Molecular Modelling of Carbonate Minerals: Studies of Growth and Morphology [and Discussion]

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Molecular modelling of carbonate minerals: studies of growth and morphology

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The aim of the work presented here is to develop a computer simulation technique which will predict the surface structure, the morphology and the rate of growth of carbonates. The technique is based on energy minimization in which all atom positions are varied until the lowest energy configuration is achieved. An important development is the incorporation of dynamics which is used to calculate the effect of temperature on the thermodynamic properties including heat capacities and free energies. The energies are calculated by using an interatomic potential based on the Born model of solids. Hence the surface structure is probed on the atomic scale. This also offers the possibility of investigating the influence of selected additives or impurities on the surface structure and the morphology. Thus having established that the technique can reliably model each surface of pure calcite, we have studied the effect of a range of additives including Li, Mg and phosphate: for example, the elucidation of the mechanism whereby phosphate inhibits nucleation. The success achieved to date shows that computer modelling can provide a valuable link between microscopic and bulk behaviour and gives us confidence in extending the technique to other carbonates.

1. Introduction

Much of the recent work on the growth and morphology of carbonates has been to determine the mechanisms controlling crystallization in a biological environment. The focus is increasingly directed towards understanding the nature of the interactions between organic molecules and the crystal surfaces (Addadi & Weiner 1989; Mann *et al.* 1990). In one example, the adsorption of acidic oyster-shell proteins onto rigid substrates has been shown to influence the orientation of calcite nuclei formed from aqueous solution (Addadi & Weiner 1985). One difficulty in interpreting this complex behaviour is the lack of suitable techniques for probing the surface structure and the growth mechanisms at the atomic level. This is particularly important as the surface structure and energy will influence the growth rate of a particular surface and the growth rates of each surface can vary dramatically. This will have a profound effect on the resulting crystal habit. Thus an important step towards understanding the crystallochemical factors responsible for nucleation and growth in inorganic and biological systems would be to predict the structure and energy of crystal surfaces at the atomic level. Molecular simulation is one technique which can probe the surface at the atomic scale and control precisely the number of additives.

Two important developments have allowed simulation techniques to be applied to this area. The first is the significant experimental advances in understanding the

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relationship between the calcite structure and its morphology which have revealed insights into the nature of calcite surfaces (Heijnen 1985; Mann *et al.* 1990). This work provides high quality and detailed results with which to compare and test the simulations. The second development is the considerable increase in computational resources which allows us to model increasingly complex systems. Despite these developments, modelling the interaction between biological macromolecules and carbonate surfaces is only now becoming feasible. However, a necessary first step is to establish whether these techniques can reliably model the effect of the addition of common salts containing anions such as phosphate and cations such as magnesium. In this paper we will outline some of the simulation approaches to modelling surfaces at the atomic scale. We will also attempt to highlight the strengths and weaknesses by focusing on recent work which aims to predict carbonate morphologies and the influence of growth additives particularly on calcite.

(*a*) *Computer simulation methodology*

The ideal approach for determining the structure and bonding in a carbonate would be by direct solution of the Schrödinger equation which treats all atoms and electrons. The complexity of such a calculation makes it computationally prohibitive for all except very simple systems or those containing small fragments of a few tens of atoms. However, the continued development and success of these techniques such as work on the defects in magnesia (De Vita *et al.* 1992) and silicate minerals (Nada *et al.* 1992), suggests that this approach will become routine in the future. Molecular simulations provide an alternative strategy which attempt to combine the reliability of the direct or *ab initio* calculation with the increased complexity associated with the treatment of many more atoms. The basis of the atomistic approach is to calculate the interaction between individual atoms and molecules by using simple parametrized analytical functions, called the potential model. This approach can build on the strengths of the *ab initio* methods by fitting the potential model parameters to the *ab initio* results. Indeed it is usually the reliability of these parameters used in describing the interatomic forces rather than the approximations in the simulation methods which determine the success of the simulation. Thus the inclusion of all the important interatomic interactions, and then the subsequent derivation of the appropriate parameters is critical in determining the outcome of the simulation.

The interaction energies between pairs or groups of atoms include a number of components. The largest component is due to the long-range Coulomb energy which describes the electrostatic interaction between charges. In addition, there are a number of short-range contributions arising from the repulsion between neighbouring charge clouds, the van der Waals attraction, and electronic polarizability. The electronic polarizability is particularly important when modelling highly polarizable anions such as oxygen. This is modelled by using the shell model (Dick & Overhauser 1958), which has a simple mechanical description where an ion is represented by a massless shell attached to a core by a harmonic spring. A final contribution is included for covalently bonded molecules and polyanions where three body and torsional forces are important.

