

MINERALOGICAL MAGAZINE

VOLUME 39 NUMBER 302 JUNE 1973

The origin and petrogenetic significance of hour-glass zoning in titaniferous clinopyroxenes

SUZANNE Y. WASS

School of Earth Sciences, Macquarie University, North Ryde,
N.S.W., 2113, Australia

SUMMARY. Tertiary alkali basaltic rocks from the Southern Highlands, New South Wales, contain two types of clinopyroxene crystals, which exhibit excellent morphological development of hour-glass zoning. These are small, quench clinopyroxene crystals and large, abundant, euhedral phenocrysts. Electron microprobe analyses show that the different zone sectors derive from compositional differences, with variation in TiO_2 and Al_2O_3 contents inversely with SiO_2 content being most significant. Increased depth of colour of titanogites depends on increased coupled substitution of Al for Si in tetrahedral sites and of Ti^{3+} in an M_1 site, while pleochroism is enhanced by increasing Fe content. It is suggested that the formation of hour-glass zoning is determined by an environment of crystallization where initial crystal growth is rapid relative to ionic diffusion in the melt, resulting in different chemistry for different growth directions within the crystal. This implies that, under certain conditions, kinetic factors, as well as the chemical composition of the host magma, may be significant in determining the chemical composition of phases precipitated, particularly where more than one crystallographic direction of growth is possible.

CLINOPYROXENE of low-pressure origin in Tertiary alkali basaltic rocks from the Southern Highlands, N.S.W., can usually be subdivided into intratelluric and quench phases. Both types may exhibit hour-glass zoning. One rock in particular, chemically a nepheline hawaiite but relatively coarse-grained, was used to obtain the main chemical data on the hour-glass zone sectors and to establish crystallographic relationships between the sectors. This was because of the perfection of the hour-glass sectors in the clinopyroxenes in this rock and also because use of only one rock type ensures that any chemical variations in the pyroxenes are not due to intrinsic composition differences between different host rocks. However, clinopyroxenes in numerous other basaltic flows from the same alkali-basaltic province show development of hour-glass zoning and these were studied in somewhat less detail chemically, to provide an overall concept of such zoning and to eliminate the possibility that a type of zoning is peculiar to a given rock.

The crystallization history of the flow studied in most detail is significant to the formation of the good hour-glass zonation in its clinopyroxenes. A reasonably long

period of shallow intratelluric crystallization can be inferred as this flow is a late-stage differentiate of a basaltic lava pile about 200 feet thick. It appears to have been erupted as a crystal mush from a final vent, and represents the most fractionated effusive rock of this sequence. In this¹ rock (45100), large euhedral titaniferous clinopyroxene phenocrysts, dominantly displaying prismatic and pinacoidal forms and elongate parallel to *c*, are up to 6 mm long and 3 mm wide and comprise about 25 % of the rock. Other flows studied in less detail include another flow derived by moderate high-level differentiation and numerous flows containing abundant quench grains set in a glassy or cryptocrystalline mesostasis.

Morphology of hour-glass zoning

Similar morphological development was evident in all examples of hour-glass zoning examined. The typical hour-glass form (figs. 1, 2) is best developed in the (010) plane, and appears in thin section as four triangular segments all with apices

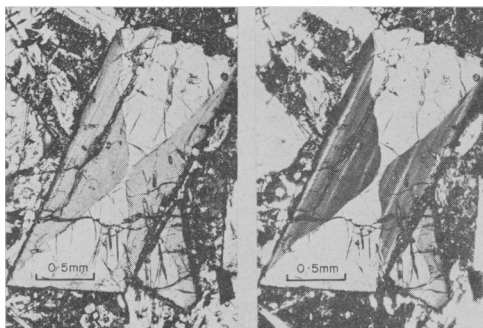


FIG. 1a, left: Hour-glass zoning in titanite on an (010) section. Note that in this crystal, the paler sectors are contiguous. (Plane polarized light.) *b*, right: Same crystal as in *a* with crossed polars. Concentric zones, most clearly seen in the dark sectors are continuous across all sectors. Note the stepped nature of the boundaries between light and dark sectors. Each step coincides with the width of a concentric zone.

pointing towards the mid-point of the crystal. Opposite zone sectors (i.e. triangles) are chemically and optically identical. In plane polarized light hour-glass zone sectors are clearly evident by colour difference. On (010) sections (fig. 1a), sectors with triangular bases parallel to (001) are pale brownish-pink and sectors with bases parallel to (100) are deep reddish-pink. Either both dark or both pale sectors may be contiguous, indicating that either may nucleate initially. Difference in birefringence and dispersion characterize the two sector types under crossed polars. No significant optical discontinuity, other than that due to the compositional differences, occurs across sector boundaries. (010) sections (figs. 1a, 1b, 4) show evenly

developed sectors; (100) and (001) sections, depending on where the crystal is cut, show irregular sectorial arrays (fig. 3), although a few (100) sections show shallow hour-glass shapes. Examination of many sections on the universal stage shows that the type and degree of perfection of the zoning morphology depends on crystallographic orientation. In particular, the boundaries between pale and deeply coloured sectors are in the (011) zone. In several sections large plagioclase crystals cut across the zoned pyroxenes, but this has no optically detectable effect on the morphology of the hour-glass zoning.

