American Mineralogist, Volume 58, pages 986–990, 1973

Origin of Sector-Zoning of Igneous Clinopyroxenes

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Abstract

A protosite is defined as a partially formed structural site on a crystal surface. When a crystal grows rapidly from a magma, protosites but not structural sites are in equilibrium with the magma. The geometry of each protosite on each growth surface differs from that of the corresponding true structural site in variable degree. The geometry of the $M(1)$ and $M(2)$ protosites on {100} surfaces of augite deviate most from the true structural sites, and are effectively the most flexible. Consequently the composition of the {100} sector can deviate most prominently from the equilibrium composition. Several types of sector-zoning are interpreted, based on this concept of protosites.

Introduction

Accumulation of a tremendous amount of analytical data on pyroxenes by use of the electron probe microanalyser in the last decade has revealed that compositional sector-zoning is not uncommon in both terrestrial and lunar igeneous rocks. According to Hollister and Gancarz (1971), a crystal which is compositionally sector-zoned has regions or sectors which have significant differences in composition, and these chemical differences are probably produced on the surfaces of crystal faces simultaneously growing under identical conditions of pressure, temperature, and composition of the surrounding phase. Hollister and Gancarz (1971) have applied with slight modification the theory originally developed for the interpretation of sector-zoning of staurolite (Hollister, 1970) to the sector-zoning of igneous clinopyroxenes. The application of their theory, however, is not always satisfactory, because it does not adequately explain sector-zoning with respect to Ca/(Mg + Fe) ratios. This paper presents a theory for the development of sector-zoning in clinopyroxenes.

An Example of Sector-Zoned Augite

Sector-zoning is well developed in augite in a pegmatoidal dolerite in the Tawhiroki tholeiitic dolerite sheet at Moeraki, Northeastern Otago, New Zealand (Benson, 1943, 1944). Analytical data for pyroxenes taken from several positions in the dolerite sheet will be published by Nakamura and Coombs (1973). The dolerite is about 50 m thick, and the pegmatoidal rock occurs near the center of the sheet. The augite crystals are of slender prismatic habit elongated along *c* with {100}, {110} faces. No exsolution lamellae were observed. Platy pigeonite inclusions epitaxially grown on {100} are uncommon. The augite is therefore considered to have been saturated with Ca-poor pyroxene in the early stage of crystallization. No differences in composition were observed between sectors resulting from growth on {010} and {110}. The compositional sector-zoning is most marked by deviations in the ratio Ca/(Ca + Mg + Fe), being about 0.31 in {100} sectors and about 0.38 in {110} and {010} sectors (Fig. 1 and Table 1). Decreases of Ca, Al, and Ti in the {100} sectors can be simply explained in terms of dilution of the components containing these elements by the increase in the $MgSiO_3$, $FeSiO_3$, and $MnSiO_3$ components. The compositional variation of the {010} and {110} sectors (Fig. 1) is very similar to that of Skaergaard augites (Brown, 1957). Nakamura and Coombs (1973) have concluded that the pegmatoidal dolerite was formed from liquid oozing from the surrounding rocks—the lack of pre-existing augite nuclei causing considerable supersaturation of augite—followed by sudden nucleation and rapid growth.

Structural Considerations

A partially formed structural site on a growing crystal surface is here called a *protosite*. Unlike the comparable structural site, a protosite possesses an

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incomplete second (and usually first) coordination sphere of neighbors. In the structure of augite, which resembles that of diopside (Fig. 3), Si occupies the tetrahedral sites; Mg and Fe occupy the 6-coordinated $M(1)$ sites; and principally Ca, but also Fe and perhaps minor amounts of Mg, occupy the 8-coordinated $M(2)$ sites. The shape and size of the comparable protosites will differ according to the growth surface on which they occur. Thus an $M(2)$ protosite in augite differs in size and shape depending upon whether it lies on {010} or on {100}. The incompleteness of their coordination sphere imparts a flexibility to the protosites that permits them to accommodate atoms not usually favored by the completed structural site. Consequently, the increase in excess free energy caused by their acceptance of unfavorable atoms would be less than if these atoms occupied the more rigidly defined structural sites.