The method for obtaining the parameters which is most widely used and enjoys considerable success is by empirically fitting the parameters to reproduce experimental data. These data can include a range of properties, principally the crystallographic structure and elasticity (Lewis & Catlow 1985). The difficulty in fitting potential parameters to mineral properties is that many parameters need to be derived and often there are insufficient experimental data with which to make a comparison. Hence, the approach of assuming transferability of potential parameters is adopted. This is when parameters derived for one mineral structure, such as the parameters describing the forces in the carbonate group, are transferred to other mineral systems, specifically other carbonates. The assumption of transferability has proved to be highly successful for modelling silicates (Parker & Price 1989). An advantage of *ab initio* methods is that they need not assume transferability and hence the potential parameters of even the most unusual impurity could be calculated independently. However *ab initio* methods do suffer the disadvantage that all the interactions may not be calculated explicitly. Thus before making predictions using any potential it is essential to test the reliability by calculating properties not used in the fitting and where possible to use two potentials which were derived independently. This enables us to test the sensitivity of the results to the details of the potentials. In the following section we summarize the techniques before describing recent simulations on carbonate surfaces.

2. Simulation techniques

The simulation techniques can be subdivided into two classes, static simulations and dynamic simulations. Static simulations, as the name implies, do not include any time-dependent motion. However, during a simulation the atoms are allowed to adjust their atomic positions until they achieve an energy minimum. Thus this has the advantage that an approximate trial structure can be selected (for example replacing a calcium ion in calcite with magnesium) and, after energy minimization, a new structure will be obtained along with the energy of substitution. There is now considerable evidence that this approach can reproduce experimental data on solubilities and defect formation in halides and oxides (Catlow 1987; Catlow & Mackrodt 1982), including such effects as oxygen partial pressure and defect concentrations. Despite being a static technique, this approach can yield valuable information on the morphology of the growing crystal by analysis of the component surface energies. There has been important work on the quantitative treatment for calculating the relative rates of growth with respect to morphological modifications in molecular crystals (Hartman & Heijnen 1983; Heijnen & Duijneveldt 1984; Docherty & Roberts 1988). Hartman & Bennema (1980) discussed the crystal habit controlling factors in terms of the 'attachment energy' (E_{att}) defined as the energy per molecule released when one slice of thickness d_{hkl} crystallizes onto a crystal face hkl. They found that the relative growth rate of a face increases with increasing E_{att}. Another advantage of this technique is that metastable configurations can be studied as the minimization will not necessarily access the global minimum. This has enabled us to gain many insights into the structure and reactivity before progressing to the computationally more expensive dynamic simulations. However, dynamic simulations, which involve solving Newton's Laws of Motion, are necessary because they allow the effect of temperature to be included, either in terms of the thermal contribution to the free energy or by the explicit calculation of diffusion.

(*a*) *Surface calculations*

The methodology we have adopted for modelling the surfaces structures, their stability and the effect of impurities on surfaces is based on the work of Tasker & Mackrodt (Mackrodt & Tasker 1985; Mackrodt *et al.* 1985; Tasker *et al.* 1985). Their work has demonstrated the viability of the approach by successfully modelling the surface properties of a number of ceramic oxides (Mackrodt & Tasker 1989; Davis *et al.* 1989).

Our approach is first to consider the low energy and hence the most common surfaces of a crystal which are generally those of low Miller index. These planes are the closest packed with large interplanar spacings. However, in ionic crystals other constraints also apply. If the Madelung sums are not to diverge with increasing crystal size then the crystal must not only be electrically neutral but must also have no net dipole moment perpendicular to the surface. Bertaut (1958) demonstrated that when there is a dipole moment perpendicular to the surface, the surface energy diverges and is infinite. Such surfaces are therefore unstable, and cannot occur naturally without the adsorption of foreign atoms or surface roughening.

The final structure (and energy) of a surface is determined by the requirement that the system is in mechanical equilibrium. This is achieved by allowing the ions in the surface region to relax to the point at which they experience net zero force. The number of relaxed surface planes is increased to the point at which the surface energy converges. Defects and impurities can be accommodated in the surface but only such that the net charge is zero.

The equilibrium crystal morphology of a material can be determined by applying Wulff's Theorem (Wulff 1901), although it was Gibbs (1928) who first proposed that the equilibrium form of a crystal should posses minimal total surface energy for a given volume. Wulff proposed that a polar plot of surface energy as a function of the orientation of normal vectors would give the crystal morphology. This assumes that the crystal is small and that it can rearrange during growth due to the short distances over which ions have to travel.

(*b*) *Modelling the effect of temperature*

There are two approaches for modelling temperature using either lattice dynamics or molecular dynamics. Lattice dynamics is best suited for calculating spectroscopic and thermodynamic properties of solids at or below the Debye temperature whereas molecular dynamics is most appropriate for simulating time dependent properties, particularly diffusion and high temperature phenomena.

Lattice dynamics is based on an analytical solution of Newton's Laws of Motion which gives the vibrational frequencies. The major limitation of our calculations using lattice dynamics is the use of the quasi-harmonic approximation, in which the vibrational motions in the solid are assumed to arise from independent quantised harmonic oscillators whose frequencies vary with cell volume. These frequencies can be used to interpret infrared and Raman spectroscopic data. In addition, thermodynamic functions such as the vibrational entropy, S, free energy, F, and heat capacity, C_p can be determined, e.g.

$$F = k_{\mathrm{B}} T \sum_i \left(\tfrac{1}{2}x + \ln\left(1 - \mathrm{e}^{-x}\right)\right),$$

where each property is summed over the total number of phonon frequencies, M, and where $x = h\omega_i / k_{\mathrm{B}} T$. The zero point energy $\Sigma \tfrac{1}{2} h\omega_i$ is also included. Thus the crystal surface structure at a given temperature can be predicted by minimizing the free energy, F (Parker & Price 1989).

