observed to form completely ordered structures, but monticellite, $MgCaSiO_4$, does. Thus a further test of our modeling procedure can be obtained by comparing the optimum distance model for monticellite with the observed structure. Table 4 displays model versus observed cation–oxygen interatomic distances. The mean deviations between monticellite model cation–oxygen distances and the average of the two observed sets of distances are 0.006Å (0.4%) for the Si tetrahedron, 0.026Å (1.2%) for the M1 octahedron, and 0.032Å (1.3%) for the M2 octahedron. Si–O model distances did not change significantly during DLS refinement, which is not unexpected due to their high weights relative to other prescribed distances. The differences between those distances and the observed ones simply reflect the degree to which averages of forsterite and Ca_2SiO_4 Si–O distances do not correspond to an accurate model of the Si tetrahedron in monticellite.

Comparison of M–O distances in the ordered monticellite optimum-distance model with observed distances on the one hand and with the original prescribed distances on the other reveals that the DLS procedure altered the model structure so as to cause all prescribed M–O distances to change in the direction that would make them closer to the corresponding distance actually observed in monticellite. Except for the M1–O(2) and M2–O(3) dis-

Table 3. Cell parameters for optimum-distance ordered intermediate olivines and observed olivines

	M1	M2	a(Å)	b(Å)	c(Å)
DLS	Ni	Mg	4.734	10.169	5.949
DLS	Mg	Ni	4.742	10.129	5.946
Observed	$Ni_{.77}$ $Mg_{.23}$	$Mg_{.74}$ $Ni_{.26}$	4.737	10.172	5.937
DLS	Co	Mg	4.774	10.207	5.997
DLS	Mg	Co	4.762	10.275	5.981
Observed	$Co_{.73}$ $Mg_{.27}$	$Mg_{.63}$ $Co_{.37}$	4.775	10.258	5.996
DLS	Fe	Mg	4.811	10.203	6.047
DLS	Mg	Fe	4.755	10.428	6.036
Observed	$Fe_{.52}$ $Mg_{.48}$	$Mg_{.52}$ $Fe_{.48}$	4.794	10.339	6.042
DLS	Mg	Mn	4.766	10.625	6.107
DLS	Mn	Mg	4.842	10.279	6.059
Observed	$Mg_{.65}$ $Mn_{.35}$	$Mn_{.67}$ $Mg_{.33}$	4.818	10.447	6.130
DLS	Fe	Mn	4.832	10.648	6.176
DLS	Mn	Fe	4.859	10.503	6.120
Observed	$Fe_{.66}$ $Mn_{.33}$*	$Mn_{.63}$ $Fe_{.37}$	4.844	10.577	6.146
DLS	Mg	Ca	4.810	11.106	6.450
DLS	Ca	Mg	4.989	10.535	6.134
Observed	$Mg_{1.0}$	$Ca_{1.0}$	4.822	11.108	6.382
DLS	Fe	Ca	4.906	11.129	6.519
DLS	Ca	Fe	4.993	10.832	6.198
Observed	$Fe_{.85}$ $Ca_{.15}$	$Ca_{.98}$ $Fe_{.02}$	4.892	11.180	6.469
DLS	Mn	Ca	4.878	11.117	6.486
DLS	Ca	Mn	4.983	10.984	6.311
Observed	$Mn_{.91}$ $Mg_{.09}$	$Ca_{.98}$ $Mn_{.02}$	4.913	11.147	6.489

*Includes 0.04 Mg.

