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Crystal structure and crystal growth: II. Sector zoning in minerals

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Abstract

A model for sector zoning is based on the premise that each face will have an adsorption layer of characteristic composition on its surface during growth, part of which may be metastably incorporated by lateral spread of growth steps. The adsorption layer will be superimposed on a distinct surface within the crystal structure: this surface is that one across which the potential bonding energy is at a minimum. Adsorption of cations into different types of partially-completed sites, or protosites (Nakamura, 1973) on this surface is critical. When a favorable protosite is available, it is assumed that (1) highly charged, small ions (or strongly bonding atoms in general) will be preferred over normal occupants, but if there is little difference among possible cations in this respect, (2) the cation partition coefficient protosite/growth-medium will be closer to one than the coefficient completed-site/growth-medium. Charge-compensating cation substitutions on the surface are not assumed to be necessary, since temporary charge balance could be attained by adsorption of additional anions, and permanent charge balance by substitutions within the new, permanent growth step. Rationalizing the sector zoning in a mineral involves locating the exposed surface within the crystal structure for each face, identifying the favorable protosites thereon, and considering the possible substituent cations. The model has been applied with apparent success to titanaugite, staurolite, quartz, andalusite, brookite, plagioclase, and other minerals.

Introduction

Chemical sector zoning may be described as the existence of different compositions in different growth sectors of a single crystal. A growth sector (Hollister, 1970) or face locus (Frondel *et al.* 1942) is defined by the face on which the growth has taken place; thus growth sectors are essentially pyramidal in form, with the given face at the base, and a point in the interior of the crystal, usually the center or seed, at the apex.

Sector zoning has been described in many minerals and synthetic compounds; a classic example is titanaugite (*e.g.* Pelikan, 1896; Holzner, 1934; Hollister and Gancarz, 1971). Many examples described in older literature are cited by Frondel *et al.* (1942), and more recent studies are cited by Hollister and Gancarz (1971). Most early descriptions relied mainly on optical observation or very limited chemical analysis; not until the advent of the electron microprobe was it possible to study sector zoning systematically and completely.

Attempts to explain sector zoning in structurally complex minerals have also been made only recently. Hollister (1970) constructed a model for staurolite based mainly on concepts of local charge balance. Hollister and Gancarz (1971) extended this model to titanaugite. Leung (1974) attempted to explain sector zoning in titanaugite by local metastable variation in liquid composition near the faces, while Nakamura (1973) proposed that a critical factor in augite is the geometric flexibility of the partially exposed cation sites or *protosites.*

This paper presents a model for sector zoning based on partial incorporation of an adsorption layer, which is assumed to have different compositions on different faces. Some rules for determining the composition of the adsorption layer are tentatively proposed. The model is tested on all known well-documented cases of major-face sector zoning in minerals.

The model

In most cases, the forms developed on sector-zoned crystals are relatively limited in number, and are those forms which are normally developed on that particular mineral. Furthermore, the morphology of a crystal may be predicted to a first approximation from its structure, using any of several methods as discussed in Part I (Dowty, 1976), and the forms which are actually developed on sector-zoned crystals of augite, staurolite, quartz, *etc.* are usually those predicted. For such prominent faces it is reasonable to suppose that growth takes place by propagation of growth steps or layers (*e.g.* Buckley, 1951). Thus these forms are usually the flat or *F* forms as defined by Burton and Cabrera (1949), Hartman and Perdok (1955), or in Part I. In such a mode of growth, there will be a certain surface parallel to each rational face which is exposed to the growth medium before it is covered over by a new step. The growth steps are presumed to have thickness *d*, the interplanar spacing, or some integral multiple of *d*, so that the level in the crystal structure which is thus exposed is always the same. It is an important assumption of the present model that there will usually be only one such surface (sometimes a small number), and that it will be a *surface of least bonding* (Part I). The location of the surface of least bonding within the crystal structure may be found by the computational method given in Part I, by the periodic-bond-chain method (Hartman and Perdok, 1955), or by inspection of projections if the structure is not too complicated.

When a crystal face grows rapidly, concentration gradients may be set up in the growth medium adjacent to the face, resulting in nonequilibrium partitioning of elements between medium and crystal face (Burton *et al.* 1953). If this phenomenon is responsible for sector zoning, it is predicted that the fastest-growing faces should have the highest content of impurities, if growth rate perpendicular to the face is the controlling parameter, or perhaps that the slowest-growing faces should have the highest impurity content, if the lateral spreading rate of layers is the critical factor (Kröger, 1973, p. 12). Neither prediction appears to be consistent with all the examples discussed below.

This paper will assume a mechanism for incorporation of foreign ions similar to that proposed by Hall (1953). In Hall's model, there is an adsorption layer present on the surface of each face, which may have a composition distinctly different from either the interior of the crystal or the growth medium. If growth is moderately rapid, part of the adsorption layer is incorporated into the crystal. On *F* faces, this will occur when the exposed surface is covered over by lateral spread of a new layer. The problem of sector zoning thus becomes that of specifying the composition of the adsorption layer, which is assumed to be superimposed on, or to modify, the surface of least bonding. In most mineralogical cases, we are concerned with cations (metals), since oxygen (or sometimes sulfur) is generally the only anion present. Cations will tend to be adsorbed onto the exposed surface in locations that correspond at least roughly to regular sites of the crystal. Cations may be adsorbed into other positions, but these are unlikely to be incorporated when a new layer covers the surface. Thus the key to sector zoning is considered to be the occupancies of partly exposed cation sites or *protosites* (Nakamura, 1973) on the surface of least bonding.

