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THE STRUCTURAL MORPHOLOGY OF OLIVINE. I. A QUALITATIVE DERIVATION: DISCUSSION

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In his paper on a qualitative derivation of the growth habits of olivine, 't Hart (1978) considers the surface compositions represented in my article on the same topic (Fleet 1975) to be incorrect, arguing that the surface populations of *M*1 and *M*2 cations are too high. However, I feel that the inconsistency between the surface I represented and that required by the *PBC* theory (Hartman & Perdok 1955) points to possible conceptual limitations in the latter. Discussion of these will be prefaced by a distillation of my own understanding of the process of crystal growth, as this has not been covered in previous publications.

The habit of a crystal grown from solution is a compromise between i) the tendency to minimize specific surface energy, and ii) growth kinetics. Crystal faces develop parallel to, and are defined by, surfaces of minimum surface energy. For any particular face $(h'k'l')$, such surfaces are separated by a distance d_{hkl}, where *hkl* is an integer multiple of $h'k'l'$, as required by space lattice and translational symmetry requirements. Probable growth surfaces can usually be assigned by inspection of appropriate structural projections. This was attempted for important pinacoid and prism faces in my study on olivine (Fleet 1975). The field of crystal-growth kinetics is quite complex and, in general, little understood. However, those kinetic factors that are exclusively structure-related may be anticipated quite readily. Dominant amongst these is the facility with which the components of the crystal (particularly the polyatomic ones such as molecules and complex ions) may be organized on the various growth surfaces presented by the crystal. Clearly, it must be easier to assemble structural repeat units on growth surfaces of high surface-energy than on surfaces of low surface-energy. The stereochemical properties of a growth face and of the structural components attached to it are of paramount importance in this connection. These criteria were examined in a qualitative way in my discussion of the morphology of olivine. The present concepts lead to a physical interpretation of the Donnay–Harker law (Donnay & Harker 1937) as, in general, the probability of a low-energy surface and the ease of assembly of structural repeat units will tend to, respectively, increase and decrease with increase in d_{hkl}.

The surface composition of a growth layer of a multicomponent crystal may not lend itself to precise definition, particularly when 'free' cations have to be accommodated. For olivine, the problem is simplified by considering a crystal of forsterite, Mg_2SiO_4, growing from a liquid of the same composition. As discussed in my article, the nearest-neighbor coordination polyhedra must be similar in both solid and liquid. Thus, virtually all the surface oxygens must be bonded to nearest-neighbor Mg^{2+} cations and virtually *all* of the *M* protosites, which accommodate the surface Mg^{2+}, have to be occupied. In defining the surface compositions in Figure 2 of my article, *M*-site cations in protosites having three or more surface oxygens were associated somewhat arbitrarily with the crystalline phase. A more precise definition seems unnecessary and irrelevant to my crystal-growth model. The surface composition represents neither that of a vacuum-dried crystal nor that of a hypothetical detached and isolated individual growth-layer.

In the *PBC* theory the attachment energy (E_{att}) of individual growth layers is used as a measure of growth rate. Whereas this theory has played an important role in the development of our understanding of the process of crystal growth, it does appear to have certain conceptual limitations: (1) An isolated growth layer is a purely hypothetical concept. Some degree of prestructuring must occur adjacent to the crystal surface, perhaps to the extent of forming a definite transition zone on the crystal-liquid interface. However, such prestructured components would not be in the form of a detached growth-slice having broken bonds complementing broken bonds on an adjacent surface. A growth layer must form through nucleation and subsequent progressive assembly of structural components on a developing substrate. Thus, where inappropriately arranged, prestructured material might actually hinder crystal growth rather than promote it. (2) The *PBC* theory does not take into account the detailed stereochemical properties of growth faces and, therefore, ignores what may be the most significant factor controlling the development of growth habit. (3) The 'growth habit' determined from E_{att} is precisely defined, yet the development of an individual form associated with a particular habit characteristically varies with the conditions of crystallization. In calculating the E_{att} habit, a term that approximates the specific surface energy is normalized with respect to d_{hkl}. Although this could be interpreted as adding a kinetic factor to the equilibrium habit, its physical significance is somewhat obscure and there seems no basis for referring to the E_{att} habit as *the* growth habit. (4) The *PBC* theory is intrinsically inapplicable to crystals with noncentrosymmetric structures. A ready explanation of this limitation is that the differential development of non-equivalent forms related by a centring operation is directly or indirectly a function of the stereochemical properties of the corresponding growth faces.

The hypothesis of crystal growth which I have outlined above does not allow for simple mathematical description. This may seem somewhat incongruous in view of the organized nature of the crystalline state. However, the development of a growth habit is not, in general, an equilibrium phenomenon. I believe this discussion has emphasized that the process of crystal growth is, at least in part, reaction-path dependent. Hence, in common with many facets of chemical kinetics, meaningful quantification may only be forthcoming through empirical means.

REFERENCES

The references are listed after the reply.

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