

On hour-glass sector zoning in clinopyroxene

A. K. FERGUSON

School of Geology, University of Melbourne, Parkville, Victoria, Australia, 3052

SUMMARY. The observations of hour-glass sector zoning from four selected clinopyroxenes in under-saturated lavas best fit a model in which the sector zoning is formed due to a structural requirement in a growth direction normal to $\{100\}$ where a high concentration of silicate units, required to build the silicate chains, is unsatisfied. In these sectors Al substitutes for Si, the charge balance being maintained by octahedral substitutions, of which Ti contributes to the deeper colour of the sectors. The presence of concentric zoning only reflects a change in temperature and a change in the composition of the liquid during crystallization of the pyroxene.

HOURLASS sector zoning has been observed in leucite-bearing volcanic rocks and four clinopyroxene crystals have been examined in detail:

- A Titanaugite phenocryst in lava, Bufumbira, Uganda;
- B Titanaugite phenocryst in lava, New South Wales, Australia;
- C Aluminous augite crystal lining a cavity in lava, Vulsinian volcanoes, Italy;
- D Aluminous augite phenocryst in lava, Sabatinian volcanoes, Italy.

The hour-glass structures in clinopyroxenes A, B, and D are observable optically and in titanaugites A and B the hour-glass structure is defined by two strongly coloured sectors (α buff, γ violet-brown) separated by two pale-coloured sectors (fig. 1, i and ii). In aluminous augite D, where two pale-coloured sectors (α colourless, γ pale green) are separated by two colourless sectors, the hour-glass structure is less obvious but under crossed-polars the typical hour-glass structure is easily observed (fig. 1, iii). No optical evidence of hour-glass structure is observed in sections of aluminous augite C; but sector zoning is revealed by microprobe analysis. In addition to hour-glass sector zoning, concentric zoning parallel to the crystal outline was observed in titanaugites A and B and in aluminous augite D.

The hour-glass sector zoning observed in pyroxenes A, B, and D is best developed in sections cut parallel to $\{010\}$ (fig. 1, i and iii). Sections parallel to $\{001\}$ show a poorly defined hour-glass structure (fig. 1, ii), while only concentric zoning is observed in sections parallel to $\{100\}$. O'Reilly (1972) and Schorer (1970) have also observed the best-developed hour-glass structures in sections parallel to $\{010\}$ in titanaugites and, in addition, O'Reilly has observed a 'suggestion of an hour-glass shape' in sections parallel to $\{100\}$, but no sector zoning in sections perpendicular to the c -axis. Strong (1969) concludes that the 'H' of the hour-glass structure lies in a plane parallel to $\{001\}$ and orientated parallel to either the a - or b -axis.

A model of the orientation of the sectors consistent with the observations of the pyroxenes A, B, and D is shown for a typical augite crystal in fig. 1 (iv). In the following discussion, sectors opening on to the $\{100\}$ faces are called $\{100\}$ -sectors (i.e. the

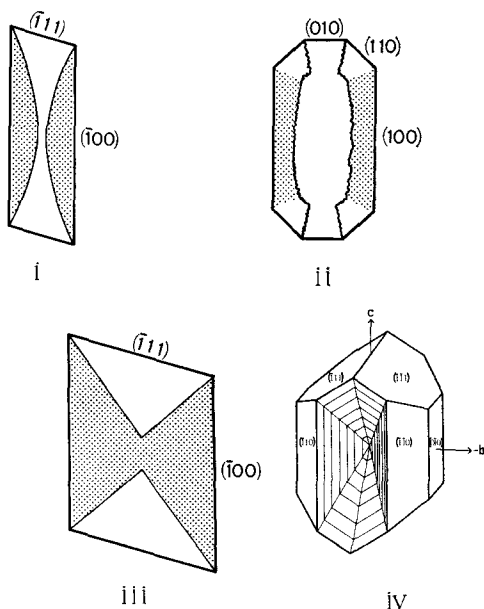


FIG. 1. (i) and (ii) Hour-glass sector zoning observed in titanites occurring in lavas from Bufumbira, Uganda (A, table I). (i) is orientated perpendicular to the b -axis and (ii) is perpendicular to the c -axis. The deeply coloured, more pleochroic sectors are represented by stippling. (iii) Hour-glass sector zoning observed under crossed polars in an aluminous augite occurring in a lava from the Sabatinian volcanoes, Italy (D, table I). The stippled areas show similar chemical composition to the stippled areas in (i) and (ii). (iv) A typical augite crystal (from Brauns, 1908, Fig. 238) with the $\{100\}$ -sectors, corresponding to the deeply coloured sectors in the titanites, removed.

Note, $-a$ axis is towards the front.

Bas, 1962), the charge balance would be maintained most easily by Ti^{3+} , rather than by Ti^{4+} substitution for Mg and Fe in MI sites (Verhoogen, 1962). Thermodynamically, Verhoogen (1962) has in fact shown that Fe^{3+} and Ti^{3+} are more stable than Fe^{2+} and Ti^{4+} . Thus the sectors characterized by high Al^{IV} are likely to contain significantly higher amounts of Ti^{3+} and Fe^{3+} , the remaining Fe (approximately 80 % of the total Fe) being present as Fe^{2+} .