As discussed by Nakamura (1973), one of the principal factors that will govern the admission of foreign cations is the geometric flexibility of protosites. For the propose of defining this flexibility, protosites may be classified on the basis of the number of bonds in the first coordination sphere that are directed to atoms on the crystal side of the surface of least bonding compared to the total number of potential bonds for the site, which would include those directed toward atoms that have not yet become firmly attached to the crystal (the "dangling bonds"). The most common and important case is that of an octahedral site. Probably the most advantageous configuration for adsorption is the 3/6 or half site (Fig. 1a). This case is particularly interesting, because if it is assumed that all six bonds are roughly equivalent it makes little difference to the template fraction (see Part I) whether or not a cation is present; the number of bonds crossing the surface of least bonding is the same in both cases, three. Thus cations in such sites may be regarded as completely "replaceable." If four of the bonds are directed to the crystal, producing a 4/6 site (Fig. 1b), then the cation site is almost certainly occupied, and the environment around the cation is probably fairly close to that in the interior of the crystal. However, it appears from the examples below that a certain amount of replacement of the preferred cations by impurity cations can take place in 4/6 sites. A 5/6 site (Fig. 1c) is probably very close to the configuration within the crystal, and foreign cations are presumably not usually tolerated. When the site is 2/6 or 1/6 bonded to the crystal (Figs. 1d, e), it is quite possible for some cation to be adsorbed onto the face in the general neighborhood of the site, but if such cations do not suit the internal structure, their relatively weak bonding probably allows them to be expelled by surface diffusion as the new growth begins to cover the exposed face. In the classification

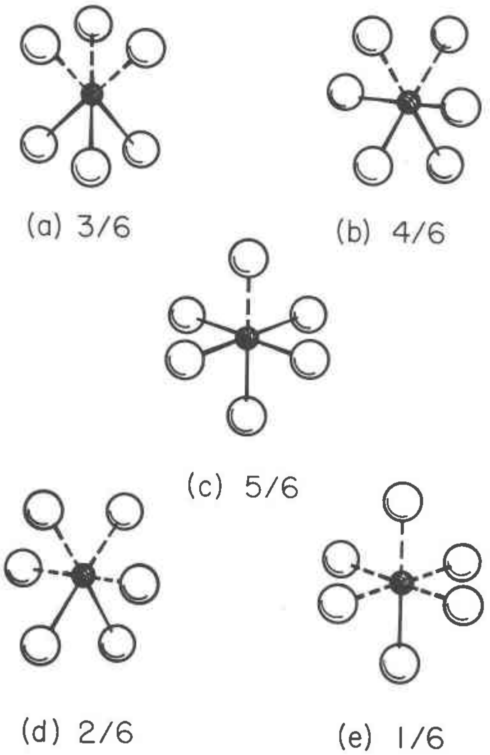

FIG. 1. Classification of exposed octahedral cation sites.

of four-coordinated (tetrahedral) sites, and sites with coordination number higher than six, the possibilities are somewhat analogous to those of six-coordination.

Factors governing the population of adsorbed cations

Atoms in the adsorption layer are probably rather mobile, so that cations are not permanently attached to protosites. Nevertheless, those cations which are bound most firmly to a protosite are those which will spend the most time there, and which are most likely to be incorporated into the crystal. In covalent crystals, the most firmly held atoms will presumably be those which have the strongest bonds crossing the surface of least bonding. In ionic crystals, the exposed protosites represent regions of negative electric potential, hence we may expect that *the cations which will be bound most firmly are those which have high charge and small size* (Rule 1). This first criterion bears a certain resemblance to Goldschmidt's rules for the substitution of minor elements in crystals. It is assumed that coupled substitutions of cations on the surface will not be necessary to maintain charge balance, since a temporary balance could be attained by adsorption of greater or lesser numbers of anions. The necessary compensation within cations sites could occur in a subsequent growth layer. For example, Ti^{4+} could replace Al^{3+} in a protosite on the surface, and the compensating substitution of Al^{3+} for Si^{4+} could occur in the next layer. In this respect, the present model differs from that of Hollister (1970) and Hollister and Gancarz (1971), who assumed that coupled substitutions would be necessary on the surface.

In the absence of charge, size, and other bonding limitations, *the composition of the adsorption layer probably tends to approach that of the growth medium more closely than does the interior of the crystal* (Rule 2). That is, the partition coefficients between growth medium and adsorption layer will tend to be closer to one than those between the growth medium and the interior of the crystal. If growth is sufficiently rapid and diffusion slow, there may also be effects due to diffusion gradients, as in the Burton *et al.* (1953) theory, but this can never lead to an actual crystal/medium impurity partitioning of greater than one if the equilibrium partition coefficient is less than one.

This second rule appears to have been the principal criterion used by Nakamura (1973), who did not consider charges or differential bonding. However, sector zoning in most of the minerals examined below seems to be governed by the first rule. The influence of second and higher coordination spheres, to which Nakamura ascribed sector zoning in some cases, is not considered to be important in this paper.

Even if a cation site is favorably exposed, some adsorbed atoms may be so unsuitable to the completed site that they are expelled during or immediately after the covering of the surface by a new layer. Thus in addition to the above rules for adsorption, the intrinsic cation preferences of each site must also be considered. In many cases, independent data may not exist on this question, and it is sometimes necessary to make *ad hoc* assumptions about site preferences. A further problem, if site occupancy data are available, is that the observed cation distributions may themselves have been determined partially by growth history.

