

## Stable and metastable pyroxene crystallization in layered komatiite lava flows

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### Abstract

Pyroxenes in the rapidly-cooled upper portions of thick, layered komatiite lava flows have significantly different compositions and structures from pyroxenes in the cumulate lower portions of the same flows. Rocks in the flow tops contain composite pyroxene megacrysts made up of needles with cores of pigeonite and margins of subcalcic, aluminous augite. The pigeonite is more magnesian [ $Mg/(Mg + Fe) \approx 0.84$ ] than any previously reported in terrestrial rocks. In the cumulate zones, the pyroxenes are bronzite and augite.

The pigeonite probably formed under conditions of strong undercooling developed during the solidification of the upper parts of the flows, whereas the cumulus pyroxenes formed under conditions approaching equilibrium in the more slowly-cooled central parts of the flows.

### Introduction

In thick, layered komatiite lava flows, the compositions and the types of pyroxenes in flow top zones differ considerably from those in lower cumulate layers of the same flows. Magnesian pigeonite and subcalcic augite are present in the flow top zones, whereas bronzite coexists with augite in the cumulate layers. Furthermore, the pigeonite has crystallized from magmatic liquids, which, under experimental equilibrium conditions (Arndt, 1977a), would have crystallized olivine. In this paper, the crystallography, mineral habit, and chemistry of pyroxenes from the upper and central parts of two layered komatiite lava flows are described and contrasted, and the conditions that controlled their formation are investigated.

#### *Thick, layered komatiite lava flows*

The principal features of the two lava flows are illustrated in Figure 1a,b. One of them, Fred's Flow, from Munro Township in northern Ontario, has been described in detail in other publications (Arndt, 1976, 1977b; Arndt *et al.*, 1977). The other, which will be referred to as the Alexo Flow, is in Dundo-

nald Township about 70 km west of Munro. It has been discussed very briefly by Arndt (1977a).

Fred's Flow can be divided into four units: a brecciated or spinifex-textured uppermost unit; a gabbroic unit; a cumulate unit; and a basal, olivine-depleted marginal unit (Fig. 1a). The flowtop breccia is made up of fragments of porphyritic lava containing olivine phenocrysts and skeletal olivine in a matrix of fine-grained acicular augite and devitrified glass. Spinifex is the name given to textures dominated by skeletal olivine on pyroxene grains, which form when ultramafic or highly mafic magmas crystallize relatively rapidly, as in the upper sections of lava flows (Nesbitt, 1971; Donaldson, 1976; Arndt *et al.*, 1977). In Fred's Flow, a thin layer of olivine spinifex-textured rock containing thin wafers of olivine in a pyroxene-glass matrix overlies a thicker pyroxene spinifex-textured layer, in which large composite pigeonite-augite needles (described below) are oriented perpendicular to the flow margins, and lie within a pyroxene-plagioclase matrix. The gabbroic unit, which has a normal, medium-grained, sub-hedral-granular texture, is underlain by a thin interval of alternating layers of augite plus bronzite

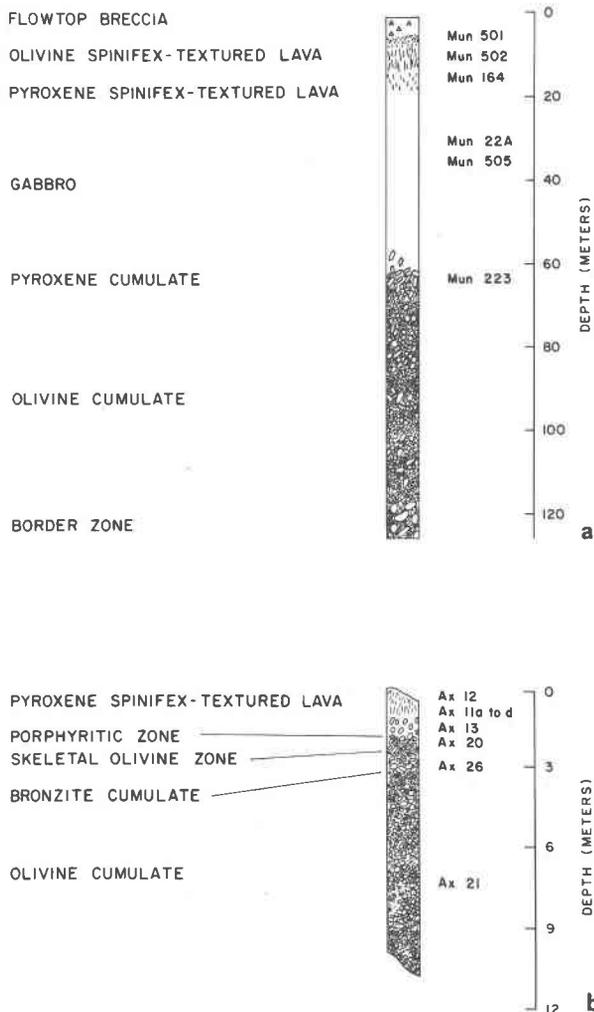


Fig. 1. Diagrammatic section through (a) Fred's Flow and (b) the Alexo Flow. Sample locations are shown on the right of the columnar section.

cumulates, and by a thicker interval of olivine cumulate.