In the following discussion, crystal growth is assumed to occur by addition of molecular units to a step formed by a screw dislocation in the lattice (see Verma and

the more strongly coloured sectors in titanite augites A and B) and likewise the other sectors will be called $\{010\}$ -sectors and $\{\bar{1}\bar{1}\bar{1}\}$ -sectors.

The compositional variation between sectors was studied with an electron microprobe in crystals cut parallel to $\{010\}$. The analyses (table I) refer to areas close to the rims of the crystals in order to reduce the effect of concentric zoning. The $\{100\}$ -sectors of all four pyroxenes contain higher Ti, Al^{IV} , Fe^{2+} , and Al^{VI} and lower Si and Mg than the $\{\bar{1}\bar{1}\bar{1}\}$ -sectors (table I); Ca and Na show no consistent variation. A direct correlation is found between colour and Ti content, the $\{100\}$ -sectors of titanite augites A and B being more titaniferous than the coexisting $\{\bar{1}\bar{1}\bar{1}\}$ -sectors.

From measurements of polarized spectra on a titanite, Manning and Nickel (1969) conclude that its pleochroism is due to the charge transfer $Fe^{2+} \rightarrow Fe^{3+} + e$, while the observed colour is attributed to a combination of this with Fe^{2+} and Ti^{3+} $d-d$ electron transitions (Ti^{4+} is colourless).

In the present case the more pleochroic $\{100\}$ -sectors (i.e. the deeply coloured sectors in the titanite augites A and B) are higher in Ti, Al^{IV} , Fe^{2+} , and Al^{VI} . Since the Ti content increases with Al^{IV} (Verhoogen, 1962, and Le

Krishna, 1966, ch. 7 for a complete discussion). The step height is thought to be of the order of a unit cell dimension and, all other factors being equal, the rate of growth of a spiral inversely proportional to the step height. Surface diffusion is the main mechanism by which molecular units are transported to a step where they are bound

TABLE I. *Electron microprobe analyses of rim compositions of $\{\bar{1}11\}$ - and $\{100\}$ -sectors of hour-glass clinopyroxenes*

	A		B		C		D	
	$\{\bar{1}11\}$	$\{100\}$	$\{\bar{1}11\}$	$\{100\}$	$\{\bar{1}11\}$	$\{100\}$	$\{\bar{1}11\}$	$\{100\}$
SiO ₂	47.2	42.7	53.2	52.0	51.8	46.1	47.5	43.3
TiO ₂	2.82	4.37	1.29	3.38	0.64	1.61	1.02	1.87
Al ₂ O ₃	5.7	8.9	1.05	2.80	4.3	9.8	6.2	10.0
FeO†	7.7	8.4	6.6	7.3	5.0	7.6	9.0	11.0
MnO	0.16	0.15	0.16	0.16	0.08	0.09	0.19	0.15
MgO	12.1	11.2	15.0	11.8	14.3	11.7	11.8	9.6
CaO	24.3	23.5	22.0	22.3	23.3	22.9	23.5	23.7
Na ₂ O	0.53	0.45	1.16	1.08	0.16	0.16	0.31	0.35
K ₂ O	*	*	*	*	*	*	*	*
Cr ₂ O ₃	*	*	*	0.03	0.04	*	*	*
NiO	*	*	*	*	*	*	*	*
Total	100.51	99.67	100.46	100.85	99.62	99.96	99.52	99.97
<i>Cations (based on 6 oxygen atoms)</i>								
Si	1.77	1.63	1.96	1.92	1.91	1.72	1.80	1.66
Al ^{iv}	0.23	0.37	0.04	0.08	0.09	0.28	0.20	0.34
Al ^{vi}	0.02	0.03	0.01	0.04	0.09	0.15	0.08	0.11
Ti ⁴⁺	0.08	0.12	0.04	0.09	0.02	0.05	0.03	0.05
Fe ²⁺	0.24	0.27	0.20	0.23	0.15	0.24	0.29	0.35
Mn	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01
Mg	0.68	0.64	0.82	0.65	0.78	0.65	0.67	0.55
Ca	0.98	0.96	0.87	0.88	0.92	0.92	0.96	0.97
Na	0.04	0.03	0.08	0.08	0.01	0.01	0.02	0.03
Z	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ΣXY	2.05	2.06	2.03	1.98	1.97	2.02	2.05	2.07

A Phenocryst in lava, Bufumbira, Uganda.

B Phenocryst in lava, New South Wales, Australia.

C Euhedral crystal lining a cavity in lava, Vulsinian volcanoes, Italy.

D Phenocryst in lava, Sabatinian volcanoes, Italy.

* Below lower limit of detection.