Exposure of tetrahedral sites

Although partial exposure of tetrahedral sites is probably not common on the major faces of many types of silicates, in other cases it is unavoidable. However, it appears unlikely that cations other than silicon would be adsorbed onto such protosites, because there are no common cations which have both higher charge and suitable size. The most common substituent for silicon—aluminum—is larger and has a smaller charge. On the other hand, when a tetrahedral site is occupied partly by aluminum at equilibrium, it seems possible that the aluminum could be replaced by silicon.

Although direct substitution for silicon on the surface is thus not expected to be important, those coupled substitutions which involve a tetrahedral cation (*e.g.* octahedral Al for Mg on the surface and tetrahedral Al for Si in a subsequent layer) are nevertheless more likely to be preserved. As pointed out by Hollister (1970), in order for the mineral to reequilibrate, simultaneous diffusion of both cations is necessary, and diffusion of tetrahedral cations is in general rather slow.

Examples

The following examples represent all reasonably-well documented cases of sector zoning in minerals which could be located in the literature. The general morphology of each mineral is discussed in Part I (Dowty, 1976), and references to structural data are also given there.

Titanaugite

Essentially all accounts of sector-zoned or hourglass titanaugite demonstrate that the prism sectors are enriched in Ti with respect to the basal sectors. The prism sectors are normally under the forms {110}, {100}, and {010}, while the basal sectors are usually under the form $\{11\bar{1}\}$, although terminations cannot always be identified. Hollister and Gancarz (1971) found that the order of decreasing concentration of Ti, Al, and Fe^{3+} is {100}, {010} {110}, and $\{11\bar{1}\}$.

The surfaces of least bonding for all three major prism forms do not cross any Si–O bonds, but do expose *M*1 and *M*2 sites (Fig. 2). The form {100} has 3/6 half sites exposed for both *M*1 and *M*2, and it is therefore predicted that this form could very easily adsorb and incorporate the highly charged and relatively small Al, Ti, and Fe^{3+} ions. Titanaugites generally have *M*2 sites nearly filled with Ca, and if we assume that *M*2 does not tolerate Al, Ti, and Fe^{3+} ions, we do not expect much replacement of Ca. However in cases in which the augite is more subcalcic, and presumably saturated (at equilibrium) with Mg and Fe^{2+}, it may be that excess amounts of Mg and Fe^{2+} could be adsorbed and incorporated into *M*2 on {100}, by virtue either of their smaller size or their greater abundance (or both), as proposed by Nakamura (1973).

Although the crystal boundary for the (110) face is drawn in Figure 2 with a zig-zag line, this is done for clarity only; a strict plane may be passed through the structure parallel to (110), intersecting the same bonds shown in Figure 2. This is not quite the case for {010}, however; the O2 oxygen atoms terminating the Si–O bonds at the edges of the silicate chains all have the same *y* coordinate, so that if a surface of least bonding is to be obtained, it must be bent an infinitesimal amount around the centers of the O2 oxygen atoms (the amount of bending is greatly exaggerated in Fig. 2). Both the {110} and {010} surfaces expose *M*1 sites, but only as 4/6 configurations. Presumably, this allows some adsorption and incorporation, but not as much as on {100}.

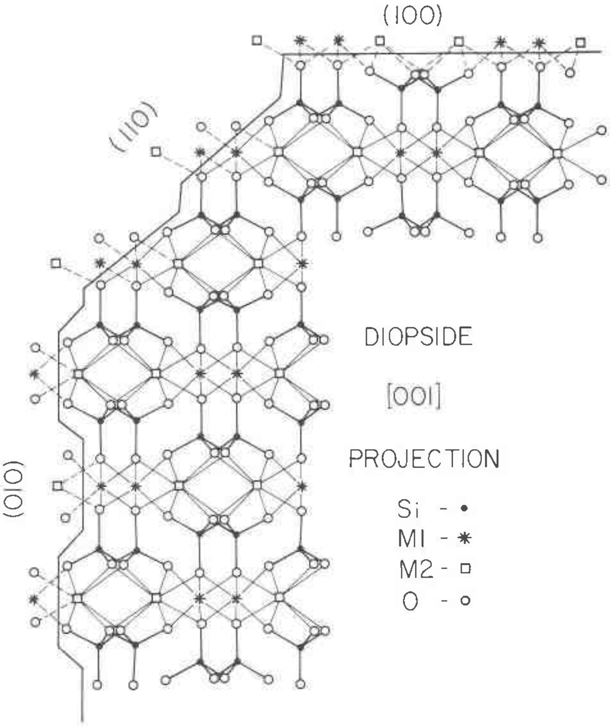

FIG. 2. Projection of the diopside structure down [001].

A projection parallel to face $(\bar{1}11)$ is shown in Figure 3. The surface of least bonding marked $(\bar{1}11)a$ was located by the computer technique and intersects *M*1 sites as 4/6 sites. However, the plane marked $(\bar{1}11)b$, which exposes only *M*2 sites, is also a possibility, and it becomes the surface of least bonding if the *M*2 bonds are made slightly weaker relative to the *M*1 bonds. These two planes thus have about the same total bond strength, and it might be conjectured that each is the exposed surface about half the time.