An alternative method for calculating the vibrational properties of solids is to use molecular dynamics where Newton's Laws of Motion are solved numerically (Jacobs

Table 1. *Interatomic potential parameters for calcite simulations*

(Buckingham potential: $V = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/\rho_{ij}^6$; three body potential, $V = \frac{1}{2}K(\theta - \theta_0)^2$; O–C–O $K = 2.6$ eV rad^{-2}, $q = 120.0°$.)

(i) PJ (shell ion model)

atoms	A_{ij}/eV	ρ_{ij}/Å	C_{ij}/(eV Å^{-6})	charge/e
Ca–O	1111.0	0.30926	0	Ca:2+
O–O	6959.0	0.23654	0	O: −0.97310
C–O	527.5	0.1550	0	C:0.91930

Oxygen core shell spring constant, 74.92 eV Å^{-2}.

(ii) PP (shell ion model)

atoms	A_{ij}/eV	ρ_{ij}/Å	C_{ij}/(eV Å^{-6})	charge/e
Ca–O	1605.415	0.296540	0	Ca:2+
O–O	20431.768	0.212650	3.47	O:1.09478
C–O	0.13258E+13	0.041521	0	C:1.28434

Four body torsion, $K = 0.11294$ eV rad^2; oxygen core shell spring constant, 177.4 eV Å^{-2}.

et al. 1991; Watson *et al.* 1992). The major advantage of molecular dynamics is that the atoms are in motion and hence this method can model diffusing atoms or molecules. This is particularly necessary when dealing with ions in solution where they are in constant motion. On calculating the energies for the ions leaving solution we use the free energy perturbation method (Singh *et al.* 1987). This enables us to find the free energy difference for exchanging ions in solution with the surface.

3. Applications and results

(*a*) *Modelling perfect lattice properties*

In an attempt to assess the reliability of the simulations we have considered various calcite potentials and applied them to selected surfaces. The order of preference depends on the measure of agreement with experimentally observed crystal properties. The results of two of the calcite ($CaCO_3$) potentials are described below. These were supplied by Pavese *et al.* (1992), PP, and Jackson & Price (1992), PJ. The parameters are given in table 1. These potentials were derived by adjusting the parameters to fit the calcite structure and elastic constants to the experimentally observed values. The addition of impurities such as Mg to the calcite surfaces requires an additional Mg–O interatomic potential, see table 2. In this case we derived parameters which best reproduced the structure and elastic constant tensor of dolomite (Landholt & Bornstein 1966) while maintaining those parameters in common with calcite.

(*b*) *Carbonate surfaces and morphology*

We considered first the low index faces $\{1\,0\,\bar{1}\,4\}$, $\{1\,0\,\bar{1}\,0\}$, $\{1\,1\,\bar{2}\,0\}$ and $(0\,0\,0\,1)$ of calcite, where the Miller indices are based on the simplest hexagonal unit cell of $a = 4.99$ Å and $c = 17.06$ Å. A schematic representation of the stacking sequence is given in figure 1. The surface energies were calculated by using energy minimization with the potentials given in table 1. The surface energy is the difference in energy, per unit surface area, of a block of crystal before and after cleaving, and hence represents a small difference between two large numbers which can magnify any

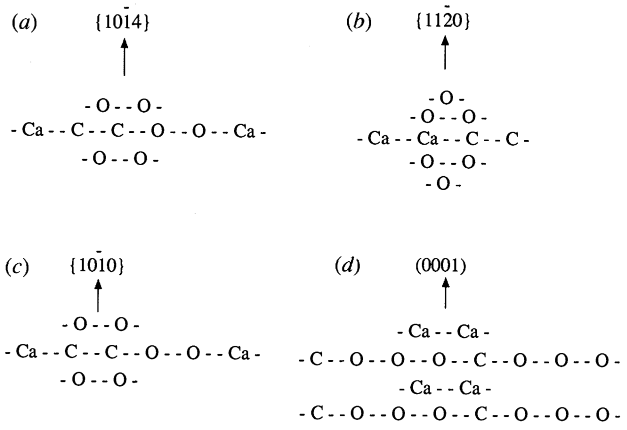

Figure 1. Schematic representation of the stacking sequences for the low-index surfaces of calcite.

Table 2. *Interatomic potential parameters used for the additives on calcite*

(Charges on P, +3.4; O, −1.46667; OH, −1.0. O_c is the carbonate oxygen, O_p is the phosphate oxygen.)

