

Prediction of Mineral Structure by Energy Minimisation Techniques

S. C. Parker, C. R. A. Catlow, and A. N. Cormack

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Energy minimisation techniques in conjunction with ionic model potentials can now be used to predict the crystal structures of many classes of inorganic solids; the present communication, which is concerned with their application to mineral systems, in particular forsterite and beryl, demonstrates their viability as a technique in structural mineralogy.

Recent developments in computational techniques together with the availability of increasingly accurate interatomic potentials for inorganic solids, open up the possibility of

making reliable predictions of crystal structures using energy minimisation methods. In an earlier study reported elsewhere¹ we developed potential models for silicates which we found

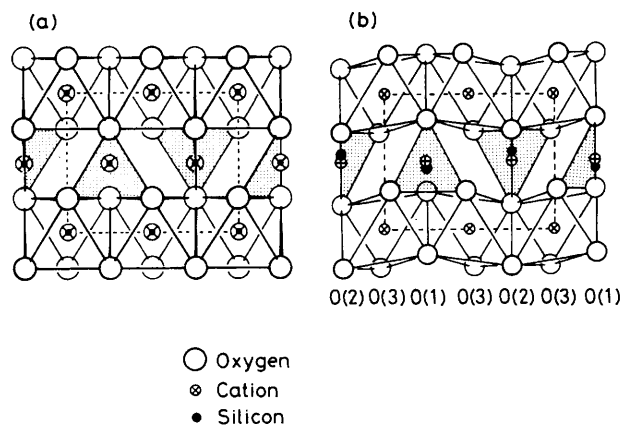


Figure 1. (a) 'Ideal' olivine structure. (b) Observed olivine structure; note rumpling of the oxygen sublattice.

Table 1. Comparison of experimental and calculated atomic co-ordinates for Mg olivine (Mg_2SiO_4 , $a = 4.7534$, $b = 10.1902$, $c = 5.9783$ Å, space group $Pbnm$).

	Experimental			Calculated		
	x/a	y/b	z/c	x/a	y/b	z/c
Mg(1)	0.0	0.0	0.0	0.0	0.0	0.0
Mg(2)	0.99169	0.27739	0.25	0.99323	0.28481	0.25
Si	0.42645	0.09403	0.25	0.45655	0.10909	0.25
O(1)	0.76594	0.09156	0.25	0.76914	0.09442	0.25
O(2)	0.22164	0.44705	0.25	0.20747	0.44018	0.25
O(3)	0.27751	0.16310	0.03304	0.29382	0.16270	0.04429

could usefully discriminate between alternative structural models for pyroxenoids. The present note considers applications of these and closely related models to predictions of the structures of minerals. Our results show that accurate predictions of the structure of this class of compound can now be made—a facility that could be of considerable value in view of the complexity and variety of the structural chemistry of these systems. The present note illustrates the results which may be obtained with two important minerals, the olivine forsterite (Mg_2SiO_4) and beryl ($Al_2Be_3Si_6O_{18}$).

The method used in the calculations, described in detail elsewhere,^{2,3} is conceptually simple: using specified interatomic potentials, the co-ordinates of all the atoms within the unit cell of a compound are adjusted until the minimum energy configuration is attained. The minimisation procedure is not constrained by symmetry considerations, *i.e.* no assumptions are made as to the space group of the crystal. (Unit cell dimensions may also be adjusted; this was not done in the work summarised here, although the structures examined were close to equilibrium with the observed cell dimensions.) The use of this method with large complex structures requires highly efficient summation and minimisation procedures. These are available in the computer code (METAPOCS)³ used in the present study. The interatomic potentials employed in our study are based on an ionic model description with parameterised, two-body short-range potentials. Parameters are taken from the work of Catlow *et al.*¹ and Parker.² The ionic model is clearly an approximation for silicate systems; but our work establishes that it is acceptable for crystal structure prediction.

The first example considered is the mineral forsterite, Mg_2SiO_4 . The structure contains distinct isolated SiO_4 groups; it may be described in terms of a hexagonal close packed array

Table 2. A comparison of the calculated with experimentally determined (ref. 7) co-ordinates of the mineral beryl ($Al_2Be_3Si_6O_{18}$) which has six-membered silicate rings ($a = 9.212$, $b = 9.236$ Å, space group = $P6/mcc$ ref. 143).