All observed data from Brown (1980) except Co-Mg from Ghose and Wan (1974), Fe-Mg from Ghose et al. (1976), Mg-Mn occupancy from Lumpkin et al. (1983)

Table 4. Comparison of DLS-model and observed interatomic distances (in Å) for monticellite, $MgCaSiO_4$

	Prescribed	DLS-model	Brown (1970)	Lager and Meagher (1978)
Si-O(1)	1.626	1.626	1.615(4)	1.617(5)
Si-O(2)	1.647	1.647	1.656(3)	1.656(4)
Si-O(3) 2x	1.637	1.636	1.640(2)	1.637(4)
<Si-O>	1.637	1.636	1.638	1.637
M1-O(1) 2x	2.130	2.142	2.194(2)	2.186(3)
M1-O(2) 2x	2.076	2.107	2.091(2)	2.089(3)
M1-O(3) 2x	2.140	2.130	2.120(2)	2.113(3)
<M1-O>	2.115	2.126	2.135	2.129
M2-O(1)	2.442	2.453	2.478(3)	2.484(5)
M2-O(2)	2.286	2.297	2.309(4)	2.316(5)
M2-O(3) 2x	2.426	2.406	2.411(3)	2.414(4)
M2-O(3)' 2x	2.385	2.359	2.289(2)	2.291(4)
<M2-O>	2.392	2.380	2.364	2.368

tances whose changes during DLS were greater than the original discrepancy between prescribed and observed values, the model M–O distances lie between the originally prescribed and the observed values. The small discrepancies between optimum model and observed M–O distances may be due, at least in part, to either of two reasons. As described earlier, the weight assigned to all M–O distances was 0.33, which corresponds to the classical Pauling bond strength; force-constant data suggest that weights in the range 0.10–0.15 might be more appropriate for M^{2+}–O bonds. Lower weights would have permitted them greater compliance during DLS and could have yielded larger changes. Alternatively it is conceivable that our model distances are, in fact, closer to expectation for a truly fully ordered monticellite, and that the slightly larger M1–O polyhedron and slightly smaller M2–O polyhedron in the observed structures are due to some disordering of Mg and Ca. Brown (1970) carried out a site-occupancy refinement that yielded complete ordering with reported errors of 1%, although the 0.1 atoms of Fe^{2+} plus Mn^{2+} per 4 oxygens in the analysis were not taken into account (Onken, 1965; Moehlman and Gonyer, 1934); Lager and Meagher (1978) simply assumed complete ordering of Ca on M2. One should keep in mind that of all the olivine pairs modeled, ordered and anti-ordered monticellite correspond to the worst-case situations because the difference in size between Mg^{2+} and Ca^{2+} is the largest of any of the cation pairs.

Small discrepancies with observed distances notwithstanding, the differences between the M–O polyhedra in the optimum distance model and the prescribed end-member polyhedra permit an observation with rather far-reaching consequences: For stereochemical reasons related to the topology of the olivine structure, the Mg-filled M1 octahedron in monticellite is larger than the M1 octahedron in forsterite, likewise the Ca-filled M2 octahedron in monticellite is smaller than the M2 octahedron in pure calcic olivine, γ-Ca_2SiO_4. This observation holds not only for ordered monticellite but for most of the ordered and anti-ordered structures we examined. Table 5 lists for all 16 structures (8 ordered, 8 anti-ordered) the mean M1–O and M2–O distances in the optimum-distance structures and compares them with the corresponding M1–O and M2–O mean distances in the appropriate end-member structures. Observe that in all cases where there is a difference between ⟨M1–O⟩ and ⟨M2–O⟩ of the end members, the mean distance in the intermediate structure is either larger or smaller than the corresponding distance in the end-member structure depending on whether the accompanying M^{2+} cation has larger or smaller M–O distances, respectively. In some cases the difference between intermediate and corresponding end-member ⟨M–O⟩ is insignificant (Mg–Co, Co–Mg, Ni–Mg, Fe–Mn), in two cases (Mg–Fe, and Fe–Mg) the difference is small and probably of marginal significance, whereas for Mg–Ni and Mn–Fe no difference would be expected because the corresponding end-member ⟨M1–O⟩ and ⟨M2–O⟩ are identical or nearly so.

One can generalize, therefore, that in divalent cation silicate olivines the size and distortion of the M1 octahedron, while clearly depending on the atomic species occupying that site, may also depend significantly on the atomic species occupying M2. Likewise the size and distortion of the M2 octahedron may depend on the atomic species occupying M1. The data in Table 5 show that the degree of this dependence is related qualitatively to the size difference between the species occupying M1 and M2, but it is a complex relationship not conducive to simple analysis. The reasons for this dependence, when it occurs, are related in ways we cannot at this time connect to the geometric limitations or requirements of the olivine structure's topology.