If we assume that growth is laid down in layers or slices of thickness *d*, the interplanar spacing, we can compute the number of sites of each type exposed on each face per unit-cell volume. We obtain four *M*1

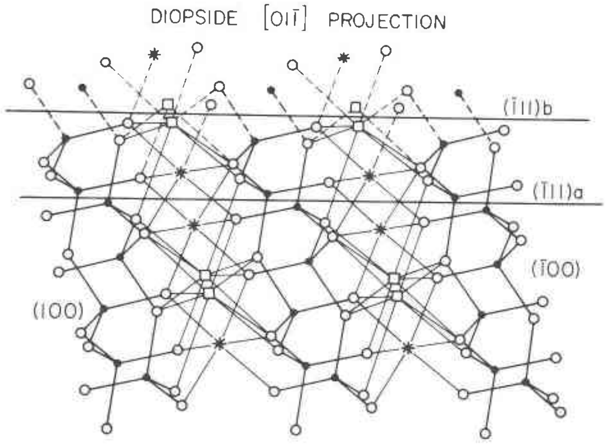

FIG. 3. Projection of the diopside structure down $[01\bar{1}]$. Symbols are the same as in Fig. 2.

half-sites on {100}, two *M*1 4/6 sites on both {110} and {010}, and on $\{11\bar{1}\}$ we take the average of the two possible planes, which is one *M*1 4/6 site. These numbers correlate well with the relative concentrations of highly charged cations in the various sectors found by Hollister and Gancarz (1971). Presumably, the small differences between {110} and {010} sectors are due to some rather subtle difference in potential or geometric nature of the exposed sites. Again, it is assumed that the exposure of *M*2 and Si sites on the surfaces of the faces is essentially irrelevant, and that the excess charge of the cations in *M*1 can be compensated by substitution of Al for Si within the new growth step or layer.

Staurolite

As described by Hollister and Bence (1967) and Hollister (1970), the sector zoning is rather complex, but the principal phenomena are: (1) the {001} sectors, compared to the others, have abundant substitution of excess Al in the Al(3) sites (which are normally partially vacant), compensated by the replacement of Si by Al; (2) the {010} sectors have an abundance of the coupled substitution Ti plus Mg for 2Al; and (3) the {001} sectors appear to be less distinctly monoclinic than the {010} sectors (Dollase and Hollister, 1969).

A projection of the structure down *c* is shown in Figure 4. The {110} surfaces have only 5/6 octahedral sites exposed, hence minimal incorporation of foreign ions is to be expected. Perhaps these sectors may be taken as the standard or normal composition of staurolite, representing the closest approach to equilibrium. The {010} faces have Al(2) sites exposed as 4/6 protosites, in which the normal Al could be replaced by Ti. Note that the compensating substitution of Mg for Al need not occur in the Al(2) sites exposed on this face, but could presumably occur in any of the Al sites in the structure (but in the same sector).

The {001} surfaces expose both Al(1) and Al(3) sites as half-sites (Fig. 5), a very favorable situation for adsorption. In the monoclinic structure, the Al(3) sites, which form chains parallel to *c*, are alternately Al(3*A*) and Al(3*B*) sites, with the Al(3*A*) sites tending to be occupied, and the Al(3*B*) sites vacant. The surface of least bonding would presumably expose the ideally vacant Al(3*B*) sites, which could therefore adsorb and metastably incorporate aluminum. Note that the surface structure shown in Figure 5 is distinctly different from that proposed by Hollister (1970), who considered that Si sites would be exposed. Exposure of Si sites is considered unlikely in this paper, but Hollister's explanation of the different symmetries of the {001} and {010} sectors needs little modification; on {001} the adsorption of Al into exposed Al(3*B*) sites tends to make these sites equiva-

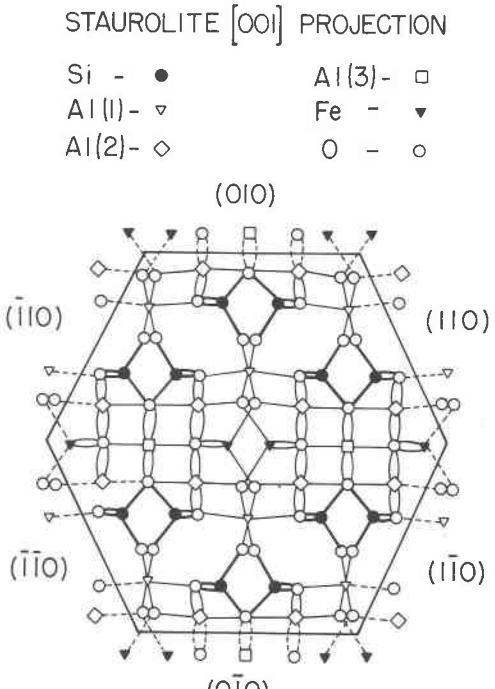

FIG. 4. Projection of the staurolite structure down [001]. *Note added in proof.* A more plausible surface of least bonding for {010} would curve around the SiO_4 groups, intersecting only Al(1)–O bonds. This change would not affect the morphology predicted in Part I, or the analysis in this paper, except that Al(1) rather than Al(2) sites would be exposed.

lent to Al(3*A*) sites, and leads in effect to stacking faults, which result in average orthorhombic symmetry as found by Dollase and Hollister (1969). On {010}, the substitution in the Al(3) sites must follow more closely the established (monoclinic) pattern.