The idealized 3-dimensional shapes of hour-glass sectors appear to be triangular

¹ Numbers refer to the catalogue of the Rock Collection of the Geology Department, the University of Sydney.

prisms parallel to b with lateral slopes approximating to the (101) plane (fig. 3*k*). Such ideal development is not always evident; unequal growth rates of each sector, and irregularity of growing surfaces can produce the patchy zoning on (001) and patchy to sub-hour-glass zoning on (100) (see fig. 3*b*). This inferred morphology of zoning on (100) and (001) is similar to the complex zoning described by Wilkinson (1957).

Quench clinopyroxenes show identical hour-glass morphology (figs. 4, 5, 6). The presence of deeply indented swallow-tail terminations does not preclude the formation of hour-glass zoning (figs. 5, 6), and as in the large phenocrysts, either both dark or both pale sectors may be mutually contiguous; the pale sectors are also always elongate parallel to c .

Concentric zoning and marginal rims

As well as the hour-glass zoning, two other types of zoning are present in many of these clinopyroxenes. One type occurs as narrow bands concentric with the euhedral crystal outline; these are distinguishable by change in colour intensities and slightly different extinction angles, and occur continuously throughout all sectors of the hour-glass zones (figs. 1*b*, 2). Hour-glass zone sector boundaries are sometimes stepped and indented (figs. 1*b*, 2). These irregularities always occur where concentric zones intersect hour-glass sector boundaries, suggesting a relationship between crystal growth and formation of concentric zones.

Many of the hour-glass zoned crystals are completely rimmed by a narrow zone (up to 0.01 mm wide) of dark purplish-red strongly pleochroic clinopyroxene, which is optically and chemically equivalent to quench groundmass clinopyroxene in the same rock. This outer rim is continuous, non-sectorial and is probably due to late-stage precipitation of a clinopyroxene layer concomitant with precipitation of groundmass clinopyroxene.

Chemistry of zones and quench clinopyroxenes

Hour-glass zones: Numerous traverses and spot analyses by electron microprobe were carried out on five separate crystals showing hour-glass zoning. A corresponding

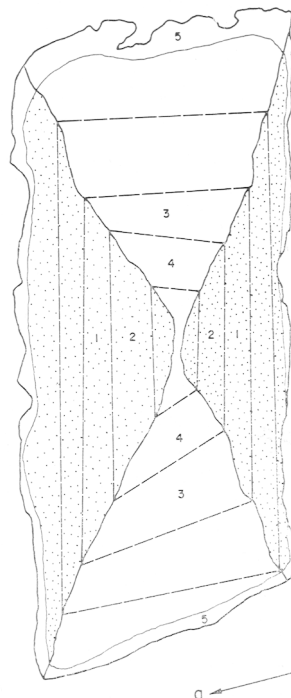


FIG. 2. Diagram traced from fig. 1*b*, showing the configuration of concentric normal and oscillatory zones by dashed lines. Stippling indicates the more deeply coloured hour-glass sectors while the outermost concentric rim is a late-stage overgrowth compositionally equivalent to small groundmass clinopyroxene grains. Numbered areas bounded by dashed lines (normal and oscillatory zones) and continuous lines (hour-glass sector boundaries) refer to analyses given in table I.