Table 5. Mean ⟨M1–O⟩ and ⟨M2–O⟩ distances (in Å) in intermediate DLS model structures versus those in corresponding end-member structures

End-member	M1	Intermediate		M2	End-member
<M1-O>	Occupant	<M1-O>	<M2-O>	Occupant	<M2-O>
2.101	Mg	2.104	2.179	Fe	2.182
2.157	Fe	2.154	2.129	Mg	2.126
2.101	Mg	2.102	2.139	Co	2.142
2.119	Co	2.118	2.127	Mg	2.126
2.076	Ni	2.078	2.124	Mg	2.126
2.101	Mg	2.100	2.102	Ni	2.102
2.157	Fe	2.159	2.224	Mn	2.227
2.185	Mn	2.184	2.186	Fe	2.182
2.101	Mg	2.107	2.220	Mn	2.227
2.185	Mn	2.181	2.132	Mg	2.126
2.101	Mg	2.126	2.380	Ca	2.392
2.346	Ca	2.332	2.143	Mg	2.126
2.185	Mn	2.198	2.360	Ca	2.392
2.346	Ca	2.338	2.239	Mn	2.227
2.157	Fe	2.210	2.372	Ca	2.392
2.346	Ca	2.329	2.203	Fe	2.182

Two consequences of this M1–M2 interdependence deserve mention. First, for olivine compositions in which the interdependence is large, especially Ca-containing ones, determination of M1 or M2 site occupancies using mean M–O distance-versus-occupancy curves calibrated with appropriate end members will be subject to significant error. Second, for any given cation pair the degree to which mixing is not ideal along the binary join will be dependent primarily on the magnitude of the M1–M2 size and distortion interdependence. Static enthalpies and entropies of mixing will arise from changes of M1 polyhedral geometry in response to changing M2 occupancy and vice versa; vibrational contributions to the mixing terms will be associated with the concomitant frequency shifts, which are likely to become significant as the cation pair size contrast increases.

Cation exchange energies

If the energies of ordered versus anti-ordered olivine structures are approximated using linear combinations of end-member site energies, clearly the interdependence between M1 and M2 polyhedral geometries is ignored. Individual site energies for M1 and M2 in six different end-member olivines are listed in Table 6a. In Table 6b we list the energy difference between ordered and anti-ordered arrangements for eight intermediate olivine compositions, approximated as the sum of end-member M1 and M2 site energy differences obtained using values listed in Table 6a. The calculated exchange energies have the wrong sign (compared with observed distributions, see last column of Table 7) in seven out of eight cases. For example, the linear combination of Ca in M1 and Mg in M2 yields an energy configuration lower by 24.1 kcal/gfw than Mg in M1 and Ca in M2. In the eighth case, that of Mg–Mn, even though the sign is correct, the magnitude is clearly too small since Mg is substantially smaller than Mn and the observed intermediate is strongly ordered. We conclude, therefore, that this approximation using only end-member site energies is generally invalid and gets worse as the size difference between the two cations increases. The failure of this approach to predict, even qualitatively, the cation arrangement in olivines must stem from the differences in the M1 and M2 environments between end-member structures and ordered intermediates. This is yet another illustration of the interdependence between M1 and M2.

A better approximation to the cation exchange energy requires that the interdependence of M1 and M2 polyhedral geometries be taken into account. We have, therefore, calculated the total structure energy for optimum-distance models of ordered and anti-ordered olivines using the method outlined earlier. The results of these calculations are listed in Table 7 together with observed cation distributions of natural and synthetic olivines. The calculated energy differences obtained using the complete electrostatic model with both Coulomb and cation–anion repulsive energy terms match well the observed configuration for every intermediate olivine. The energy difference, ΔU, is small for those pairs with little difference in ionic radii and large for those pairs with large ionic radii differences. Olivines observed to be ordered have large positive ΔU values with observed (ordered) configuration more stable than the hypothetical (anti-ordered) one.