To account for the difference in Ti and Mg content between {010} and {001}, we apparently must call on a rejection of Ti from the exposed half-sites on {001}. Perhaps the Al(1) and Al(3) sites exposed on {001} are inherently much less receptive to Ti than the Al(2) sites exposed on {110}. Alternatively, the abundant excess Al adsorbed onto Al(3) on {001} may play a role. Hollister (1970) considered that Al(1) and Al(2) sites would not be likely to accept foreign cations, because they are in a part of the structure which is essentially identical to that of kyanite, normally a rather pure mineral. However, kyanite is known to be sector-zoned also (Hollister, 1970), and a detailed investigation of it may throw some light on the sector zoning of Ti and Mg in staurolite.

Quartz

This paper will be concerned only with zoning under the three major forms, *m* {$10\bar{1}0$}, *r* {$10\bar{1}1$}, and *z* {$01\bar{1}1$}. Few quantitative data exist, although there are many reports of sectoral color variations. According to Frondel (1934), the purple color of amethyst, which is known to be related to the presence of Fe^{3+} (*e.g.* Barry *et al.*, 1965) is almost always stronger in the *r* sectors than the *z* sectors, and stronger in the *z* sectors than in the *m* sectors. This pattern seems to apply to most coloring agents, and thus, presumably, to most impurities.

A projection of the structure parallel to [10·0] is shown in Figure 6. Most of the cation substitutions in quartz probably involve substitutions into interstitial sites, with replacement of Si by Al or Fe^{3+} to balance the charge. The approximate locations of the interstitial sites may be obtained from the position of the Li site in β-eucryptite, $LiAlSiO_4$, which is a stuffed derivative of the quartz structure (Buerger, 1954). All the possible interstitial positions are shown in Figure 6; only half of these are occupied in β-eucryptite.

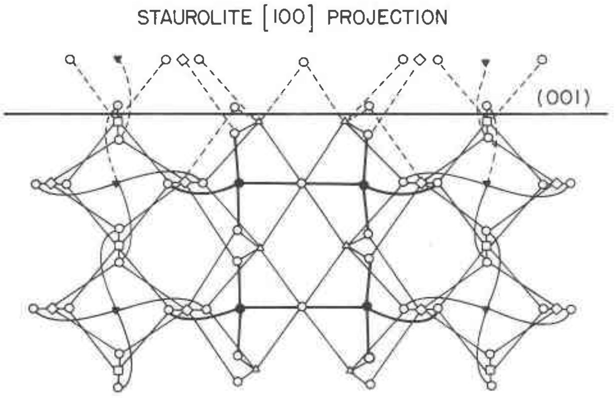

FIG. 5. Projection of the staurolite structure down [100]. Symbols are the same as in Fig. 4.

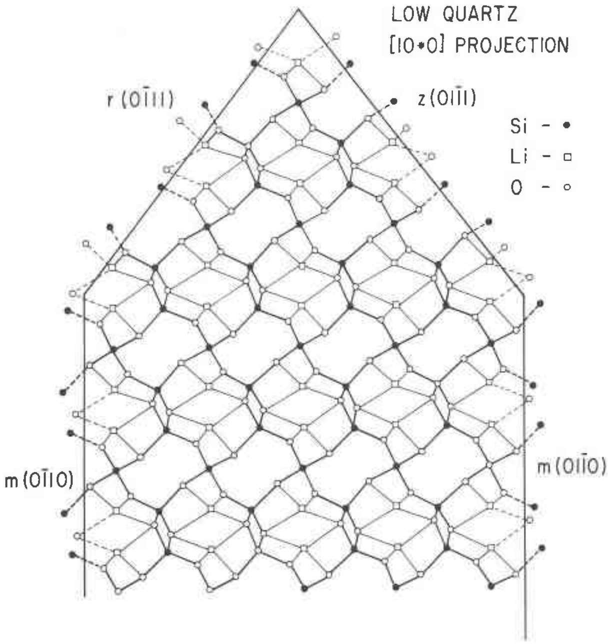

FIG. 6. Projection of the low quartz structure down [100]. The approximate locations of the interstitial sites are denoted by the symbol for Li.

There is some ambiguity in choosing the location of the crystal boundary parallel to the major faces. In each case, the boundary could be moved inward across one or two sets of oxygen atoms without changing the total surface energy or template fraction (neglecting the interstitial sites, which are occupied so seldom as to have little effect). If we do this, however, several Si sites are exposed on the surface as 3/4 sites. Now it seems very probable that the fourth oxygen atom would be permanently attracted to this incomplete site, thus bringing us back to the configuration shown in Figure 6, which has oxygen atoms exposed on the surface. These oxygens could bond to silicon atoms in 1/4 sites, but it is considered unlikely that silicon atoms would favor this configuration because silicon is less abundant than oxygen in the growth medium and is presumably surrounded by its own set of complexed oxygen atoms.