Si atoms are considered to exist in the magma as SiO_4^{4-} tetrahedra or more polymerized anions but not as independent Si^{4+} ions. For silicate minerals, the SiO_4 tetrahedron may, therefore, be regarded as the smallest unit to be taken into account at the time of deposition of an Si atom on the crystal surface over considerable ranges of temperature, pressure, and composition of melt. It is most unlikely that Si atoms not covered by oxygen atoms are exposed on crystal surfaces to surrounding silicate melts.

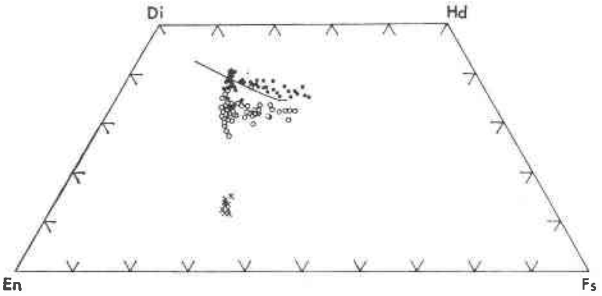

FIG. 1. Ca–Mg–Fe plot of the compositions of {100}, {010}, and {110} sectors of augites from a pegmatoidal dolerite from Moeraki. Open circles, {100} sector; solid circles, {010} and {110} sectors; crosses, pigeonite inclusion. The solid line shows the compositional changes of the Skaergaard augites coexisting with Ca-poor pyroxenes (Brown, 1957).

Accordingly we may assume that a crystal grows

TABLE 1. Electron Probe Analyses of an Augite Grain in the Pegmatoidal Dolerite*

	{100} sector					{110} sector		{010} sector			
	1	3	2	21	12	20	11	7	8	9	10
SiO_2	50.7	51.2	51.4	50.7	50.8	50.8	50.8	50.4	50.7	50.9	50.7
Al_2O_3	2.04	1.67	1.18	1.83	1.27	2.48	1.36	2.60	2.40	1.52	1.09
Cr_2O_3	0.03	0.01	0.00	0.00	0.00	0.05	0.00	0.06	0.02	0.00	0.00
TiO_2	1.20	1.14	0.78	1.12	0.83	1.52	0.84	1.52	1.50	1.08	0.73
FeO**	12.7	13.3	17.8	13.5	17.3	10.6	16.4	10.7	10.2	13.6	18.1
MnO	0.34	0.31	0.41	0.31	0.38	0.23	0.36	0.24	0.22	0.29	0.37
MgO	16.5	16.1	12.8	16.9	13.7	14.8	12.3	14.9	14.4	13.7	11.0
CaO	15.2	15.5	15.1	14.7	14.8	19.2	17.1	18.7	19.4	18.2	17.1
Na_2O	0.26	0.27	0.27	0.24	0.27	0.31	0.30	0.31	0.31	0.29	0.33
Total	99.0	99.5	99.7	99.3	99.4	99.9	99.5	99.4	99.2	99.6	99.4
Si	1.914	1.928	1.967	1.913	1.950	1.902	1.951	1.897	1.910	1.934	1.963
Al_z	0.086	0.072	0.033	0.081	0.050	0.098	0.049	0.103	0.090	0.066	0.037
Al_y	0.005	0.002	0.020	--	0.007	0.012	0.013	0.012	0.016	0.002	0.013
Cr	0.001	--	--	--	--	0.001	--	0.002	0.001	--	--
Ti	0.034	0.032	0.023	0.032	0.024	0.043	0.024	0.043	0.042	0.031	0.021
Fe	0.401	0.419	0.569	0.427	0.555	0.331	0.527	0.337	0.322	0.431	0.585
Mn	0.011	0.010	0.013	0.010	0.012	0.007	0.012	0.008	0.007	0.010	0.012
Mg	0.930	0.903	0.730	0.951	0.782	0.824	0.706	0.834	0.810	0.776	0.638
Ca	0.616	0.626	0.620	0.592	0.607	0.771	0.702	0.755	0.784	0.740	0.710
Na	0.019	0.020	0.020	0.018	0.020	0.022	0.022	0.023	0.023	0.022	0.024
Z	2.00	2.00	2.00	1.99	2.00	2.00	2.00	2.00	2.00	2.00	2.00
WXY	2.02	2.01	2.00	2.03	2.01	2.01	2.01	2.01	2.01	2.01	2.00
Ca	31.7	32.1	32.3	30.1	31.2	40.0	36.3	39.2	40.9	38.0	36.7
Mg	47.7	46.4	38.0	48.3	40.2	42.8	36.5	43.3	42.3	39.9	33.0
Fe	20.6	21.5	29.7	21.6	28.6	17.2	27.2	17.5	16.9	22.1	30.3