Table 6a. M1 and M2 site energies for observed olivine end-member structures, kcal/gfw

	Mg_2SiO_4	Ca_2SiO_4	Mn_2SiO_4	Fe_2SiO_4	Co_2SiO_4	Ni_2SiO_4
M1	-880.0	-775.0	-842.2	-878.7	-886.3	-897.0
M2	-964.9	-835.8	-929.9	-971.3	-982.1	-996.1

Table 6b. End-member site energy differences for ordered and anti-ordered olivines, $M1M2SiO_4$, kcal/gfw. Positive values indicate the cation distribution shown has the lower energy; negative values indicate the opposite (anti-ordered) distribution has the lower energy.

M1	M2	ΔU	M1	M2	ΔU
Fe	Mg	-7.7	Mg	Mn	+2.8
Co	Mg	-10.9	Mg	Ca	-24.1
Ni	Mg	-14.2	Mn	Ca	-26.9
Fe	Mn	-4.9	Fe	Ca	-31.8

Several compositions have significant energy terms that have not been taken into account. Both Ni–Mg and

Table 7. Structure energy differences between optimum-distance models of ordered and anti-ordered olivines. $M1M2SiO_4$ (kcal/gfw). Positive values indicate the cation distribution shown (ordered) has the lower energy; negative values indicate the opposite (anti-ordered) distribution has the lower energy.

M1	M2	ΔU, Coulomb only	ΔU, Coulomb + repulsive	Observations
Fe	Mg	-5.0	-0.1	Fe usually in M1 - very slight ordering; some LFSE from Fe^{2+}
Co	Mg	-2.7	+0.1	Co in M1 - partial ordering; LFSE from Co^{2+}
Ni	Mg	+4.3	+2.3	Ni in M1 - strong ordering; LFSE from Ni^{2+}
Fe	Mn	+1.3	+6.8	Fe in M1 - partial ordering some LFSE from Fe^{2+}
Mg	Mn	+11.1	+11.0	Mg in M1 - nearly complete ordering
Mg	Ca	+11.0	+17.1	Mg in M1 - complete ordering
Mn	Ca	+16.7	+6.6	Mn in M1 - nearly complete ordering
Fe	Ca	-6.7	+10.5	Fe in M1 - strong ordering; some LFSE from Fe^{2+}

Co–Mg olivines possess ligand field stabilization energies (LFSE) favoring Ni and Co in M1 (Burns, 1970). These terms, if included, would make the values in Table 7 more positive. There is a small LFSE favoring Fe^{2+} in M1 as well (Walsh et al., 1974), and this, if included, would undoubtedly cause the negative ΔU for FeMg olivine to become slightly positive in agreement with observation.

Our calculations contain no covalency or polarization contributions, which may be significant in alkaline earth-transition metal intermediate olivines. Charge density determinations (Fujino et al., 1981) suggest that the bonding at M1 is more covalent than at M2. However, the success of our method in semi-quantitatively reproducing observed ordering schemes in intermediate olivines suggests that the electrostatic model provides the bulk of the cation exchange energy.

Summary

Distance least-squares models of eight ordered and anti-ordered intermediate olivines show that the detailed geometries of M1 and M2 polyhedra are not independent. The fact that M1–O distances are affected by the content of M2 and vice versa explains why the ordered and anti-ordered intermediate structures exhibit excess volumes of mixing, some positive and some negative.

Cation exchange energies calculated as the differences between electrostatic energies of optimum distance models of ordered versus anti-ordered intermediate olivines correctly predict the observed cation distributions for all eight compositions examined. This contrasts with predictions based only on differences between end-member M1 and M2 site energies, which are incorrect for seven of eight cases. Intermediate olivines for which the cation exchange energy is large are strongly ordered, whereas those for which the exchange energy is small tend to be at least partially disordered even at low temperatures.

Electrostatic energies calculated for optimum distance model structures provide a useful framework for rationalizing observed structural configurations. We believe this will prove a useful technique in a variety of applications.