Ambiguities such as this often arise in deciding the configuration of the crystal surface. When the configuration on both sides of the surface of least bonding

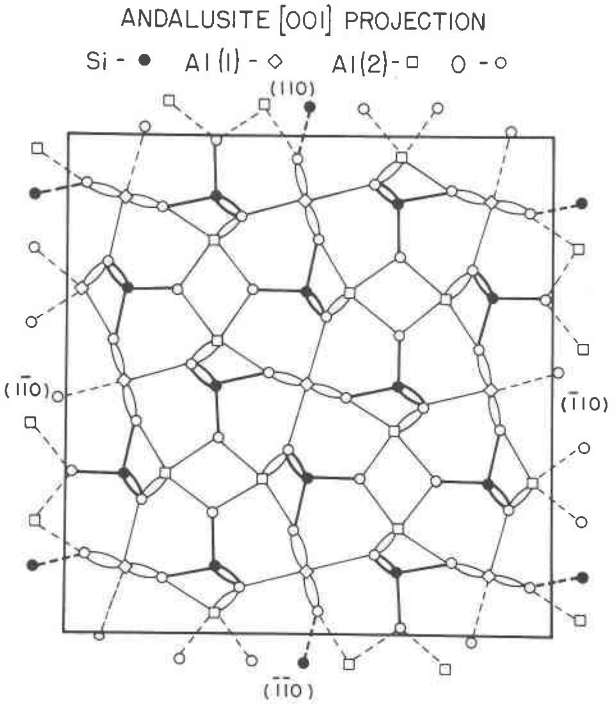

FIG. 7. Projection of the andalusite structure down [001].

is not the same, it is often necessary to decide which will be the outside of the crystal. In many such cases, the ambiguity can be resolved as illustrated in quartz, and usually leads to an excess of oxygen atoms or other anions on the surface. To compensate for this excess of negative charge, cations are presumably adsorbed onto the surface.

With the boundaries as shown in Figure 6, the rhombohedral faces have interstitial sites exposed as half sites (2/4), whereas the prism faces only expose 3/4 sites. It is assumed that the environment of the 3/4 sites is too much like that of the solid crystal to accept adsorbed cations such as Li, Al, Fe^{3+} *etc.*, whereas at least a small number may be adsorbed and incorporated on the rhombohedral faces. The two rhombohedra have the same basic topology (they are equivalent in high quartz), but they differ in exact face structure and presumably in their capacity for adsorption. In addition to giving a stronger color to *r* than to *z*, a greater amount of adsorption of foreign ions may very commonly slow the growth of *r*, making it more prominent than *z* (Frondel, 1934).

Poty (1969) made quantitative analyses of trace elements in some natural quartz crystals, and found higher concentrations of Li and Al under *r* and *z* than under *m*, in general agreement with the above analysis, but he also found different concentrations of Li and Al in the *m* faces, depending on whether they were directly adjacent to *r* or to *z* (the crystals were singly terminated). This aspect of quartz sector zoning deserves further investigation.

Brookite

Several investigators (*e.g.* Arnold, 1929; Frondel *et al.*, 1942) have described very dark zones beneath {001}, and less often under {021}. The {001} sectors were found to have relatively high concentrations of Nb and Fe. The coupled substitution of Nb or Ta plus Fe^{2+} or Fe^{3+} for Ti is a very common pigmenting substitution in all forms of TiO_2. The sector-zoned crystals are rather flat tabular on {100}, elongated parallel to *c*, and display in addition the forms {210}, and apparently {111}.

The numbers of 4/6 titanium protosites exposed per unit cell on these faces are four for {001}, two for {021}, one for {111}, and none for {100} and {210}. This provides a reasonable explanation for the dark color under {001} and {021}, although it is predicted that {111} will also show some enrichment in Nb and Fe with respect to the prism forms, apparently not enough to cause coloration. The surfaces of least bonding for these forms are planes, except for {111}, for which a deviation around one oxygen atom is necessary.

Andalusite

Hollister and Bence (1967) described crystals showing only {110}[1] and {001} sectors. Fe, Ti, and Mg concentrations were higher under {001} than {110}. The prediction of surface structure on the {110} faces is ambiguous, and the structure shown in Figure 7 (which was obtained by the computer calculations) is only one possibility. The location of the surface of least bonding depends on the relative values assigned to Al–O and Si–O bonds. It is possible to curve the surface in such a way that no Si–O bonds are intersected. However, it seems that none of the possible surfaces expose the octahedral Al(1) sites as other than 5/6 or 1/6 protosites, whereas the five-coordinated Al(2) sites may be exposed as 3/5 protosites. The surface of least bonding for {001}, on the other hand, exposes the Al(1) sites as 4/6 protosites (Fig. 8). The five-coordination of aluminum in Al(2) is very unusual, and if one makes the reasonable assumption that this site is very intolerant of foreign

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[1] The forms or sectors described by Hollister and Bence (1967) as {100} and {010} are actually the {110} form (L. S. Hollister, personal communication).

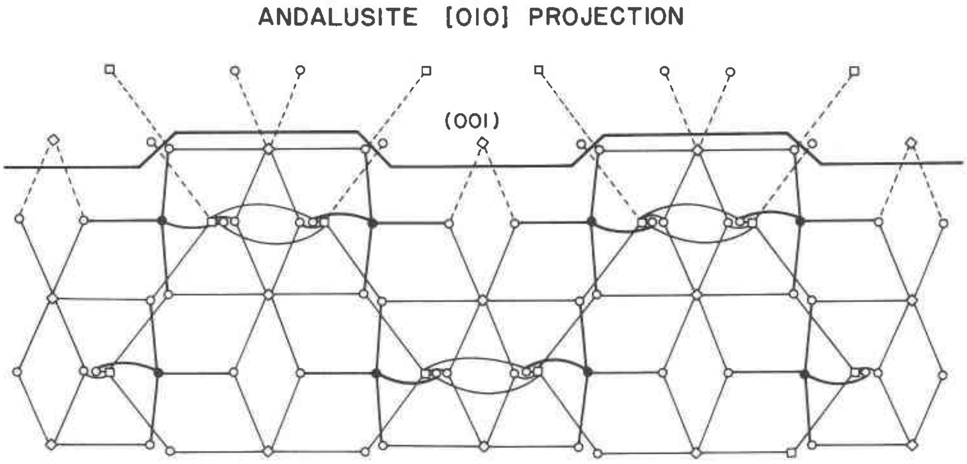

FIG. 8. Projection of the andalusite structure down [010]. Symbols are the same as in Fig. 7.

cations, it is to be expected that impurities would be concentrated in the Al(1) sites exposed on the {001}sectors. However, it is not clear from the partial analyses of Hollister and Bence (1967) what the exact stoichiometry of the substitutions is, and possibly a more complicated explanation than this will be necessary.