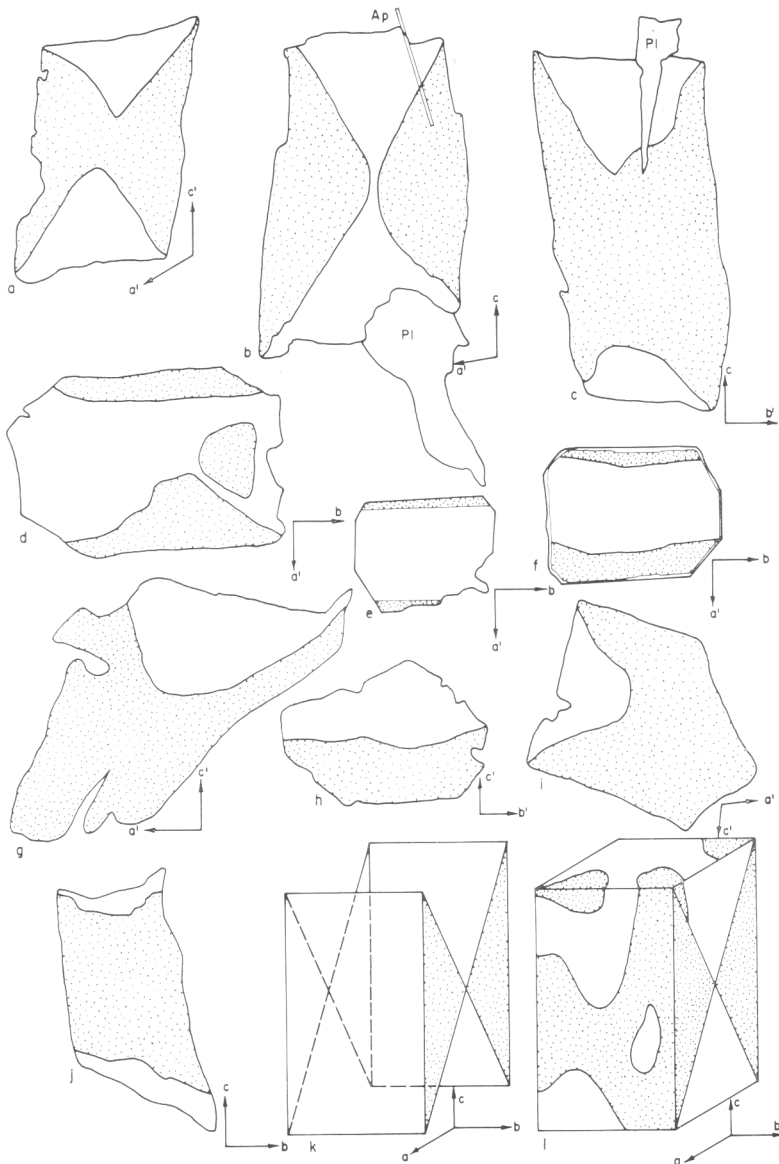
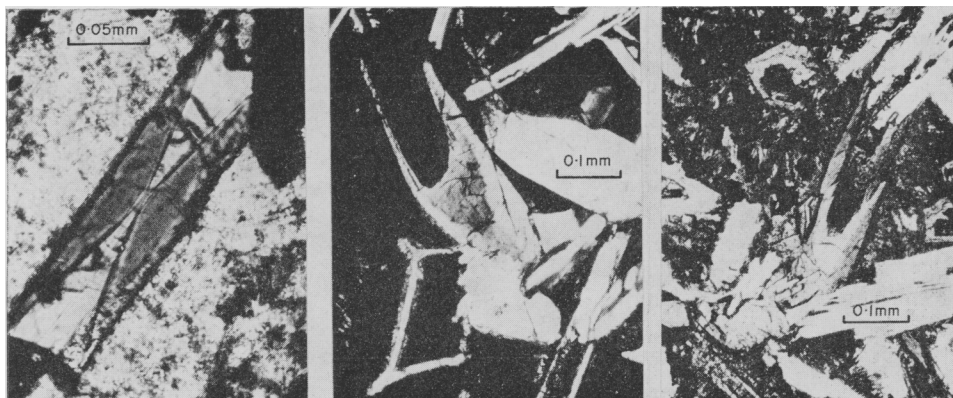


FIG. 3. *a-j*. Sketches (using camera lucida attachment) of various sections of hour-glass zoned titan-augites with axial directions. Stippled areas indicate deeply coloured zones. Pl = plagioclase, Ap = apatite. *a*, approximately (010); *b*, (010); *c*, (110); *d*, approximately (001); *e*, (001); *f*, (001), note continuous outer rim of composition equivalent to groundmass clinopyroxene; *g*, (100); *h*, (101); *i*, (011); *j*, (111). *k*, idealized 3-dimensional morphology of the hour-glass structure in titan-augites of this study. The enclosed triangular prisms (stippled on (010)) represent deeply coloured sectors. *l*, schematic diagram suggesting variation in morphology of the hour-glass structure by uneven growth of various sectors. Note the patchy nature of the zoning on (001) and (100).

relationship between depth of colour (i.e. particular zone sector) and chemical composition was established (Tables I, II, and III). Variations in TiO_2 and Al_2O_3 contents inversely with SiO_2 contents correlate with the zoning. In deeply-coloured sectors, TiO_2 ranges from 5.2 to 5.8 %, Al_2O_3 from 10.1 to 10.9 %, as SiO_2 varies inversely from 42.6 to 41.5 %. In pale sectors, TiO_2 ranges from 2.5 to 2.9 %, Al_2O_3 from 5.8 to 6.8 % as SiO_2 varies from 50.4 to 47.9 %.