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References

Alberti, A. and Vezzalini, G. (1978) Madelung energies and cation distributions in olivine-type structures. Zeitschrift für Kristallographie, 147, 167–175.

Baur, W. H. (1977) Computer simulation of crystal structures. Physics and Chemistry of Minerals, 2, 3–20.

Bertaut, F. (1952) L'énergie électrostatique de Réseaux ioniques. Le Journal de Physique et le Radium, 13, 499–505.

Bish, D. L. (1981) Cation ordering in synthetic and natural Ni–Mg olivine. American Mineralogist, 66, 770–776.

Brown, G. E. (1970) Crystal Chemistry of the Olivines. Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Brown, G. E. (1980) Olivines and Silicate Spinels. In P. H. Ribbe, Ed., Reviews in Mineralogy, Vol. 5, Orthosilicates, p. 275–381. Mineralogical Society of America, Washington, D. C.

Brown, G. E. and Fenn, P. M. (1979) Structure energies of the alkali feldspars. Physics and Chemistry of Minerals, 4, 83–100.

Burnham, C. W. (1973) Order–disorder relationships in some rock-forming silicate minerals. Annual Reviews of Earth and Planetary Science, 1, 313–338.

Burns, R. G. (1970) Mineralogical Applications of Crystal Field Theory. Cambridge University Press, Cambridge, England.

Chang, Z. P. and Graham, E. K. (1977) Elastic properties of oxides in the NaCl-structure. Journal of Physics and Chemistry of Solids, 38, 1355–1362.

Cohen, A. J. and Gordon, R. G. (1976) Modified electron-gas study of the stability, elastic properties, and high-pressure behavior of MgO and CaO crystals. Physical Review, B 14, 4593–4605.

Czaya, R. (1971) Refinement of the structure of γ-Ca_2SiO_4. Acta Crystallographica, B27, 848–849.

Davies, G. F. (1976) The estimation of elastic properties from analogue compounds. Geophysical Journal of the Royal Astronomical Society, 44, 625–647.

Dempsey, M. J. and Strens, R. G. J. (1976) Modelling crystal structures. In R. G. J. Strens, Ed., Physics and Chemistry of Rocks and Minerals, p. 443–458. Wiley, New York.

Dollase, W. A. (1980) Optimum distance model of relaxation around substitutional defects. Physics and Chemistry of Minerals, 6, 295–304.

Francis, C. A. and Ribbe, P. H. (1980) The forsterite–tephroite series. I. Crystal structure refinements. American Mineralogist, 65, 1263–1269.

Fujino, K., Sasaki, S., Takéuchi, Y., and Sadanaga, R. (1981) X-ray determination of electron distributions in forsterite, fayalite and tephroite. Acta Crystallographica, B37, 513–518.

Ghose, S. and Wan, C. (1974) Strong site preference of Co^{2+} in olivine, $Co_{1.10}Mg_{0.90}SiO_4$. Contributions to Mineralogy and Petrology, 47, 131–140.

Ghose, S, Wan, C., and McCallum, I. S. (1976) Fe^{2+}–Mg^{2+} order in an olivine from the lunar anorthosite 67075 and the significance of cation order in lunar and terrestrial olivines. Indian Journal of Earth Sciences, 3, 1–8.

Hazen, R. M. (1976) Effects of temperature and pressure on the crystal structure of forsterite. American Mineralogist, 61, 1280–1293.

Hazen, R. M. (1977) Effects of temperature and pressure on the crystal structure of ferromagnesian olivine. American Mineralogist, 62, 286–295.

Iishi, K. (1978) Lattice dynamics of forsterite. Amerian Mineralogist, 63, 1198–1208.

Jackson, I. and Liebermann, R. C. (1978) The elastic properties of $(Mg_xFe_{1-x})O$ solid solutions. Physics and Chemistry of Minerals, 3, 11–31.

Jones, R. E. and Templeton, D. H. (1956) Optimum atomic shape for Bertaut series. Journal of Chemical Physics, 25, 1062–1063.

