

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

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In his discussion, Fleet (1979) raises two major points: the surface composition of olivine crystal faces and conceptual limitations in the *PBC* theory. We shall consider the latter first and in the same order as Fleet.

1. The first concept discussed is that of an isolated growth layer. We have the impression that Fleet's idea of the growth mechanism advocated in the *PBC* theory is one in which 'a detached growth slice' is formed in the non-crystalline phase adjacent to the crystal surface, hovers there, and then suddenly attaches itself onto the surface. However, no such concepts exist in the *PBC* theory. The growth layer, or slice, is a layer formed either through nucleation or created by a screw dislocation, expanding laterally on the surface during the growth process. We agree with Fleet that some degree of prestructuring could occur, but as yet this aspect is highly speculative.

2. The second limitation would be that the *PBC* theory does not take into account the detailed stereochemical properties of growth faces. We think it does, as we take into account (i) the chemical bonds formed during crystallization and (ii) the surface energies of the faces (Hartman 1973, 't Hart 1978b), the latter being based on a model of the atomic surface configuration of those faces. Further comments are given below.

3. Fleet finds the physical significance of the 'growth habit' as determined from E_{att} somewhat obscure. The growth rate R_{hkl} of a face (hkl) is determined not only by the conditions of crystallization (*e.g.*, supersaturation, temperature and impurities) but also by the crystal structure. Calling the former the external factors and the latter the internal factor, then we can find the former by theoretically deriving the latter. For the internal factor several assumptions exist. A quantified Donnay-Harker

law assumes that R_{hkl} is proportional to $(1/d_{hkl})^m$, where $m \geq 1$ (Hartman 1978a, b). The *PBC* theory assumes, for lack of a better expression, that R_{hkl} is proportional to $E_{att}(hkl)$. Only on the basis of this assumption is the E_{att} habit called *the* (theoretical) growth habit. Incidentally, it should be remarked that E_{att} does *not* approximate the specific surface energy γ , but rather

$$E_{att} \approx 2 V \gamma / (Z d_{hkl}) \quad (1)$$

where Z is the number of molecules or formula units in a primitive cell of volume V .

4. It is incorrect to say that the *PBC* theory is inapplicable to crystals with noncentrosymmetric structures. A qualitative classification into *F*, *S* and *K* faces is always possible, because for polar faces the condition that a *PBC* or a slice should not have a dipole moment has to be dropped. Actually, such work has been done for quartz (Hartman 1978a) and for $\text{Hg}(\text{CN})_2$, with space group $I\bar{4}2d$ (Lédésert & Monier 1965). For a quantitative approach E_{att} is evidently not the only factor to be considered, as it is the same for (hkl) and ($\bar{h}\bar{k}\bar{l}$). On the basis of the spiral growth mechanism Cadoret & Monier (1967) found that the different electronic polarizability of the outermost atoms must be one of the main causes of the different growth rates of opposite faces.

We now turn to the surface populations of M cations on faces of olivine as represented by Fleet (1975) and by 't Hart (1978a). We disagree with Fleet's assertion that 'the surface composition of a growth layer of a multicomponent crystal may not lend itself to precise definition'. Indeed, as Fleet states in his discussion, crystal faces are defined by surfaces of minimum surface energy. This surface energy can be calculated using some model for the interatomic forces, such as, *e.g.*, electrostatic forces. Thus, it is possible to decide which surface configuration will be the most stable one by computing the lowest value of the specific surface energy or of E_{att} , both

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quantities being proportional to each other for a given face (*cf.*, eq. (1); Hartman 1973, 't Hart 1978b).

The surface composition as considered by Fleet (1975) originates from his assumption that nearest-neighbor coordination polyhedra must be similar in both solid and liquid and that therefore, all of the surface oxygens must be bonded to nearest-neighbor Mg^{2+} cations so that virtually all of the M protosites have to be occupied. We have three remarks.

1. Why do only the oxygens need Mg^{2+} cations and not these Mg^{2+} cations other oxygens as well? Evidently no definite surface composition will be obtained when the coordination polyhedra are to be maintained.

2. The Mg^{2+} ions on the surface of (010) are all linked to three surface oxygens. Then why associate these arbitrarily with the crystalline phase? Considering only the number of $Mg-O$ bonds as Fleet does, it would be more logical to say that half of the Mg^{2+} ions are associated with the crystal, the other half being associated with the fluid. In that case the surface composition as derived by 't Hart (1978a) is obtained. The ions associated with the fluid are not fixed in the crystallographic M positions, but subject to the common diffusion process in the fluid. This means that in the fluid the coordination polyhedra are not present as static entities, but constantly disintegrated and formed again.

3. The occupation of all M protosites creates a dipole moment at the surface and therefore a very high electrostatic surface energy. This is obviously in conflict with the condition of minimum surface energy.

Finally, we agree with Fleet that the growth habit is not an equilibrium phenomenon. Yet, the surface configurations of faces that grow by a layer mechanism are determined by the specific surface-free-energy of the interface crystal-fluid. In using the specific surface energy (or E_{att}) we make two constraints: (i) entropy effects are ignored, which is presumably

correct for temperatures well below the melting point, and (ii) the fluid is considered as isotropic, in the sense that its interaction with the crystal is either ignored or assumed to be the same for the crystal faces considered.

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