(i) Buckingham potential: $V = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r^6$

atom	A_{ij}/eV	ρ_{ij}/A	$C/(\text{eV Å}^{-6})$	reference
O_p–O_p	1388.773	0.36231	175	van Beest *et al.* (1990)
P–O_p	9034.208	0.19264	19.8793	van Beest *et al.* (1990)
O_p–O_c	3627.500	0.28749	0	Titiloye *et al.* (1992)
O_p–Ca	2396.800	0.29202	0	Titiloye *et al.* (1992)
Mg–O_c	583.754	0.29654	0	Titiloye *et al.* (1992)
Li–O_c	510.092	0.29654	0	Titiloye *et al.* (1992)

(ii) Morse potential: $V = D_b[(1-\exp(-\alpha(r_{ij}-r_0)))^2] - D_b$

O_p–H	$D_b = 5.896$ eV, $\alpha = 2.277$ A^{-1}, $r_0 = 0.948$	Saul *et al.* (1985)

Table 3. *Calculated energies for the selected low-index surfaces of calcite using different interatomic potentials*

surface	energies/(J m^{-2}) PJ	 PP
{1 0 $\bar{1}$ 4}	0.23	0.53
{1 1 $\bar{2}$ 0}	0.50	0.84
{1 0 $\bar{1}$ 0}	0.52	0.92
(0 0 0 1)	1.60	0.83

small discrepancies. The energies (at 0 K and neglecting zero point energy) are given in table 3. These results show that the {1 0 $\bar{1}$ 4} surface is the most stable of all the faces considered by 0.3 J m^{-2}. Both potentials show the first-order prismatic faces {1 0 $\bar{1}$ 0} and {1 1 $\bar{2}$ 0} to be about equal in stability. The (0 0 0 1) basal plane consists of alternate layers of Ca^{2+} and CO_3^{2-} ions in successive planes thereby creating a dipolar surface. The surface dipole was removed by transferring half the surface atoms from the top (i.e. 1 Ca^{2+} ion in figure 1*d*) surface to form a new plane at the

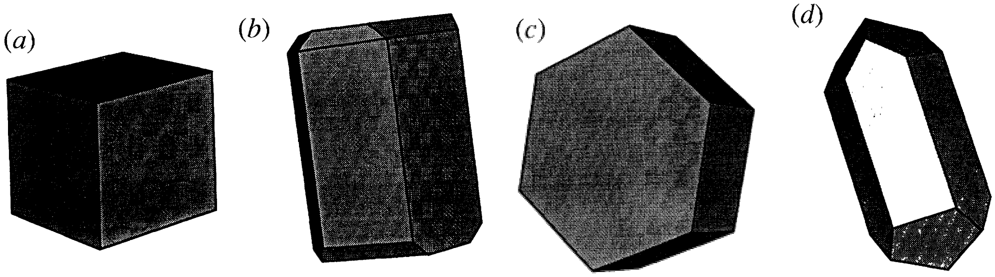

Figure 2. Predicted crystal morphologies showing (a) $\{1\,0\,\bar{1}\,4\}$ rhombohedral, (b) $\{1\,0\,\bar{1}\,0\}$ face stabilized with Mg^{2+}, (c) (0 0 0 1) face stabilized with Li^{+} and (d) $\{1\,0\,\bar{1}\,0\}$ face stabilized with HPO_4^{2-} additives.

bottom of the crystal using the scheme devised by Kummer *et al.* (1967). The removal of the surface dipole allows the energy to converge and to be calculated but this also creates surface vacancies which destabilizes the crystal face. The two potentials differ as to the extent of the destabilization. In addition to being the most stable surface the atomic arrangement at the $\{1\,0\,\bar{1}\,4\}$ surface shows negligible surface reconstruction after relaxation. This indicates that the surface structure is a simple termination of the bulk crystal. The resulting rhombohedral habit (figure 2*a*) has been shown to be consistent with experimental observations of calcite crystallization (Titiloye *et al.* 1991; Mann *et al.* 1990).

We have also extended the range of carbonates considered. Two straightforward applications are to dolomite and magnesite. For dolomite the simulations show that the prismatic faces $\{1\,0\,\bar{1}\,0\}$, $\{1\,1\,\bar{2}\,0\}$ are stabilised with respect to the $\{1\,0\,\bar{1}\,4\}$. The calculated surfaces energies for the three faces $\{1\,0\,\bar{1}\,0\}$, $\{1\,1\,\bar{2}\,0\}$ and $\{1\,0\,\bar{1}\,4\}$ are 0.22, 0.16 and 0.31 $J\ m^{-2}$ respectively. However, on further increasing the magnesium content to magnesite the $\{1\,0\,\bar{1}\,4\}$ again becomes the most stable surface to stabilize a rhombohedral morphology.

(c) *Influence of additives on calcite morphology*

When modelling the effect of additives we consider the segregation energy. This is defined as the difference in energy in substituting an impurity or defect at the surface compared to the bulk. The variation of the segregation energy with surface coverages has been discussed by Mackrodt and Tasker (Tasker 1979; Mackrodt & Tasker 1989; Mackrodt 1989). They have established that for the few cases where there is good experimental data, both experiment and simulation are in good accord. In addition, the heat of segregation can also be considered as segregation from the solution to the surface. This enables us to simulate the relative stability of the additives with respect to the surface in solution conditions.

