Atomistic simulation studies of mineral surfaces and the role of impurities on their structure and stability

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The aim of our current work is to predict the structure and stability of mineral surfaces. A major difficulty when comparing with the limited experimental data is that surface properties are often dominated by impurities which segregate to the surface. Thus we must also determine the extent to which different impurities segregate and their effect on the surface structure and stability. The approach we have adopted is to use atomistic simulation where the interaction between each atom is described by parameterised potential functions based on the Born model of solids. Once the total interaction energy is obtained, energy minimisation is used to determine the structure and stability of each surface.

We illustrate these methods by describing work on three minerals. (1) $MgAl_2O_4$ (spinel) where the surface structures of the pure material are calculated to be different from the bulk (2) quartz where the surface structures and stabilities are modified by the presence of dissociatively adsorbed water. (3) $CaCO_3$ where impurities segregating to the surfaces can dramatically modify the surface stability. This is best visualised by considering the simulated equilibrium morphologies where the enhanced stability of certain crystal faces cause them to be expressed in the crystal habit.

The surfaces of spinel ($MgAl_2O_4$)

Spinel structured materials show a range of cation distributions from the *normal* distribution where the divalent ion occupies only tetrahedral sites to the *inverse* distribution where they are found in octahedral co-ordination. The most common surfaces of a crystal are generally those with a low Miller index, and experimental work has shown that the low index surfaces do indeed dominate the crystal morphology. We considered the {100}, {110} and {111} surfaces, which in general represent the lowest energy structures[1]. The first unexpected result, was that on cleaving spinel, in all of the orientations considered the surfaces were dipolar i.e. all surfaces must therefore contain defects. This was unexpected because defects normally have the effect of destabilising the surfaces. As defect formation by oxidation is unlikely for spinel as neither magnesium or aluminium have variable oxidation states the surfaces are stabilised by surface vacancies. In addition, the majority of the surfaces of spinel terminate with Al^{3+} cations. This can lead to an unstable surface due to the high charge and low co-ordination. This effect can be reduced if the local surface structure is inverted so as to swap the surface Al^{3+} with Mg^{2+} in the layer below. The resulting inversion of the structure layers leads to the surface energies that are lower than the normal surfaces, with the exception of the most stable {100}[2]. Thus we predict that most of the surfaces of spinel show the structurally distinct inverse-spinel structure. This is exemplified by comparing the energy to exchange an isolated pair into the inverse configuration which is unfavourable in the bulk (137 kJ/mol), slightly unfavourable for the {100} surface at 12 kJ/mol but for the {110} and {111} becomes energetically preferred at –28kJ/mol and –66 kJ/mol respectively. Thus if the crystals were grown at sufficiently low temperatures to prevent cation exchange we might envisage that the inverse structure could be 'frozen' into the crystal structure.

The surface structure of quartz

In contrast to spinel cleaving a framework silicate will result in silicon and oxygen dangling bonds. These can be removed by either allowing the surface to reconstruct or by the addition of water. We modelled the stoichiometric low index surfaces of quartz, including the {00.1}, {01.1}, {01.0} & {01.2}. We found that the addition of water, i.e. $H^+ + OH^-$ across the Si-O bonds greatly stabilised most surfaces, e.g.. the {01.0} the surface energy

Table 1 The segregation energies in kJ/mol of Mg^{2+} and Li^{+} to the surfaces of calcite

Surface	Mg^{2+}	Li^{+}
10.4	127.3	128.3
11.0	130.3	87.7
10.0	84.9	65.6
00.1	115.7	−208.3

was reduced from 2.7 J/m^2 to 1.7 J/m^2. In addition, atomistic simulation also reveals the detailed surface structure. For example the {01.0} surfaces have two possible cuts and the addition of water results in either the terminating silicon atom having a single OH or two OH groups whereas the {00.1} surface silicon atoms all have two OH groups. The resulting morphology, favouring {01.0} over {00.1}, is simply a result in the relative reactivity of the surface silicon and OH groups[3].

The effect of additives on calcite morphology

In this section we describe the influence of Mg^{2+}, Li^{+}, SO_4^{2-} and HPO_4^{2-} additives on the surface stability and morphology of calcite[4]. The surface energies for the low index faces {10.4}, {10.0}, {11.0} and (00.1) were calculated. These results show that the {10.4} surface, which has the smallest surface area is the most stable face, while the first order prismatic faces {10.0} and {11.0} are about equal in stability. Of the low index faces the (00.1) was found to be the least stable. This is not surprising as the basal plane is comprised of alternating layers of Ca^{2+} and CO_3^{2-} ions in successive planes revealing it to be a dipolar surface, and hence it contains surface defects. The predicted rhombohedral morphology agrees well with the experimentally observed morphology[5].

The segregation energies of Mg^{2+} or Li^{+} ions to the different faces of calcite were evaluated and are shown in Table 1. A positive segregation energy indicates a preferential dissolution of magnesium into the bulk of the calcite crystal, while a negative value suggests that magnesium ions prefer to stay at the surface. The results suggest that magnesium ions prefer to dissolve into the bulk from the stable faces. This result is not surprising given that magnesium and calcium carbonates can form a solid solution. However, as calcite is grown in a comparatively low temperature solution it is unlikely that magnesium can diffuse rapidly through the solid, and hence remain at the surface The simulations predicted that incorporation of Mg^{2+} stabilises the first order prismatic faces {10.0} relative to other faces. The substitution of Ca^{2+} ions with Li^{+} ions results in the stabilisation of the polar (00.1) surface. One possible explanation is that for the {10.4}, {10.0} and {11.0} surfaces, lithium substitutes into an interstitial site. This is in contrast to the (00.1) surface where the lithium can interact with the vacant cation sites. The morphological consequence of the increased stability of the (00.1) face is to predict a tabular crystal habit comprising basal (00.1) and {10.4} side faces, which agrees with recent experimental studies of calcite crystallisation in the presence of Li^{+} ions[6].

We next used the same procedure for simulating the effect of the sulphate and hydrogenphosphate anions. The only difference was that only 50% of the carbonate ions were replaced due to the size of the sulphate and hydrogenphosphate anions. These anions were observed to stabilise the {10.0} surface compared to {11.0} or {10.4} with the hydrogenphosphate making a more marked effect. Hence the morphology is dominated by the first order prism face, {10.0} and the extent to which it is stabilised is dependent on the anion and surface concentration. This suggests that morphologies may be a sensitive tool for determining impurity concentrations.

Summary

In summary, the predictions made in this work are consistent with experimental observations and demonstrate the use of atomistic simulations in predicting the effects of additives in crystal growth technology. Future studies will focus improving interatomic potentials, considering a wider range of additives and incorporate the influence of pH and ionic strength on surface selectivity.

References

1. Oliver P.M., Parker S.C., Mackrodt W.C. (1993) *Modelling Simul. Mater. Sci. Eng.*, **1**, 755–60.
2. Davies, M. J., Parker, S. C. and Watson, G. W. *J. Mater. Chem.*, in Press.
3. Baram, P. and Parker, S. C. Submitted to *Phys. Chem. Miner.*
4. Parker, S. C., Titiloye, J. O. and Watson, G. W. (1993) *Phil. Trans. R. Soc. Lond.*, **A344**, 37–48.
5. Mann, S., Didymus, J. M., Sanderson, N. P., Heywood, B. R. and Aso Samper, E. J. (1990) *J. Chem. Soc. Faraday Trans.*, **86**, 1873–80.
6. Rajam, S. and Mann, S. (1990) *J. Chem. Soc. Chem. Comm.*, 1789–91.