Epidote

Shannon (1924) described some small, well-formed secondary epidote crystals from diabase, which showed pronounced hourglass zoning of birefringence (Fig. 9), presumably due to greater concentrations of Fe^{3+} versus Al in certain sectors. The crystals were tabular on {100}, and the birefringence of the crystals as a whole when lying flat on this form was less in the sector or sectors defined by the forms in the zone [010], which included {001}, {102}, and {101}. The forms terminating the crystal on *b*, at least one of which presumably incorporates an excess of Fe^{3+}, were {111} and {011}.

The {001} faces have two $M(2)$ sites per unit cell exposed as 4/6 sites, but perhaps more importantly, {101} has one $M(3)$ site per unit cell exposed as a 3/6 site, and {111} has one $M(1)$ and one $M(2)$ site exposed as 3/6 sites. In epidote, the $M(1)$ and $M(2)$ sites prefer Al very strongly over Fe^{3+}, and the $M(3)$ site prefers Fe^{3+} (Dollase, 1971). If we assume that the growth medium had moderate amounts of both Al and Fe^{3+}, and that the adsorption of trivalent cations onto the exposed half sites is less selective than the solid crystal at equilibrium, it may be conjectured that the {101} sectors would have more than the equilibrium amount of Al in the $M(3)$ site, and that the {111} sectors would have more than the equilibrium amount of Fe^{3+} in the $M(1)$ and $M(2)$ sites. In the {001} sectors, there might be a slight excess of Fe^{3+} in the $M(2)$ site, by virtue of the exposed 4/6 protosites. This, of course, needs to be checked by microprobe measurements of the amount of Fe and Al in all sectors; Mössbauer (or X-ray diffraction) measurements of the site distribution of iron might also be useful.

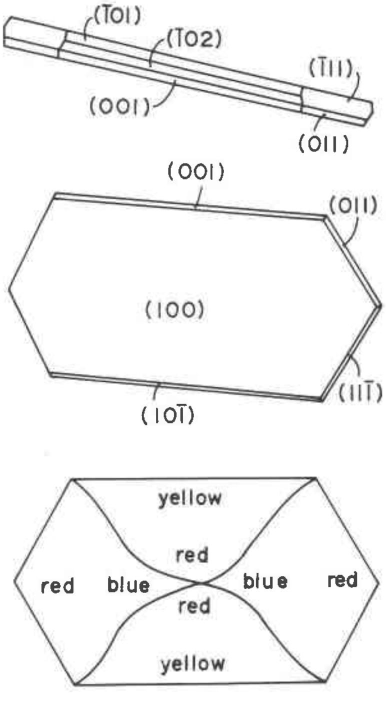

FIG. 9. Sector zoning in epidote, after Shannon (1924). The lower figure shows the birefringence observed on the flat-lying plate.

Galena

Frondel *et al.* (1942) found higher concentrations of the impurities Ag and Si in the {111} sectors versus the {100} sectors. Possibly this represents the coupled substitution $2Ag^+$ and Si^{4+} for $3Pb^{2+}$. As pointed out by many investigators, the {111} faces in the NaCl structure are susceptible to adsorption because ions all of one kind are exposed on the surface. Furthermore, the cation sites exposed on {111} are half sites (3/6) in the terminology of this paper, whereas those on {100} are 5/6 or 1/6, which may be more significant for a crystal like galena in which the bonds are mainly covalent.

Plagioclase

Bryan (1972) reported some rapidly-grown skeletal plagioclase crystals from deep sea basalts that showed {001} and {010} growth sectors. The {010} sectors had higher calcium content than the {001} sectors. If the Ca–Na site is considered to be 9-coordinated, then the surface of least bonding on {001} exposes two 4/9 sites per unit-cell volume, whereas {010} exposes four 4/9 sites. Calcium is presumably preferentially adsorbed onto the exposed sites, by virtue of its higher charge than sodium. However, this tendency is not very pronounced, since crystals with less skeletal morphology, which apparently grew more slowly, did not show sector zoning.

Conclusions

Success and applicability of the model

The proposed model appears to explain the major features of sector zoning in the examples available, although problems remain in some cases. No other model has been applied to this many examples. The apparent success of the analyses is considered to support the assumption made in Part I and this paper that any surface exposed on a crystal face will be a surface of least bonding, and it seems that the prediction of surface structure usually has been successful.

It should be emphasized, however, that the model is not necessarily applicable to all types of sector zoning. For faces which do not grow layer by layer the situation is more complicated (*e.g.* Kröger, 1973, p. 56), and predictions are more difficult. Also, a high degree of prestructuring in the growth medium may upset the prediction of the surface of least bonding, as discussed in Part I, and may itself cause the introduction of foreign atoms as parts of complexes.