* *The positions of analyses are shown in Figure 2.*
***Total Fe as FeO*

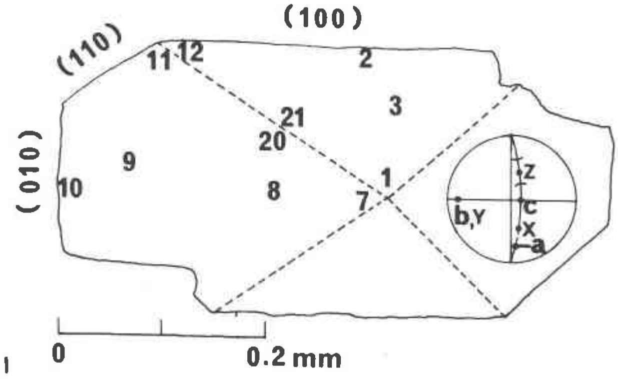

FIG. 2. Sketch of a sector-zoned augite crystal cut roughly normal to *c*. The numbers express the positions of analyses given in Table 1.

in a particular direction by the accretion of layers as thick as the height of an SiO_4 tetrahedron measured normal to the surface, rather than by atom-by-atom accretion. Such layers, if parallel to {100} in diopside, do not contain Mg and Ca atoms, which are present in the gaps between the layers. These gaps may be regarded as independent growth layers.

The growth layers can thus be defined parallel to {100} and {010} (Fig. 3). Parallel to {100}, there are alternating cationic and SiO_3-chain layers. The $M(1)$ and $M(2)$ protosites on the {100} growth layer, which respectively coordinate to three and four oxygens of the underlying SiO_3-chain layer, may be regarded as half-formed $M(1)$ and $M(2)$ sites. Each growth layer parallel to {010}, on the other hand, contains $M(1)$, $M(2)$, and tetrahedral protosites. The $M(1)$ protosite on the {010} growth surface is coordinated to four oxygens, two from the underlying layer and two from the same layer, and constitutes 4/6 of an $M(1)$ site. There are two $M(2)$ protosites, one coordinated to 8 oxygens and the other to 6 oxygens. With respect to the first coordination sphere they may thus be regarded as fully-formed and 6/8 formed $M(2)$ sites. The $M(1)$ and $M(2)$ protosites on the {100} surface, being only half-formed, deviate more from the $M(1)$ and $M(2)$ sites than the $M(1)$ and $M(2)$ protosites on the {010} surface. These {100} protosites may therefore be expected to accept cations having a greater range of ionic size than the better defined sites on the {010} surface. They may be regarded as more flexible in size and shape.

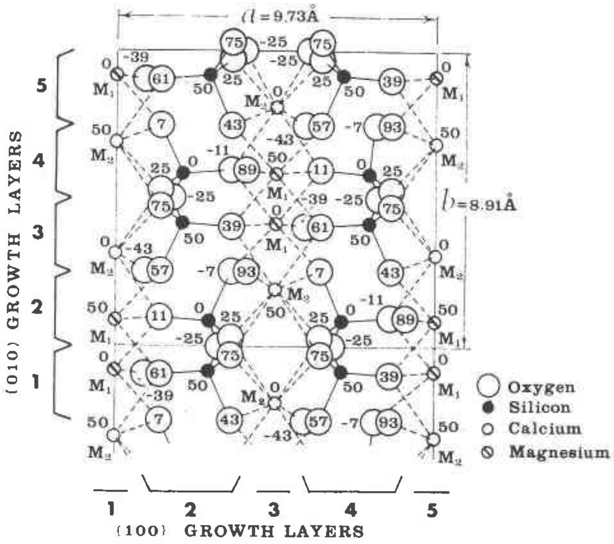

FIG. 3. Idealized structure of diopside as viewed along the *c* direction (Warren and Bragg, 1928). {010} growth layers 1 to 5 are indicated by horizontal strips of structure to the right of these numbers, and {100} growth layers 1 to 5 are vertical strips located above these numbers. Copied from Deer, Howie, and Zussman (1963).