Kittel, C. (1971) Introduction to Solid State Physics, fourth edition. John Wiley and Sons, Inc., New York.

Lager, G. A. and Meagher, E. P. (1978) High-temperature structural study of six olivines. American Mineralogist, 63, 365–377.

Lasaga, A. C. (1980) Defect calculations in silicates: Olivine. American Mineralogist, 65, 1237–1248.

Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. American Mineralogist, 39, 92–96.

Lumpkin, G. R. and Ribbe, P. H. (1983) Composition, order-disorder and lattice parameters of olivines: relationships in silicate, germanate, beryllate, phosphate and borate olivines. American Mineralogist, 68, 164–176.

Lumpkin, G. R., Ribbe, P. H., and Lumpkin, N. E. (1983) Composition, order–disorder and lattice parameters of olivines: determinative methods for Mg–Mn and Mg–Ca silicate olivines. American Mineralogist, 68, 1174–1182.

Matsui, Y. and Syono, Y. (1968) Unit cell dimensions of some synthetic olivine group solid solutions. Geochemical Journal, 2, 51–59.

Meier, W. M. and Villiger, H. (1969) Die Methode der Abstandsvergeinerung zur Bestimmung der Atomkoordinaten idealisierter Geruststrukturen. Zeitschrift für Kristallographie, 129, 411–423.

Moehlman, R. S. and Gonyer, F. A. (1934) Monticellite from Crestmore, California. American Mineralogist, 19, 474.

Morimoto, N., Tokonami, M., Watanabe, M., and Koto, K. (1974) Crystal structures of three polymorphs of Co_2SiO_4. American Mineralogist, 59, 475–485.

Naray-Szabo, I. (1969) Inorganic Crystal Chemistry. Akademiai Kiado, Budapest.

Ohashi, Y. and Burnham, C. W. (1972) Electrostatic and repulsive energies of the M1 and M2 cation sites in pyroxenes. Journal of Geophysical Research, 77, 5761–5766.

Onken, H. (1965) Verfeinerung der Kristallostruktur von Monticellit. Tschermaks Mineralogische und Petrographische Mitteilungen, 10, 34–44.

Rajamani, V., Brown, G. E., and Prewitt, C. T. (1975) Cation ordering in Ni–Mg olivine. American Mineralogist, 60, 292–299.

Shannon, R. D. and Prewitt, C. T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B24, 925–946.

Smyth, J. R. (1975) High temperature crystal chemistry of fayalite. American Mineralogist, 60, 1092–1097.

Spetzler, H. (1970) Equation of state of polycrystalline and single-crystal MgO to 8 kilobars and 800 K. Journal of Geophysical Research, 75, 2073–2087.

Templeton, D. H. (1955) Rate of convergence of Madelung series by the method of Bertaut. Journal of Chemical Physics, 23, 1629–1630.

Templeton, D. H. and Johnson, Q. C. (1961) Computation of Madelung sums and crystal energies. In R. Pepinsky and J. M. Robertson, Eds., Computing Methods and the Phase Problem in X-ray Crystal Analysis, p. 150–153. Pergamon Press, New York.

Tosi, M. P. (1964) Cohesion of ionic solids in the Born model. Solid State Physics, 16, 1–120.

Tossell, J. A. (1980) Calculation of bond distances and heats of formation for BeO, MgO, SiO_2, TiO_2, FeO, and ZnO using the ionic model. American Mineralogist, 65, 163–173.

Walsh, D., Donnay, G., and Donnay, J. D. H. (1974) Jahn–Teller effects in ferro-magnesian minerals: pyroxenes and olivines. Bulletin de la Société francaise de Minéralogie et de Cristallographie, 97, 170–183.

Walsh, D., Donnay, G., and Donnay, J. D. H. (1976) Ordering of transition metal ions in olivine. Canadian Mineralogist, 14, 149–150.

Whittaker, E. J. W. (1971) Madelung energies and site preferences in amphiboles. I. American Mineralogist, 56, 980–996.

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