FIGS. 4, 5, 6: FIG. 4 (left). Hour-glass zoning in a titanite in the rapidly chilled glassy lining of a vesicle. Shallow swallow-tail terminations are evident. (Plane polarized light.) FIG. 5 (middle). Hour-glass development in titanite in the chilled marginal phase of a basaltic flow. Note the extremely deep swallow-tail structure. The hour-glass sector with triangular base parallel to (001) appears dark due to crossed polars. In plane polarized light this is actually the pale sector. FIG. 6 (right). Hour-glass structure in titanite in a glassy basaltic flow. Swallow-tail terminations are well developed. Note the invariable configuration of dark and pale sectors. (Plane polarized light.)

Concentric zones are also distinct chemically. Microprobe data indicate that Fe/Mg substitution on a smaller scale than that of groundmass clinopyroxenes (about 0.5 % FeO) characterizes these zones. However, they are otherwise chemically identical with the particular hour-glass sector in which they lie—i.e. in the deeply coloured sectors, the concentric zones are higher in Al_2O_3 and TiO_2 , and lower in SiO_2 than the corresponding concentric zone in the pale sectors (table I, fig. 2). Thus concentric zones appear to arise in a manner completely analogous to that which produces normal zoning in plagioclases (Vance, 1962). Small fluctuations either in chemistry or pressure and temperature conditions in the melt result in corresponding Fe/Mg fluctuations within the growing clinopyroxenes. The concentric zones are thus time boundaries within the crystals. It is therefore necessary that analyses of dark and pale sectors of the same crystal are carried out within the same concentric zone. Otherwise it may easily appear that FeO concentration is also significant in the formation of different zone sectors.

The *outer-rim* of the large phenocrysts is chemically distinct from the main hour-glass sectors in its relative enrichment in iron at the expense of magnesium (analysis 5, table I), although TiO_2 and Al_2O_3 values are high and SiO_2 relatively low. This

compositional trend is normal for late-crystallizing clinopyroxenes from alkali-basaltic magmas (Yagi and Onuma, 1967), and arises from a process quite distinct from that which produces the hour-glass zoning, although some elemental trends are common to both.

TABLE I. *Representative electron microprobe analyses of different sectors and zones in one titanaugite grain from rock 45100*

	1	2	3	4	5
SiO ₂	41.7	43.1	47.3	47.4	43.0
TiO ₂	5.40	5.76	2.92	2.84	5.51
Al ₂ O ₃	10.7	10.1	6.27	6.04	9.34
Cr ₂ O ₃	0.02	0.04	0.02	0.02	0.03
*FeO	7.81	8.39	7.07	7.20	9.17
MgO	9.54	9.19	12.0	12.3	9.07
CaO	22.9	22.3	22.4	22.4	22.0
Na ₂ O	0.69	0.77	0.52	0.55	0.94
Total	98.0	99.7	98.5	98.7	99.1

* Total Fe as FeO

Cation contents on basis of 6 oxygen.

Si	1.599	1.635	1.792	1.790	1.647
Al ^{iv}	0.401	0.365	0.208	0.210	0.353
Al ^v	0.083	0.086	0.069	0.058	0.102
Ti	0.157	0.164	0.084	0.082	0.158
Cr	0.000	0.001	0.001	0.001	0.001
Fe	0.251	0.267	0.223	0.227	0.294
Mg	0.546	0.519	0.678	0.695	0.518
Ca	0.938	0.907	0.910	0.908	0.906
Na	0.051	0.055	0.018	0.041	0.069
x+y	2.02	2.00	1.98	2.01	2.05

1. Deeply-coloured hour-glass sector.
2. Same hour-glass sector as (1) but on a concentric, continuous paler zone
3. Pale pink hour-glass sector adjacent to (2).
4. Same hour-glass sector as (3) but on a concentric, continuous paler zone.
5. Continuous outer rim of pyroxene phenocryst.

Numbers of analyses refer to numbered areas on fig. 2. Each analysis is the average of at least ten points within each area.

'Groundmass' clinopyroxene in 45100 includes small, commonly skeletal, prismatic quench crystals and larger euhedral crystals (up to 0.5 mm long) that texturally do not appear to be quench products. The quench clinopyroxene is strongly pleochroic from deep purplish red to light brownish pink and is chemically similar to the quench rims on the hour-glass zoned phenocrysts (analyses 3 and 4, table I).