The heats of segregation of Mg^{2+} from the crystal at 100% coverage of different surfaces are shown in table 4. The positive segregation energy indicates that magnesium prefers to dissolve into the bulk calcite crystal lattice. This is not unexpected as the magnesium is known to form a solid solution with calcite. However, at ambient temperatures magnesium will not diffuse into the crystal, and any loss of magnesium at the surface will be replenished from solution. Indeed using the molecular dynamics to model the segregation from solution we find the segregation energy from solution to be highly exothermic which suggests that the magnesium ions will saturate the solid surface. The calculation of the modified surface energies show that the first-order prismatic faces $\{1\,0\,\bar{1}\,0\}$ are stabilized

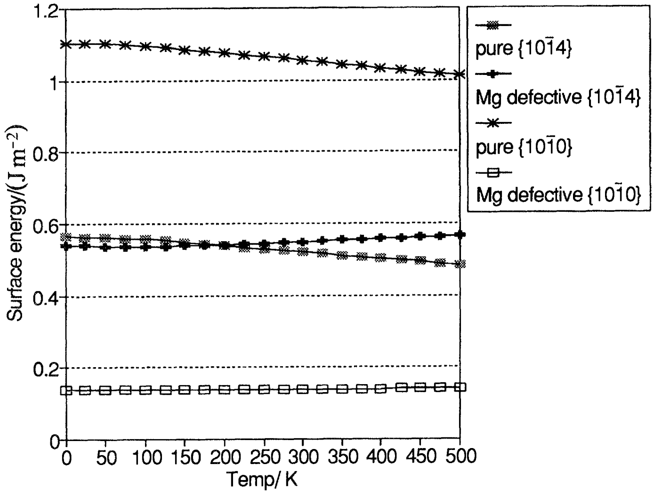

Figure 3. Variation in the harmonic surface free energy as a function of temperature for pure calcite and for calcite with Mg additives on the {1 0 $\bar{1}$ 4} and {1 0 $\bar{1}$ 0} surfaces using the PP potential.

Table 4. *Heats of segregation of* Mg^{2+} *and* Li^{+} *ions on the calcite surface from the bulk* (kJ mol^{-1}) *using the PJ potential*

	100 % coverage	
surface	Mg^{2+}	Li^{+}
{1 0 $\bar{1}$ 4}	127.3	128.3
{1 1 $\bar{2}$ 0}	130.2	87.7
{1 0 $\bar{1}$ 0}	84.9	65.6
(0 0 0 1)	115.7	−208.3

relative to other faces. This is best illustrated by comparing the surface free energies of the {1 0 $\bar{1}$ 0} and the {1 0 $\bar{1}$ 4} in figure 3. The free energies calculated using lattice dynamics show a significant increase in stability of the {1 0 $\bar{1}$ 0} and little change in the {1 0 $\bar{1}$ 4}. On calculating the crystal morphology from the surface energies we found that it is modified to give a first-order prism capped with rhombohedral end faces as shown in figure 2*b*. This morphology is similar to that observed experimentally (Didymus 1992; Didymus *et al.* 1993; Leitmeier 1910).

The substitution of Ca^{2+} ions with Li^{+} ions results in an effective negative charge which was compensated by the addition of a Li^{+} interstitial. The calculated segregation energies are given in table 4 and show that the polar (0 0 0 1) surface is stabilized in contrast to the other faces. Our simulations suggest that the interstitial is energetically unfavourable and that the (0 0 0 1) is stabilized because it can be formed without recourse to interstitial formation. The reason is that the surface has one occupied and one unoccupied calcium site after the reconstruction to remove the dipolar surface. Hence replacing both cation sites with Li^{+} increases the surface density and hence stabilizing the surface. The predicted morphology for the incorporation of lithium ions on the surface is shown in figure 2*c*. The predicted morphology was tabular comprising basal (0 0 0 1) and {1 0 $\bar{1}$ 4} side faces. This is also in complete agreement with recent experimental studies of calcite crystallization in the presence of Li^{+} ions (Rajam & Mann 1990).

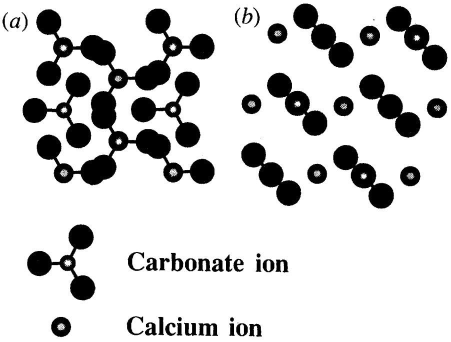

Figure 4. Projection of the (*a*) (0 0 0 1) plane showing a side view of the $\{1\,0\,\bar{1}\,0\}$ surface and (*b*) $(1\,1\,\bar{2}\,0)$ plane showing a side view of the $\{1\,0\,\bar{1}\,4\}$ surface of calcite showing the atomic arrangement of calcium and carbonate ions.

In simulating the presence of hydrogenphosphate on the surfaces, the CO_3^{2-} ions at the surfaces were replaced with HOP_4^{2-}. The phosphorus atom was centred on the vacant lattice site created by the removal of the carbonate ion and the defect surface energy calculated. The HPO_4^{2-} anion was observed to energetically prefer the $\{1\,0\,\bar{1}\,0\}$ surface compared to $\{1\,1\,\bar{2}\,0\}$ or $\{1\,0\,\bar{1}\,4\}$. The consequence of this is to lower the surface energy of $\{1\,0\,\bar{1}\,0\}$ compared to the other faces which results in a modified crystal morphology. Figure 2*d* shows the morphology predicted for the effect of HPO_4^{2-} anions on calcite surfaces. The morphology is that of a first-order prism face, $\{1\,0\,\bar{1}\,0\}$, similar to that predicted for the Mg^{2+} additives.

