MATTERS ARISING

Simulating silicate structures and structural chemistry of pyroxenoids

CATLOW *ET AL.*[1] have recently described a way of calculating lattice energies of different silicate structures in an attempt to predict which single-chain silicate structure would be the most stable for a particular metal cation or for a particular pair of cations. The stabilization energy (the difference of lattice energies calculated) of one structure with respect to another is often a very small fraction ($\sim 0.1\%$) of the total lattice energy (calculated per Si atom) and therefore a considerable degree of confidence in the values calculated is required.

The essentially ionic model presented has an empirical correction for 'short-range' interaction—presumably for orbital overlap or covalency effects. This correction does not appear to take account of the fact that in some cation environments not all oxygen ligands are equivalent; some oxygens are so-called bridging oxygens between silica tetrahedra and some are directly bonded to one Si atom only. Whether the neglect of this variation in short-range interaction is significant enough to cause appreciable error is not clear.

Nevertheless, there are many further tests Catlow *et al.* could make to clarify the quantitative validity of their model. For example, it is misleading to conclude that the most energetically favoured pyroxene or pyroxenoid structure for Mg^{2+} cations is the diopside structure when it is known that a pure Mg pyroxene has an ortho- or clino-enstatite structure and not a diopside structure. A lattice energy calculation for Mg^{2+} in an ortho- or clino-enstatite structure should therefore show that the latter structures are more stable than the diopside one. (The same argument applies to Fe^{2+}.)

However, the most intriguing point is whether such lattice energy calculations are refined enough to predict cation ordering correctly in such silicates. There is now enough experimental evidence of cation ordering (or the lack of it) in olivines and pyroxenes to provide a testing ground for such calculations. Traditionally explanations of cation ordering have been on the basis of ionic size or, in the case of transition metals, in terms of crystal field stabilization effects. Such explanations are sometimes the result of hindsight and are often less than convincing; sometimes they fail altogether. Clearly therefore it would be very useful to be able to carry out an energy calculation from first principles. Such calculations ought then to be able to predict for example that Fe^{2+} is not ordered in the olivine structure but that Mn^{2+} has a strong preference for the M_2 site—putting Mn^{2+} in the M_2 site rather than the M_1 site should lead to greater stability whereas no appreciable stabilization should occur for Fe^{2+}.

Catlow *et al.* show that the effect of having mixed cations often has a stabilization effect on a particular structure. However, the maximum stabilization will, of course, only be achieved if the correct distribution of cations among the possible sites is chosen. Calculations with different cation distributions should therefore predict the correct one.

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1. Catlow, C. R. A., Thomas, J. M., Parker, S. C. & Jefferson, D. A. *Nature* **295**, 658–662 (1982).

CATLOW AND PARKER REPLY—The comments of Walker on our simulation study of pyroxenoids raise two issues. First, what is the 'accuracy' of the calculated lattice energies; second, what further tests of our method are possible. Regarding the question of accuracy we stress that the methods used by our calculations are exact; there are no errors (above the level of machine accuracy) attributable to our lattice summation techniques. Any 'inaccuracy' arises from inadequacies in our interatomic potentials. Here we note that our potentials perform well in predicting structures of the type of mineral discussed in our article, which supports their reliability in a study of structure discrimination. Moreover, we note that the differences between the energies of different structures are appreciable (that is ~ 1 eV). The fact that these are a small proportion of the total energy does not mean that they are insignificant; indeed the total energy contains large terms which are relatively insensitive to the structure. The position here is analogous to that in quantum mechanical studies of the energies of small molecules, where binding energies, although a small proportion of the total energy may, nevertheless, be reliably calculated. The point raised by Walker concerning the possibility of different potential parameters for bridging and non-bridging oxygen atoms is valid. However, the success of our calculations in accurately predicting structures suggests that this is not a major effect, although refinements of our potentials should clearly take this effect into account.

As further tests of our calculations Walker suggests first that we examine the enstatite structure of $MgSiO_3$ which he correctly remarks is the most stable structure of this phase. Such calculations are indeed in progress; and our results find that the enstatite structure is more stable than the diopside structure for $MgSiO_3$ and $FeSiO_3$; further details of these calculations will be reported shortly. Walker also suggests that we use our techniques to tackle problems relating to cation ordering. It was indeed with the longer-term view of investigating such problems, that we originally developed our simulation methods. The success of our work encourages the extension to the problems discussed by Walker, although we emphasize that the computational demands of such work are considerable.

Finally, we should point out that the calculations we reported had the main aim of investigating whether energy minimization techniques could usefully be applied to silicate structural chemistry. We believe that our work established the viability of the technique in this field. Subsequent studies will aim at refining our potential models and hence the accuracy of our predictions.
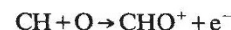
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Chemi-ionization in acetylene flames

EVIDENCE has been presented by Hayhurst and Jones[1] in favour of the preponderance of the reaction

$$CH^* + C_2H_2 \rightarrow C_3H_3^+ + e^-$$

over the reaction

$$CH + O \rightarrow CHO^+ + e^-$$
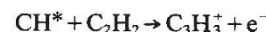
as the primary ionization process in rich acetylene/oxygen flames. This evidence is: (1) low relative concentration of CHO^+, particularly in the reaction zone; (2) double-peaked profile of $C_3H_3^+$ in rich C_2H_2/O_2 flames; (3) double-peaked profile of total ion current in rich C_2H_2/O_2 flames.

All these features may, however, be explained by a mechanism based on CHO^+ alone. It has been realized since the earliest work on mass spectroscopy of flame ions[2] that rapid proton transfer reactions will deplete CHO^+ in flames so that its concentration relative to prominent ions such as H_3O^+ (from protonation