Sector-Zoning Involving $M(1)$ and $M(2)$ Sites

Augite crystallizing from a magma saturated (or supersaturated) with Ca-poor pyroxene must have the solvus composition, if equilibrium is maintained. Considering the surface equilibria on the {100} growth surface, however, Mg and Fe atoms may well occupy the $M(1)$ and $M(2)$ protosites above the limit of this solvus composition because of their relative flexibility as discussed above. The increase of excess free energy which is caused by the introduction of Mg and Fe into the $M(2)$ protosite would be less than if they are introduced into the $M(2)$ true structural site. Amounts of the Mg and Fe atoms depositing on the {010} growth surface would be closer to those of the solvus composition than for those depositing on the {100} surface. If the crystal grows slowly enough, the excess Mg and Fe atoms at the protosites will be re-equilibrated with the surrounding liquid by diffusion after the next growth layer has been formed and the protosites have been converted to true structural sites. In the case of more rapid growth, the atomic ratios at the protosites may well be frozen in, or only partly modified, and sector-zoning may be preserved (*cf* Hollister, 1970) as in the augite in the pegmatoidal dolerite from Moeraki (Fig. 1). Under these conditions the miscibilty gap is effectively reduced in the {100} sector.

Sector-zoned augite from a pegmatite in an olivine tholeiite feeder dike from northwest Ireland (Preston, 1966) contains {001} exsolution lamellae of pigeonite in the {100} sector but not in its {010} sector, where only incipient exsolution lamellae of hypersthene parallel to {100} occur. The augite grew together with primary pigeonite and hence must have been saturated with Ca-poor pyroxene. The difference between the sectors is most easily understood on the hypothesis that the {100} sector was originally enriched in $(Mg,Fe)SiO_3$ over the equilibrium solubility limit, and subsequently this sector expelled pigeonite as exsolution lamellae during slow cooling. In contrast the composition of the {010} sector had been very close to the augite-pigeonite solvus from the beginning. Strangely, however, the microprobe analyses of Preston (1966) show that the {100} sectors are richer in Ca than in the {010} sectors. This appears to contradict the evidence of the pigeonite exsolution lamellae in the {100} sector, and is the opposite of the situation with the Moeraki pyroxenes. However, the nearly total chloritic alteration of the Ca-poor pyroxene lamellae in Preston's specimen throws some doubt on the significance of his analyses.

Complicated zonings have been reported for the clinopyroxenes from Apollo 12 basalts (Boyd and Smith, 1971; Hollister *et al,* 1971; Weill *et al,* 1971). The pigeonite continuously changes in composition toward augite normal to {100}, but remains as pigeonite normal to {010}. The difference of crystal structure between augite and pigeonite does not seem to matter at the level of precision of the present discussion. Evidently the high-temperature pigeonite structure formed first. Then the liquid became saturated with augite, and Ca atoms were accommodated in the $M(2)$ protosites of the {100} growth surface above the limit of the solvus composition. This was possible because the protosites on the {100} surface are more flexible than either the protosites on the {010} surface or the true structural sites of pigeonite. Rapid growth would have preserved the cationic distribution in the protosites. Epitaxial augite growth on {110} and not on {010} may be explained by considering the degree of structural mismatch as was suggested by Hollister *et al* (1971).

It is emphasized that sector-zonings are dependent not only on growth rates and crystal structure but also strongly dependent on the compositions of coexisting liquids. Sector-zoning with contrasting $Ca/(Mg+Fe)$ ratios would be best developed when the coexisting liquid is saturated or supersaturated with Ca-poor pyroxene. On the other hand, the clinopyroxenes from the Narce area, Italy, are sector-zoned with respect to Ti and Al (Hollister and Gancarz, 1971) but not $Ca/(Mg+Fe)$. Their host rock contains leucite and, therefore, the magma must have been far from saturated with Ca-poor pyroxenes.