The selectivity of the hydrogenphosphate anion on $\{1\,0\,\bar{1}\,0\}$ as against $\{1\,0\,\bar{1}\,4\}$ can be attributed to a combination of strong binding and minimal steric hindrance. In the $\{1\,0\,1\,0\}$ surface, the carbonate anions in each layer have one oxygen exposed and strong bidentate bonding, figure 4*a*. The exposed oxygen shows the position where much of the molecule can be free on the surface reducing the strain, while the bidentate bonding ensures good adhesion. This type of arrangement is absent in the other faces. For example, the $\{1\,0\,\bar{1}\,4\}$ (figure 4*b*) faces do not permit a bidentate bonding which is why they are less stable when compared to $\{1\,0\,\bar{1}\,0\}$.

(*d*) *Application to nucleation*

Recent simulations on very thin films of approximately 25 Å suggest that these simulation methods may also be able to aid in modelling and ultimately predicting nucleation control. Calculations on these very thin films show that certain additives can modify and sometimes totally deform the surface structure. The most notable example is observed with the addition of hydrogenphosphate ions especially on the $\{1\,0\,\bar{1}\,0\}$ surface. Simulations show that the hydrogenphosphate causes major disruption to the crystal surface with the formation of small voids (figure 5). However, once we model the effect on films thicker than about 75 Å no disruption of the lattice is predicted. These results confirm the potency of the hydrogenphosphate ions on the surface structure and are supported by nucleation of calcite crystallites as observed experimentally (Didymus 1992; Suzuki *et al.* 1992). Many more systems need to be studied before we can be confident that these results extend beyond calcite but if successful this approach does provide a simple method for screening possible nucleation inhibitors before further experimental investigation.

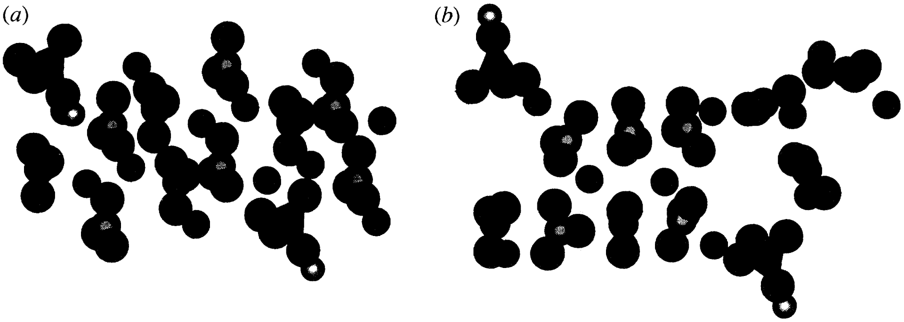

Figure 5. Projection of the $(1\,1\,\bar{2}\,0)$ plane showing the $\{1\,0\,\bar{1}\,0\}$ thin film where one carbonate is replaced by one hydrogenphosphate, (*a*) before relaxation and (*b*) after relaxation showing void formation.

4. Conclusion

There has been much recent progress in the development and sophistication of molecular simulation techniques. We can now predict the influence of growth additives on surfaces and morphology. These predictions are consistent with experimental observations. However, there is still a great need to improve the derivation of interatomic potentials. This will not only increase the accuracy and quality of results, but enable us to extend the simulations to investigate the factors which control, for example, aragonite and vaterite polymorphs in preference to calcite. Other studies aim to extend the range of these simulation techniques to investigate the effect of pH, and ionic strength which can also have a great impact on the stability of these surfaces.

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References

Addadi, L. & Weiner, S. 1985 Interactions between proteins and crystals – stereochemical requirements in biomineralisation. *Proc. natn. Acad. Sci. U.S.A.* **82**, 4110–4114.

Addadi, L. & Weiner, S. 1989 In *Biomineralization: chemical and biochemical perspectives* (ed. S. Mann, J. Webb & R. J. P. William). VCH.

Bertaut, F. 1958 The electrostatic term of the surface energy. *C.r.* **246**, 3447.

Catlow, C. R. A. & Mackrodt, W. C. 1982 *Computer simulation of solids*. Springer-Verlag.

Catlow, C. R. A. 1987 In *Solid state chemistry: techniques* (ed. A. K. Cheetham & P. Day), pp. 231–278. Oxford: Clarendon Press.

Davies, M. J., Kenway, P. R., Lawrence, P. J., Parker, S. C., Mackrodt, W. C. & Tasker, P. W. 1989 Impurity segregation to the surfaces of corundium-structured oxides. *J. chem. Soc., Faraday Trans.* II, **85**, 555–563.

De Vita, A., Gillan, M. J., Lin, J. S., Payne, M. C., Stich, I. & Clarke, L. J. 1992 Defect energetics in MgO treated by 1st principles methods. *Phys. Rev.* B **46**, 12964–12973.

Dick, B. G. & Overhauser, A. W. 1958 Theory of dielectric constants of alkali halide crystals. *Phys. Rev.* **112**, 90–103.