The larger unzoned 'groundmass' euhedra individually show optical and chemical similarities with separate sectors of the large zoned clinopyroxene crystals (analyses

TABLE II. *Electron microprobe analyses of corresponding hour-glass zone pairs from different titanaugite grains and of ground-mass titanaugite grains from rock 45100*

	1	2	3	4	5	6	7	8	9	10
SiO ₂	50.4	41.5	47.9	42.6	48.3	41.9	46.4	46.9	42.6	43.8
TiO ₂	2.48	5.61	2.90	5.23	2.90	5.45	3.67	3.10	5.49	5.69
Al ₂ O ₃	6.35	10.9	6.07	10.8	5.81	10.2	5.16	5.05	9.24	6.11
Cr ₂ O ₃	0.00	0.04	0.02	0.04	0.02	0.02	0.05	0.03	0.02	0.03
*FeO	7.25	8.08	7.07	7.87	7.18	7.96	13.5	12.5	9.70	12.6
MgO	11.6	9.62	12.0	9.49	11.8	10.1	7.91	8.44	8.58	8.38
CaO	20.8	23.0	23.1	21.7	22.5	21.9	21.7	21.5	22.6	21.6
Na ₂ O	1.08	0.66	0.56	0.72	0.60	0.56	0.99	0.80	0.74	1.21
Total	100.0	99.4	99.6	98.5	99.1	98.1	99.4	98.3	99.0	99.4

* Total Fe as FeO

Cation contents on basis of 6 oxygen.

Si	1.863	1.582	1.797	1.631	1.812	1.608	1.799	1.822	1.640	1.702
Al ^{iv}	0.137	0.418	0.203	0.369	0.188	0.392	0.201	0.178	0.360	0.280
Ti ^{iv}	0.000	0.000	0.000	0.119	0.000	0.000	0.000	0.000	0.000	0.018
Al ^{vi}	0.138	0.072	0.068	0.000	0.074	0.069	0.037	0.056	0.061	0.000
Ti	0.069	0.165	0.081	0.150	0.081	0.157	0.107	0.091	0.160	0.148
Cr	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Fe	0.224	0.256	0.221	0.253	0.226	0.256	0.438	0.406	0.310	0.409
Mg	0.637	0.547	0.670	0.541	0.661	0.593	0.450	0.488	0.492	0.486
Ca	0.822	0.941	0.927	0.888	0.900	0.901	0.901	0.897	0.934	0.900
Na	0.076	0.050	0.041	0.055	0.041	0.042	0.074	0.061	0.055	0.081
x+y	1.97	2.01	2.01	2.01	1.98	2.02	2.01	2.00	2.01	2.05

1. Pale pink sector, pyroxene A; 2. Deeply-coloured sector, pyroxene A; 3. Pale pink sector, pyroxene B; 4. Deeply-coloured sector, pyroxene B; 5. Pale pink sector, pyroxene C; 6. Deeply-coloured sector, pyroxene C; 7 and 8. Deeply-coloured euhedral groundmass grains; 9 and 10. Pale pink euhedral groundmass grains.

TABLE III. *Representative partial analyses of hour-glass zone sectors in titanaugite grains from rock 45100*

	1	2	3	4	5	6	7	8	9	10
SiO ₂	48.2	48.0	47.6	47.9	47.5	42.6	41.5	42.4	41.8	41.6
TiO ₂	2.88	2.94	2.62	2.90	2.91	5.23	5.64	5.20	5.63	5.60
Al ₂ O ₃	5.80	6.10	6.28	6.00	6.00	10.2	10.7	10.3	10.8	10.8
*FeO	7.21	7.00	7.27	7.16	7.24	7.85	7.93	7.91	8.01	8.00
MgO	11.7	12.1	11.5	11.7	11.6	9.63	10.1	10.0	9.72	9.68

* Total Fe as FeO

1-5. Pale pink sectors. 6-10. Deeply-coloured sectors.

7 to 10, table II). The implications of this are that two Ca-rich clinopyroxenes may precipitate independently but contemporaneously from a host magma, a concept further discussed below with reference to the mechanism of formation of hour-glass zones. The possibility that these larger 'groundmass' clinopyroxene crystals, identified by lack of sectorial twinning and euhedral form, may in fact be sections through

different zones of larger hour-glass zoned crystals and thus be accidental results of thin-section preparation, was considered. However, it is unlikely that random oblique sections through larger grains could consistently give euhedral crystal outlines.

Previous work on zoned clinopyroxenes

Strong (1969) gave a comprehensive survey of most of the relevant studies to that time. Where mechanisms of formation are proposed (e.g. Farquhar, 1960; Strong, 1969) resorption or original skeletal growth (of hour-glass shape) of clinopyroxene with subsequent infillings by later precipitation have been invoked. The hour-glass morphology was suggested to result from the intersection of pyramidal forms (e.g. Rosenbusch, 1905; Strong, 1969), although Preston (1966) showed that triangular prisms parallel to c , rather than intersecting pyramids, account for one type of hour-glass zoning in augite. Bence and Papike (1971) described a 'martini-glass' structure in lunar clinopyroxenes due to simultaneous precipitation of augite and pigeonite on different faces. Such explanations are not directly applicable to the present study because of the two different crystallographic structures of the two pyroxenes involved and the established immiscibility gaps such as between augite and pigeonite. However, a textural analogy exists.