Distribution coefficients

Hollister (1970), Hollister and Gancarz (1971), and Wass (1973) pointed out that sector zoning is necessarily a metastable phenomenon; Hollister and Gancarz showed in particular that the content of aluminum in clinopyroxene may be dependent on the growth history. The present model emphasizes even more the sometimes metastable nature of the incorporation of minor and trace elements (and sometimes also major elements) into crystals, because it views them as surface impurities which would ideally only be temporarily present and are not likely to be at equilibrium in the interior of the crystal. The above analysis of titanaugite permits the hypothesis that *all* the Ti, Al, and Fe^{3+} are incorporated as the result of metastable growth processes. It may be noted that as a rule titanaugites occur in volcanic rocks which are only mildly silica-undersaturated and moderately titanium-rich, but which are rapidly cooled. On the other hand, in alkalic plutonic and hypabyssal rocks, some of which may be much more undersaturated and titanium-rich (*e.g.* the carbonatite clan), the characteristic pyroxene is aegirine-augite, usually with little Ti. Of course, the composition of the growth medium (see Kushiro, 1970, on clinopyroxenes) and the temperature and pressure will also influence the equilibrium concentrations of minor elements in a crystal, and any metastable growth effects will be superimposed on these concentrations. Nevertheless, caution should be used in interpreting elemental partitioning in minerals as indicators of temperature and pressure, especially when growth was rapid.

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References

Arnold, W. (1929) Beiträge zur Kenntnis des Brookit in morphologischer und optischer Hinsicht. *Z. Kristallogr.* **71,** 344–372.

Barry, T. I., P. McNamara and W. J. Moore (1965) Paramagnetic resonance and optical properties of amethyst. *J. Chem. Phys.* **42,** 2599–2606.

Bryan, W. B. (1972) Morphology of quench crystals in submarine basalts. *J. Geophys. Res.* **77,** 5812–5819.

Buckley, H. E. (1951) *Crystal Growth.* John Wiley and Sons, New York.

Buerger, M. J. (1954) The stuffed derivatives of the silica structures. *Am. Mineral.* **39,** 600–614.

Burton, J. A., R. C. Prim and W. P. Slichter (1953) The distribution of solute in crystals grown from the melt. *J. Chem. Phys.* **21,** 1987–1996.

BURTON, W. J. AND N. CABRERA (1949) Crystal growth and surface structure. *Disc. Faraday Soc.* **5,** 33–39.

DOLLASE, W. A. (1971) Refinement of the crystal structures of epidote, allanite, and hancockite. *Am. Mineral.* **56,** 447–464.

——— AND L. S. HOLLISTER (1969) X-ray evidence of ordering differences between sectors of a single staurolite crystal. *Geol. Soc. Am. Abstr., Program* **7,** 268–270.

DOWTY, E. (1976) Crystal structure and crystal growth: I. The influence of internal structure on morphology. *Am. Mineral.* **61,** 448–459.

FRONDEL, C. (1934) Origin of the segmental coloration of amethyst and smoky quartz. *Am. Mus. Novit.* **758,** 1–15.

———, W. H. NEWHOUSE AND R. F. JARRELL (1942) Spatial distribution of minor elements in single-crystals. *Am. Mineral.* **27,** 726–745.

HALL, R. N. (1953) Segregation of impurities during the growth of germanium and silicon crystals. *J. Phys. Chem.* **57,** 836–839.

HARTMAN, P. AND W. G. PERDOK (1955) On the relations between structure and morphology of crystals. *Acta Cristallogr.* **8,** 49–52, 521–524, 525–529.

HOLLISTER, L. S. (1970) Origin, mechanism, and consequences of compositional sector-zoning in staurolite. *Am. Mineral.* **55,** 742–766.

——— AND A. E. BENCE (1967) Staurolite, sectoral compositional variations, *Science,* **158,** 1053–1056.

——— AND A. J. GANCARZ (1971) Compositional sector-zoning in clinopyroxene from the Narce area, Italy. *Am. Mineral.* **56,** 959–979.

HOLZNER, J. (1934) Beiträge zur Chemie und Optik sanduhrformiger Titanaugite. *Z. Kristallogr.* **87,** 1–42.

KRÖGER, F. A. (1973) *The Chemistry of Imperfect Crystals,* Vol. II. North Holland, Amsterdam.

KUSHIRO, I. (1970) Si-Al relations in clinopyroxenes from igneous rocks. *Am. J. Sci.* 258, 548–554.

LEUNG, I. S. (1974) Sector zoned titanaugites: morphology, crystal chemistry and growth. *Am. Mineral.* **59,** 127–138.

NAKAMURA, Y. (1973) Origin of sector-zoning of igneous clinopyroxenes. *Am. Mineral.* **58,** 986–990.

PELIKAN, A. (1896) Über den Schichtenbau der Kristalle. *Tschermaks Mineral. Petrogr. Mitt.* **16,** 1–64.

POTY, B. (1969) La croissance des cristaux de quartz dans les filons sur l'exemple du filon de La Gardette (Bourg d'Oisans) et des filons du massif du Mont-Blanc. *Science de la Terre,* Memoire no. 17.

SHANNON, E. V. (1924) The mineralogy and petrology of intrusive Triassic diabase at Goose Creek, Loudoun County, Virginia. *Proc. U. S. Natl. Mus.* **66,** 1–86.

WASS, S. Y. (1973) The origin and petrogenetic significance of hour-glass zoning in titaniferous clinopyroxenes. *Mineral. Mag.* **39,** 133–144.

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