Didymus, J. M. 1992 Morphological studies of molecular recognition in calcite crystallization. Ph.D. thesis, University of Bath.

Didymus, J. M., Mann, S., Sanderson, N. P., Oliver, P., Heywood, B. R. & Aso Samper, E. J. 1993 Modelling biomineralization: studies on the morphology of synthetic calcite. In *Mechanisms and* *phylogeny of mineralization in biological systems* (ed. S. Suga & H. Nakahara), pp. 267–271. Tokyo: Springer-Verlag.

Docherty, R. & Roberts, K. J. 1988 Modelling the morphology of molecular crystals – application to anthracene, biphenyl and beta-succinic acid. *J. Crystal Growth* **88**, 159–168.

Gibbs, J. W. 1928 *Collected works*. New York: Longman.

Hartman, P. & Bennema, P. 1980 The attachment energy as a habit controlling factor. *J. Crystal Growth* **49**, 145, 157, 166.

Hartman, P. & Heijnen, W. M. M. 1983 Growth mechanisms of a crystal face for which more than one surface structure is possible. *J. Crystal Growth* **63**, 261–264.

Heijnen, W. M. M. 1985 The morphology of gel grown calcite. *Neues Jahrbuch Mineralogie*, pp. 357–371.

Heijnen, W. M. M. & Van Duijneveldt, F. B. 1984 The theoretical growth-morphology of calcium-oxalate dihydrate. *J. Crystal Growth* **67**, 324–336.

Jacobs, P. W. M., Rycertz, Z. A. & Moscinski, J. 1991 Molecular dynamics of ionic crystals. *Adv. Solid State Chem.* **2**, 113–185.

Kummer, J. T. & Yao, Y. Y. 1967 Ionic crystal surfaces. *Can. J. Chem.* **45**, 421.

Landolt-Bornstein 1966 *Elastic, piezoelectric and related constants of crystals*. Springer-Verlag.

Leitmeier, H. 1910 Studies on carbonates. I. *Mineral. Abh.* **1**, 49.

Lewis, G. V. & Catlow, C. R. A. 1985 Potential models for ionic solids. *J. Phys.* C **18**, 1149–1161.

Mackrodt, W. C. & Tasker, P. W. 1985 Surfaces and interfaces in oxides. *Chem. Britain* **21**, 366–369.

Mackrodt, W. C., Tasker, P. W. & Colburn, E. A. 1985 The surface segregation of titania in magnesium oxide. *Surface Sci.* **152**, 940–946.

Mackrodt, W. C. 1989 Atomistic simulation of the surfaces of oxides. *J. chem. Soc. Trans.* II, **85**, 541–554.

Mackrodt, W. C. & Tasker, P. W. 1989 Segregation isotherms at the surfaces of oxides. *J. Am. ceram. Soc.* **72**, 1576–1583.

Mann, S., Didymus, J. M., Sanderson, N. P., Heywood, B. R. & Aso Samper, E. J. 1990 Morphological influence of functionalized and non functionalized-alpha, omega-dicarboylates on calcite crystallization. *J. chem. Soc. Faraday Trans.* **86**, 1873–1880.

Nada, R., Catlow, C. R. A., Dovesi, R. & Saunders, V. R. 1992 An *ab initio* Hartree–Fock study of the ilmenite structured $MgSiO_3$. *Proc. R. Soc. Lond.* A **436**, 400–509.

Parker, S. C. & Price, G. D. 1989 Computer modelling of phase transitions in minerals. *Adv. Solid State Chem.* **1**, 295–327.

Pavese, A., Catti, M., Price, G. D. & Jackson, R. A. 1992 Interatomic potentials for $CaCO_3$ polymorphs (calcite and aragonite) fitted to elastic and vibrational data. *Phys. Chem. Minerals* **12**, 80–87.

Rajam, S. & Mann, S. 1990 Selective stabilization of the (001) face of calcite in the presence of lithium. *J. chem. Soc. chem. Comm.* pp. 1789–1791.

Saul, P., Catlow, C. R. A. & Kendrick, J. 1985 Theoretical studies of protons in sodium hydroxide. *Phil. Mag.* B **51**, 107–117.

Singh, U. C., Brown, F. K., Bash, P. A. & Kollman, P. A. 1987 An approach to the application of free energy perturbation methods using molecular dynamics. *J. Am. chem. Soc.* **109**, 1607–1614.

Suzuki, T., Inomata, S. & Sawada, K. 1986 Adsorption of phosphate on calcite. *J. chem. Soc. Faraday Trans.* **82**, 1733–1743.

Tasker, P. W. 1979 The stability of ionic crystals. *J. Phys.* C **12**, 4977.

Tasker, P. W., Colburn, E. A. & Mackrodt, W. C. 1985 Segregation of isovalent impurity cations at the surfaces of MgO and CaO. *J. Am. ceram. Soc.* **68**, 74–80.

Titiloye, J. O., Parker, S. C., Osguthorpe, D. J. & Mann, S. 1991 Predicting the influence of growth additives on the morphology of ionic crystals. *J. chem. Soc. chem. Comm.* **20**, 1494–1496.