Sector-Zoning Involving Tetrahedral Sites

In SiO_3-chain growth layers along {100}, one or two non-bridging oxygens around an Si atom are not coordinated to any cations. On the other hand, no such cation-uncoordinated oxygens exist in single growth layers along {010}. This indicates that a tetrahedral protosite on the {100} growth surface can more easily change its size and shape than the tetrahedral protosites on the {010} surface. The {100} tetrahedral protosite is less similar to the true tetrahedral structural site than its {010} equivalent, and in it substitution of Al for Si will be relatively easy. The substitution requires the charge deficiency to be compensated by introducing Ti or Al into the $M(1)$ site. This again would take place more easily in the {100} $M(1)$ protosite than in the {010} $M(1)$ protosite as discussed before.

In clinopyroxenes crystallized from silica-undersaturated magmas, low silica activities force Si to be partly replaced by Al (Kushiro, 1960; Le Bas, 1962). This substitution would be most efficient on the {100} growth surface, and in the case of rapid growth, will survive as sector-zoning with respect to Al and Ti as is recorded by Hollister and Gancarz (1971) from the Narce area, but not with respect to $Ca/(Mg+Fe)$ ratio as is reported here.

Discussion

No other growth surfaces in pyroxene can have such flexible protosites as the {100} surface. Therefore, compositions of the {100} sector can deviate most from the equilibrium compositions in zoned pyroxenes. Unfortunately it cannot be stated at this time which of the various other possible growth sectors should have a composition closest to the equilibrium composition.

The present theory follows Hollister's theory of sector-zoning of staurolite (Hollister, 1970) in so far as both theories consider that equilibrium is maintained only at crystal-matrix interfaces and that the compositions on crystal surfaces are more or less preserved by rapid growth of the crystal. The difference between the two theories lies in the manner of interpretation of the surface equilibrium itself. Hollister's theory laid stress on local charge balance on the crystal surface whereas the present theory lays stress on geometrical flexibility of protosites.

Hollister and Gancarz (1971) proposed four different cases of the rate of crystal growth. The sector-zoning of clinopyroxene from Narce area was interpreted by them as representing the second most rapid growth, their case B, where surface equilibrium is achieved only between the surface of the growth step and the matrix but not between the crystal surface itself and the matrix. According to the present model, however, the sector-zoning of the Narce clinopyroxene may be interpreted as representing case C of Hollister and Gancarz (1971), where equilibrium is achieved between the growth surface and the matrix.

The present theory assumes equilibria between crystal surfaces and the surrounding liquid and is essentially independent of the manner by which each growth surface is formed. The crystal may grow by dislocation steps or by any other mechanism. Irrespective of the mechanism of growth, the atomic arrangements on a well defined crystal surface exposed to a surrounding silicate melt should be as pictured in this paper except, perhaps, at positions of dislocations. The assumption of crystal growth by accretion of layers was made to make it clear in the discussion that probable atomic arrangements on the crystal surface are limited according to the nature of the surrounding medium. This assumption neither violates generality of discussion nor contradicts any specific type of crystal growth mechanism as long as the crystal maintains its well defined outer form.

It is not uncommon that rapidly grown crystals have compositions which can never be reached at equilibrium. The protosite concept should be useful to interpret these phenomena, because the increase of excess free energy caused by the introduction of usually unfavored atoms into protosites would be less than that caused by the introduction of them into the corresponding true structural site.

Acknowledgments

I am greatly indebted to Professor D. S. Coombs for offering a chance for this work, and also for critical reading of the manuscript. Electron microprobe data were obtained on the University of Otago's new JEOL-5XA instrument which has been financed in part with grants from the New Zealand University Grants Committee, the Scientific Research Distribution Committee for New Zealand lottery profits, and Mount Isa Mines Limited.

I am indebted to Professor R. A. Howie for permission to use the figure reproduced from *Rock Forming Minerals.*

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Manuscript received, November 6, 1972; accepted for publication, March 30, 1973.