Hollister and Hargraves (1970) discussed sectorial and continuous zoning in pyroxenes from Apollo II samples. Although these pyroxenes are relatively poor in titanium compared with those of the present study, similar antipathetic variation of SiO_2 with TiO_2 and Al_2O_3 characterizes sector zoning, all sectors of which are considered to have formed at the same time. Sector zoning of augite mantles on pigeonite cores from lunar rock 12021 has been interpreted as being due to 'different trends characterising growth on (110), (100), (010) and parallel to c ' (Boyd and Smith, 1971). Smith and Carmichael (1969) mapped Ti, Al, and Si distribution in one half of an hour-glass zoned titanite. Their chemical data are in complete agreement with those of the present study, including the abrupt rather than transitional nature of the oscillatory zones.

Possible mechanisms of zoning

Any mechanism for the formation of the hour-glass zoning must be compatible with five facts established in the present study:

Pale and deeply-coloured sectors are characterized by the particular chemistry of each sector type. Variations in Al_2O_3 and TiO_2 contents, with concomitant antipathetic variation in SiO_2 content, define the two basic sector types.

As there are no large optical discontinuities across sector boundaries, sector types are not due to difference in relative crystallographic orientation.

Both the pale and deeply-coloured sectors grew contemporaneously and at similar rates in the crystals studied. This is evidenced by the presence of normal and oscillatory concentric zones, which define time boundaries within the crystal.

Sector boundaries appear to parallel (101) planes, and the zones appear to have the 3-dimensional morphology of triangular prisms.

In the two types of crystals that show development of hour-glass zoning (i.e. large, abundant, euhedral phenocrysts and quench crystals), the growth rate of the crystals relative to diffusion rates in the host magma is rapid. The large phenocrysts crystallized in a shallow magma chamber from a magma that was probably relatively viscous at this inferred late stage of fractionation. In addition, in the rock 45100, pyroxene was the major phase containing MgO, as modal olivine is less than 2 %.

Previously suggested mechanisms based on the initial formation of one set of sectors, with subsequent overgrowth of the remaining sectors (e.g. Strong, 1969) are not viable for the following reasons:

Incompletely filled hour-glass crystals were not found in the present study.

Swallow-tail terminations on quench grains cannot be interpreted in this way because such crystals commonly show good development of hour-glass sectors as well as deep swallow-tail indentations and because indentations are parallel to *c*, so that subsequent infilling of more differentiated Fe-rich pyroxene would produce deeply-coloured sectors in these positions, whereas sectors in these positions are always pale (see figs. 1*a*, 4, 6).

The nature of the concentric zones indicates that all sectors formed at the same time. In addition, either the dark or the pale sectors may be the first to form at the time of nucleation.

Chemical data does not support later infilling. The chemistry of the so-called 'later' (dark) zones is not equivalent to the fractionation trends indicated by quench pyroxenes in the same rock. Such fractionation trends involve Fe enrichment, a factor that does not distinguish pale or dark zones if analyses are carried out within the same concentric zones.

A mechanism consistent with all observed data that explains the formation of hour-glass zoning depends on the environment of crystallization. The basic requirement is kinetic—that growth of the crystal is fast relative to ionic diffusion in the melt. Evidence is threefold: the hour-glass structure occurs only in titanaugites that crystallized under conditions of relatively rapid crystal growth; rapid precipitation may be necessary to initiate simultaneous growth on two different crystallographic planes and to initiate the coupled substitution of Al for Si and of Ti³⁺ in *M*₁ sites; and a continued rapid growth rate is probably necessary to perpetuate the growth of deeply-coloured sectors, as the composition of the clinopyroxene in these sectors is unusual considering the chemical composition of the host rocks, and may represent a relatively high-energy state. If slower crystallization with continuous equilibrium adjustments followed the initial formation of the hour-glass structure, it is expected that crystallization of the paler clinopyroxene only will ensue. Thus favourable kinetic conditions may be achieved either in quenching conditions or in an environment supersaturated in potential pyroxene. Increasing viscosity of the magma as in a late-stage fractionation residue may also contribute to this kinetic balance.

The compositional differences between the sectors arise from the ability of Al to enter tetrahedral sites easily at low pressures (Yagi and Onuma, 1967). It is not necessary to invoke an immiscibility gap to explain simultaneous precipitation of two Ca-rich clinopyroxenes. Hollister (1970) has suggested that analogous sector zoning

in staurolite (which grew in the solid state) is due to 'disequilibrium between the bulk of each sector and the matrix but chemical equilibrium between the surface layers of the sectors and the matrix', with growth on different faces within the one crystal, eliminating the need for a miscibility gap in this case. Hollister and Hargraves (1970) extend this mechanism to account for compositional sector zoning in lunar clinopyroxene.