Titiloye, J. O., Parker, S. C. & Mann, S. 1993 Atomistic simulation of calcite surfaces. *J. Crystal Growth* (Submitted.)

van Beest, B. W. H., Krammer, G. J. & van Santen, R. A. 1990 Force field for silicas and aluminophosphates based on *ab initio* calculations *Phys. Rev. Lett.* **64**, 1955–1958.

Watson, G. W., Parker, S. C. & Wall, A. 1992 Molecular dynamics simulation of fluoride perovskites *J. Phys. Condens. Matter* **4**, 2097–2108.

Wulff, G. 1901 Zur frage der geschwindigkeit des wachsthums und der auflosung der krystallflachen. *Z. Kristallogr. Kristallgeom.* **34**, 949.

Discussion

K. V. Ragnarsdottir. When Mg stabilizes some calcite surfaces, are intersphere complexes formed? In the case of Pb on surfaces, are intersphere complexes expected and on what surfaces?

S. C. Parker. In the case of Mg the energetically favourable situation is where the Mg replaces Ca until the surface becomes saturated with Mg. We have not looked at Pb. If it follows the behaviour of Ba on binary oxides it will segregate to all surfaces lowering the surface energy, particularly favouring the open, less dense surfaces where repulsion between the Pb atoms will be minimized.

R. Petrovich. When the free energy difference that drives adsorption of Mg^{2+} from the solution at the calcite surface was calculated, how was the effect of the solution on the free energy of the adsorbed Mg^{2+} taken into account?

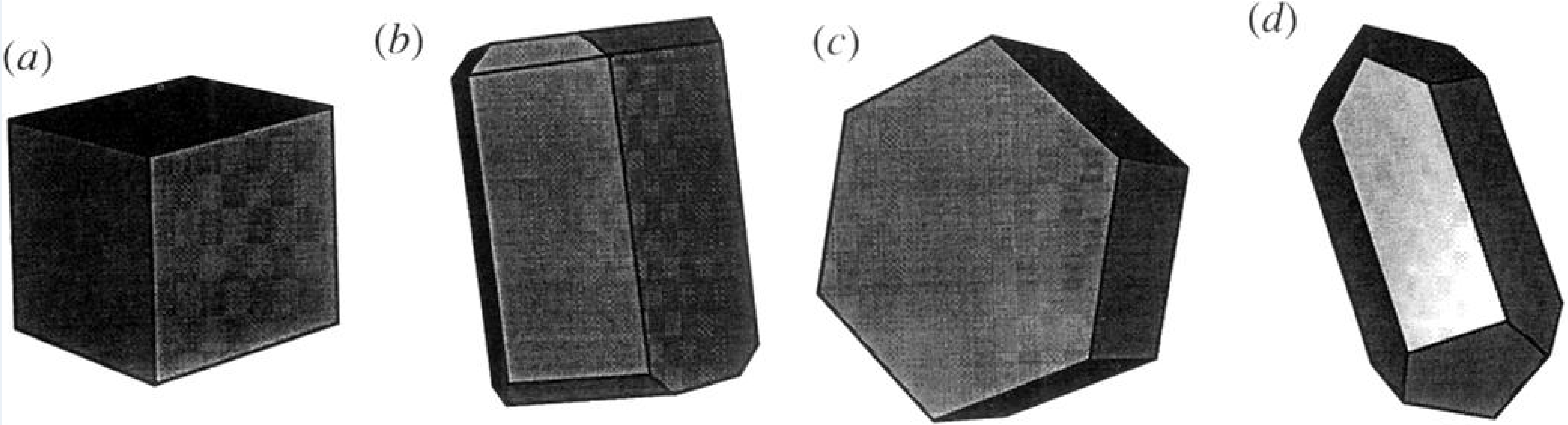
S. C. Parker. We calculated the free energy required to exchange Mg with Ca in solution and the energy required to exchange Ca with Mg at each calcite surface. The sum of the two energies gives the segregation energy from solution. Thus the effect of the solution is determined by the sign and magnitude of the first exchange term.

M. L. Coleman. Can complex ion mixtures be worked with?

S. C. Parker. Yes, but reliable descriptions of the interatomic force are required for each new ion introduced into the mixture with every other ion already present.

M. L. Coleman. Will it be possible to do the inverse problem? Using trace elements concentrations, sector zoning and morphology, could fluid composition and/or precipitation rate be constrained?

S. C. Parker. I am confident that solving the inverse problem will be possible, although this will require an order of magnitude increase in the reliability of the models. We have seen this level of improvement in the last five to ten years and as more groups use computer simulation as one of their routine tools the reliability will correspondingly increase. A further problem is trace elements of very low concentration (parts per million) can have an impact on morphology by segregating to certain surfaces. Thus there will be a requirement for increased computational resources and a lot of detailed and accurate data.



igure 2. Predicted crystal morphologies showing (*a*) $\{1\,0\,\bar{1}\,4\}$ rhombohedral, (*b*) $\{1\,0\,\bar{1}\,0\}$ face abilized with Mg^{2+}, (*c*) $(0\,0\,0\,1)$ face stabilized with Li^{+} and (*d*) $\{1\,0\,\bar{1}\,0\}$ face stabilized with HPO_4^{2-} dditives.