† Total iron as FeO.

to the growing spiral. Since the screw dislocation density is in the order of 10^6 per cm^2 (Verma and Krishna, 1966), the surface of a face is envisaged as a complexity of screw dislocations.

Other factors that also influence the rate of growth and the morphology of a crystal include internal structure, twin boundaries, lattice defects, temperature, pressure, supersaturation, impurities, and the presence of other crystals. The relative effects of many of these factors cannot be determined for a crystal forming in a lava; however,

it can be qualitatively shown that some of the above factors are clearly not related to the sector zoning, whereas others are.

The adsorption of impurities and dyes on to a crystal face resulting in an hour-glass structure and, or, habit modification (Buckley, 1951, pp. 416–19) is not applicable since there is no evidence of impurities in any of the crystals. Strong (1969) concluded that adsorption of 'unidentified impurities' on to particular crystal faces impeded crystal growth producing a skeletal hour-glass crystal, which was completed by later growth. This also is not applicable to the present case since, in addition to no impurities being present, no skeletal hour-glass crystals have been observed.

In some clinopyroxene crystals (i.e. titanaugite A and aluminous augite D) showing sector zoning, the faces of the $\{010\}$ or $\{100\}$ forms have the highest growth rates (i.e. the smallest surface area), while in other crystals, especially titanaugite B and aluminous augite C, the faces of the $\{111\}$ form have the highest growth rates. Thus the presence of sector zoning is not dependent on the relative rates of growth (or surface area) of the faces, although the final shape of the sectors in the crystal does depend on the shape of the $\{100\}$ faces (fig. 1, iv).

The possibility that two chemically different pyroxenes have formed due to a subsolidus reaction similar to the two pyroxenes present in tholeiitic lavas is unlikely in the light of current experimental data. De Neufville and Schairer (1961) have shown that up to 20 wt % $\text{CaAl}_2\text{SiO}_6$ (Ca-Ts) molecule can be incorporated as solid solution in diopside in the system $\text{CaMgSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ at 1 atmosphere. Similarly, Yagi and Onuma (1967) have found up to 11 wt % $\text{CaTiAl}_2\text{O}_6$ (Tp) molecule in solid solution with diopside in the system $\text{CaMgSi}_2\text{O}_6$ – $\text{CaTiAl}_2\text{O}_6$ at 1 atmosphere. In the pyroxenes A to D, the maximum amount of Tp molecule is 13.3 wt % (in the $\{100\}$ -sector of A) and the maximum amount of Ca-Ts molecule is 20.6 wt % (in the $\{100\}$ -sector of D). The pyroxene norm is calculated in the same order as Binns *et al.* (1970) except that acmite is the only ferric-ion-bearing molecule. Thus, because the diopside structure can readily accept large amounts of Ca-Ts and Tp molecules in solid solution, the presence of two chemically different pyroxenes, either crystallizing in equilibrium from an undersaturated alkali liquid or having a subsolidus reaction point, appear unlikely to control the formation of hour-glass sector zoning in the present case.

Effects such as pressure, size of screw dislocation steps, presence of dislocation clusters, twin boundaries, lattice defects, and the presence of other crystals may effect the final habit of the crystal but their effects are not always consistent and clearly cannot be the main factors controlling sector zoning in the present case.

For a face of the $\{100\}$ form to grow, the clinopyroxene structure requires a layer of M_1 (Mg and Fe^{2+} , etc.) and M_2 (Ca and Na) atoms followed by a layer of silicate units to form the chains (Deer *et al.* 1963, figs. 13 and 14). Since the SiO_2 content in the liquids from which each of the four pyroxenes have crystallized is low, more Al substitutes for Si in this growth direction because of the large number of silicate units required to form the chains in one layer in the growth direction perpendicular to $\{100\}$. Charge balance is maintained by Ti^{4+} , Ti^{3+} , Al^{3+} and Fe^{3+} substitution for Mg and Fe^{2+} in the M_1 sites. In other growth directions the number of silicate units required in each layer is more uniform, hence Al^{IV} substitution is less.

Predictions from the above model include a fixed orientation of the Al- and Ti-rich sectors, with the shape of the sectors being determined by the shape of the faces of the {100} form. Also, if the concentration of Al_2O_3 in the liquid is low, the growth rate of the {100} form would also be low, as is observed for titanaugite B.

Growth in the *b*-direction requires a layer of silicate units and *M1* atoms, then a layer of only *M2* atoms (Deer *et al.* 1963, fig. 13), thus {010}-sector zoning of Ca may be expected. Preliminary investigations on basal {001} sections have detected slight decreases of approximately 0.5 wt % CaO at the rim of faces of the {010} form relative to the rim at the faces of the {100} form.

The model described above requires that the SiO_2 concentration in the liquid be relatively low, which agrees with observations that chemical sector zoning occurs in undersaturated lavas where the overall rate of growth of the crystals is too fast to allow any solid state diffusion to occur. In more silica-saturated rocks, the Al and Ti contents in all sectors will depend on their own concentration relative to silica and on the temperature of crystallization and thus only concentric zoning will occur.

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