Using the diopside structure of Zussman (1968) it is evident that tetrahedral and M_1 sites would be simultaneously available for occupation on (010) and (001) layers, whereas growth parallel to (100), (110), or (101) does not permit simultaneous coupled substitution (Hollister and Hargraves, 1970). Formation of hour-glass zoning by growth parallel to certain crystallographic planes implies that specific site occupancy in one layer controls the ionic species and site occupancy for the subsequent layer. Once a compositional difference is established it is maintained by a drive towards thermodynamic equilibrium, and hence homogeneity results for that sector. Two specific growth mechanisms may account for the formation of the deeply-coloured sectors. One is simultaneous coupled substitution of Al and Ti within the same growth layer, e.g. parallel to (001). The other is a 'see-saw' effect initiated by charge imbalance in one layer, e.g. parallel to (101), satisfied by completion of the coupled Ti-Al substitution in the next. Near euhedral growth at similar rates on at least two rational planes (with relevant chemical partitioning) during formation is necessary to produce good hour-glass morphology. Imperfect sector zoning in pyroxenes may arise by a similar basic mechanism but with differential growth rates of sector types, or abrupt discontinuities resulting in growth on different crystallographic planes. Factors such as dislocation formation or erratic diffusion rates could initiate such changes in nucleation vectors.

Origin of colour in titanaugites

The determination of the chemical identity of the deeply coloured sectors in titanaugites provides a basis for interpreting the pleochroism and colour variations so commonly attributed to titanium or to aluminium. Although titanium is more abundant in the deeply-coloured than the pale sectors, the much more deeply-coloured rims and groundmass pyroxenes in 45100 do not contain a greater amount of Ti than the highly-coloured sectors. So Ti content is not solely responsible for pink colouration. Indeed, Yagi and Onuma (1967) showed that synthetic $\text{Ca Ti Al}_2\text{O}_6$ (in which all Ti is present as Ti^{4+}) is colourless.

Recent work (e.g. Burns, 1966, 1970; Burns *et al.*, 1964; Manning and Nickel, 1969) has shown that the colour of minerals arises basically from ionic charge transfer (e.g. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) and electronic transitions from ground state to higher energy levels made possible by radiation absorption in the visible region of the electromagnetic spectrum. These phenomena may be considered in terms of crystal-field theory (Orgel, 1966). A number of electronic energy levels may result from splitting of cation $3d$ in an electrostatic field due to distortion of the electronic field. Such a field surrounds every cation in the pyroxene structure.

Absorption spectra of aqueous Ti^{3+} and titanaugite show coincident peaks (Burns *et al.*, 1964) confirming that some Ti in coloured titanaugites is present as Ti^{3+} (rather than TiO_2 as conventionally reported). This is predictable from crystal field considerations, as Ti^{4+} possesses no *d*-electrons whereas Ti^{3+} possesses one *d*-electron. Ti^{3+} in octahedral co-ordination absorbs in the blue-green spectral area. This is a broad absorption shown to occur in $Ti(OH_2)_6^{3+}$ (Hartman and Schlafer, 1951), andradite (Manning, 1967), and titanaugite (Burns and Fyfe, 1967).

The presence of some titanium as Ti^{3+} in titanaugite is probably a direct result of the electronic environment of the site occupied in the crystal lattice. The fact that Ti^{3+} and Fe^{2+} are mutually incompatible in solution is not directly applicable to crystalline material because of crystal field effects in the solid lattice, as Strens (1967) demonstrates.

Two relevant recent studies have been carried out on colour in pyroxenes. Polarized absorption spectra of (001) sections of titanaugite reveal $Fe^{2+} \rightleftharpoons Fe^{3+}$ charge-transfer as well as intracationic bands of Fe^{2+} , Fe^{3+} , and Ti^{3+} in octahedral co-ordination (Manning and Nickel, 1969). The colour of this titanaugite is considered to be derived from these *d-d* electron transitions and $Fe^{2+} \rightleftharpoons Fe^{3+}$ charge transfer may cause or at least enhance the pleochroism. No available experimental data on absorption spectra support $Ti^{3+} \rightleftharpoons Ti^{4+}$ charge transfer as a potential cause of pleochroism.

Although relating to orthopyroxenes, the data of Burns (1966) fit well with the chemical data on titanaugites of this study. Burns showed that pleochroism in orthopyroxenes results from preferential occupancy by Fe^{2+} of M_2 positions, replacement of Si by Al, and the 'presence of small, high-valence cations (Al^{3+} , Fe^{3+} , Ti^{3+}) in M_1 positions and a sufficient Fe^{2+} content'.

Using published absorption spectra and chemical data combined with the information in the studies of Burns (1966) and Manning and Nickel (1969), an attempt is made to account for colour and pleochroism of titanaugites:

$Fe^{2+} \rightleftharpoons Fe^{3+}$ transitions may account for pleochroism (note the deeper colour and stronger pleochroism of quench titanaugite in 45100).