	Experimental			Calculated		
	x/a	y/b	z/c	x/a	y/b	z/c
Be	0.5	0.5	0.75	0.5	0.5	0.75
Al	0.33333	0.66667	0.25	0.33333	0.66667	0.25
Si	0.3892	0.1189	0.0	0.3878	0.149	0.0
O(1)	0.3048	0.2352	0.0	0.3199	0.2478	0.0
O(2)	0.4983	0.1473	0.1445	0.5102	0.1473	0.1440

of oxygen atoms with filling of tetrahedral sites by Si and octahedral sites by Mg. The close packed oxygen sublattice is, however, distorted as shown in Figure 1 and the distortion can best be described in terms of 'rumpling' of planes of oxygen ions. We tested therefore whether energy minimisation techniques using the potentials in refs. 1 and 2 could reproduce this mode of distortion. The starting point for the calculation was the ideal structure based on an undistorted, hexagonal oxygen sublattice, although any trial structure may be used. The co-ordinates of the minimum energy structure are compared with experiment⁴ in Table 1. The calculations are found to reproduce accurately the observed rumpling of the oxygen sublattice; and the discrepancies between theoretical and experimental values are in every case small, and within the limits expected for a 'static' simulation, *i.e.* one which omits thermal vibrations.

We next considered beryl, $Al_2Be_3Si_6O_{18}$, the structure of which was originally determined by Bragg and West.⁵ The unit cell is hexagonal: the SiO_4 tetrahedra are linked to form six membered rings with the aluminium ions occupying octahedral sites. We should emphasise that the correct prediction of the crystal structure of beryl is a more demanding test of our potentials than is the case for olivine structures because ring structured silicates contain both bridging and non-bridging oxygen atoms. Indeed it has been proposed⁶ that the oxygen atoms involved in the bridging of SiO_4 tetrahedra are more covalent owing to the difference in the extent of π -bonding between bridging and non-bridging atoms. It might therefore be expected that the potential models employed in the present study would be less reliable when applied to such structures as the models include only one type of $Si \cdots O$ potential. An additional problem arises in experimental studies of the system in that, at the centre of each silicate ring, particularly in natural samples, there are usually small amounts of water and alkali metals. Fortunately, the experimental study⁷ with which we compared our calculations had only small traces of both. The calculated minimum energy structure is given in Table 2; we note that it is also in good agreement with experiment. This suggests both that the alkali metal ions and water molecules do not contribute to the stability of the structure and more importantly that it is not necessary to invoke different bonding schemes for the bridging and non-bridging oxygen atoms in order to account for structural properties.

This work shows therefore that energy minimisation procedures combined with the potentials presented in refs. 1 and 2 are capable of yielding accurately the detailed features of the structures of minerals. Relatively simple ionic model potentials have been used; and although there are unquestionably covalent contributions to the bonding, these seem to have little direct influence on structure other than in a manner which can be assimilated into parameterised two-body potentials.

We are grateful to A.E.R.E. Harwell for generous provision of computer time and for financial support. Financial support from S.E.R.C. is also gratefully acknowledged.

Received, 27th April 1983; Com. 529

References

- 1 C. R. A. Catlow, J. M. Thomas, D. A. Jefferson, and S. C. Parker, *Nature (London)*, **295**, 658.
 - 2 S. C. Parker, U.K.A.E.A. report, A.E.R.E.—TP 968.
 - 3 S. C. Parker, C. R. A. Catlow, and A. N. Cormack, *Acta Crystallogr.*, submitted for publication.
 - 4 K. Fujino, S. Sasaki, Y. Takeuchi, and R. Sadanaga, *Acta Crystallogr., Sect. B*, 1981, **37**, 513.
 - 5 W. L. Bragg and J. West, *Proc. R. Soc. London, Ser. A*, 1926, **111**, 59.
 - 6 D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.
 - 7 F. C. Hawthorne and P. Cerny, *Can. Mineral.*, 1977, **15**, 414.
-