Replacement of Si by Al provides a favourable environment for interference of Al^{3+} and Ti^{3+} outer electrons. The presence of Ti^{3+} causes absorption in the blue-green spectral region. Preferential occupancy of the M_1 site by the highly charged Ti^{3+} ion also causes electron field distortion, which is further enhanced by substitution of Al for Si in neighbouring tetrahedral sites.

The petrogenetic significance of hour-glass zoning

Both the pale and dark sectors of hour-glass zoned titaniferous clinopyroxenes formed contemporaneously despite their compositional differences. By analogy discrete clinopyroxene phenocrysts, homogeneous within each crystal, but chemically similar to either type of hour-glass zone sector, also crystallized at the same time. The ability of clinopyroxenes to grow parallel to more than one crystallographic plane, and rapid precipitation relative to ionic diffusion in the host rock are critical factors in the simultaneous formation of two compositional types. Therefore two

clinopyroxenes may crystallize together from the liquid in alkali basaltic rocks. The petrogenetic significance of this study is that perhaps the chemistry of host magmas is not the unique controlling factor in determining the chemistry of phases precipitated. Under certain conditions, kinetic factors may assume importance, particularly where more than one crystallographic mode of growth is possible.

Acknowledgements. This study was carried out in the Department of Mineralogy, British Museum (Natural History), the facilities of which were made available by courtesy of Dr. A. A. Moss. Financial assistance from the Edgeworth David Travelling Scholarship granted by the University of Sydney is gratefully acknowledged. Dr. S. J. B. Reed and Mr. R. F. Symes provided valuable advice on use of the electron microprobe and Dr. R. Hutchison contributed lively discussion. Associate Professors T. G. Vallance and R. H. Vernon are thanked for critically reading the manuscript and for helpful suggestions.

REFERENCES

- BENCE (A. E.) and PAPIKE (J. J.), 1971. *Earth Planet. Sci. Lett.* **10**, 245–51.
 BOYD (F. R.) and SMITH (D.), 1971. *Journ. Petrology*, **12**, 439–64.
 BURNS (R. G.), 1966. *Min. Mag.* **35**, 715–19 [M.A. 17–613].
 ——— 1970. *Mineralogical applications of crystal field theory*. Cambridge (C.U.P.) [M.A. 20–1073].
 BURNS (R. G.), CLARKE (R. H.), and FYFE (W. S.), 1964. In *Chemistry of the earth's crust. Proc. Vernadsky Centen. Symp.* **2**, 88–106. VINOGRADOV (A. P.) ed. (Transl. Israel Progr. Sci. Transl., Jerusalem, 1967, 93–112).
 ——— and FYFE (W. S.), 1967. In *Researches in Geochemistry*, ABELSON (P. H.) ed., **2**, 259–85, New York (Wiley) [M.A. 19–87].
 FARQUHAR (O. C.), 1960. *Rept. 21st. Sess. Int. Geol. Congr., Norden*, **21**, pt 21, 194–200 [M.A. 15–100].
 HARTMAN (H.) and SCHLAFFER (H. L.), 1951. *Zeits. phys. Chem.* **197**, 116–42.
 HOLLISTER (L. S.), 1970. *Amer. Min.* **55**, 742–66 [M.A. 21–3348].
 ——— and HARGRAVES (R. B.), 1970. *Geochimica Acta, Proc. Apollo II Lunar Science Conf.* **1**, 541–50 [M.A. 22–2108].
 MANNING (P. G.), 1967. *Canad. Min.* **9**, 237–51 [M.A. 20–2643].
 ——— and NICKEL (E. H.), 1969. *Ibid.* **10**, 71–83 [M.A. 22–484].
 ORGEL (L. E.), 1966. *An Introduction to transition metal chemistry: ligandfield theory*. London (Methuen).
 PRESTON (J.), 1966. *Amer. Min.* **51**, 1227–33 [M.A. 19–47].
 ROSENBUSCH (H.), 1905. *Mikroskopische Physiographie I* pt. 2. Stuttgart. (Verlagshandlung.)
 SMITH (A. L.) and CARMICHAEL (I. S. E.), 1969. *Amer. Min.* **54**, 909–23 [M.A. 21–846].
 STRONG (D. F.), 1969. *Min. Mag.* **37**, 472–9 [M.A. 21–598].
 VANCE (J. A.), 1962. *Amer. Journ. Sci.* **260**, 746–60 [M.A. 16–189].
 WILKINSON (J. F. G.), 1957. *Geol. Mag.* **94**, 123–34. [M.A. 14–206].
 YAGI (K.) and ONUMA (K.), 1967. *Journ. Fac. Sci. Hokkaido Univ. Ser. 4*, **13**, 463–83.
 ZUSSMAN (J.), 1968. *Earth Sci. Rev.* **4**, 39–67.

[Manuscript received 31 May 1972]