The uppermost part of the Alexo Flow appears to have been eroded away by younger lava flows (Fig. 1b). The present top is pyroxene spinifex-textured like the lower spinifex layer in Fred's Flow. Olivine (now completely chloritized) appears sporadically in the spinifex layer, not at the top, but generally about a meter below the present surface. No gabbro is present in the Alexo Flow, and the transition from spinifex-textured lava to underlying olivine-rich rock usually is abrupt. In some areas, however, there is a narrow interval of porphyritic rock containing 10–60 percent of solid or skeletal, equant olivine phenocrysts in a fine-grained basaltic (augite + plagioclase)

groundmass. The upper 3–4 meters of the olivine-enriched layer contain skeletal, hopper olivine grains (Donaldson, 1976) in an augite-devitrified glass matrix. A thin band of bronzite cumulate separates this type of rock from the lower olivine cumulate which contains solid, polyhedral olivine grains.

The lava flows are believed to have been erupted at very high temperatures (1300–1350°C, the liquidus of olivine spinifex-textured lavas; Arndt, 1977a,b) as highly magnesian (15–20 percent MgO) liquids containing a small proportion of olivine phenocrysts. Following eruption, the lavas differentiated to form the olivine and pyroxene cumulates at the base of each flow. At the same time, spinifex-textured lava grew downwards from the top of each flow. In Fred's Flow, the quartz-normative basaltic liquid that resulted from this differentiation solidified as the gabbroic layer.

The calcium-poor pyroxenes in the pyroxene spinifex and cumulate layers of Fred's Flow have completely altered to chlorite; olivine is partially serpentinized in the cumulate layers and completely altered to chlorite and serpentine in the flow top layers. In the Alexo Flow, most mafic minerals have escaped complete alteration. The exception is olivine in the spinifex layers, which is completely altered to chlorite. Augite rarely is altered, and bronzite in the cumulate layer also is quite fresh. The state of preservation of pigeonite, however, varies from sample to

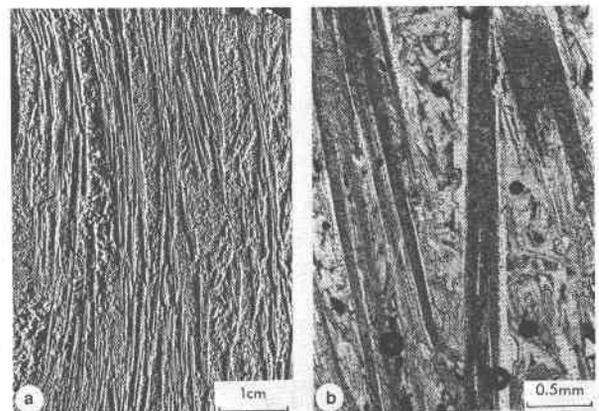


Fig. 2. (a) Photograph of a hand sample of clinopyroxene spinifex-textured lava from Fred's Flow showing pigeonite-augite megacrysts. Note the pronounced curvature of needles in the bottom left of the picture. The surface shown was polished, then etched in HF, and illuminated with highly oblique lighting. (b) Photomicrograph of a composite pigeonite-augite needle and interstitial splaying sheaths of augite and plagioclase. Pigeonite in the core of the needle has altered to chlorite. The augite mantle is unaltered.

sample. In some samples it is quite unaffected by alteration, and in others it has been pseudomorphically replaced by chlorite.

### Composite clinopyroxene megacrysts in the spinifex-textured layers

The pyroxene spinifex-textured lava is composed of 25 to 40 percent composite pigeonite-augite needles set in a matrix of dendritic augite and plagioclase. These needles are oriented roughly parallel to one another, perpendicular to the flow top (Fig. 2). They are 0.1 to 1.0 mm in diameter, and most are at least 2 cm in length. Their maximum length is difficult to estimate because they are usually inclined at a low angle to thin sections or fractured hand-sample surfaces. In many cases, however, individual needles exceed 5 cm in length. There is a tendency for their size to be fairly uniform in a single hand sample and to increase downward toward the middle of the spinifex layer.

In thin section, the needles can be seen to be organized into colonies of individuals in near-optical continuity. In fact, they form highly complicated, skeletal megacrysts that are coarse-grained equivalents of the feathery dendritic or spherulitic grains interstitial to olivine in peridotitic komatiite lavas (Fleet, 1975). Each megacryst consists of one or more parallel rows of needles, the whole appearing in three dimensions like the stems of a bunch of flowers (Fig. 2).

The megacrysts, in turn, are arranged to form sheaths or columns that extend for distances of up to several meters. Although they maintain an average orientation perpendicular to the flow top, the columns are gently curved, kinked, and warped (Fig. 2). This structure appears to be equivalent to that of the "folded columnar spinifex" of Nisbet *et al.* (1977). However, the curvature of the pyroxene columns is similar to that observed in comb-layered rocks (Lofgren and Donaldson, 1975) and probably has a similar origin: *i.e.* individual grains probably are slightly curved as a result of rapid growth from super-saturated liquids.

The individual clinopyroxene needles that make up the megacrysts are elongated parallel to the *c* axis and are bounded predominantly by {110} prism faces, with minor development of {010}. They consist of hollow cores of pigeonite, generally box-shaped in cross section, mantled and partly lined by augite (Fig. 3). A few megacrysts show well-developed augite {110} growth sectors (Figure 3e), and others show birefringence differences indicating sec-

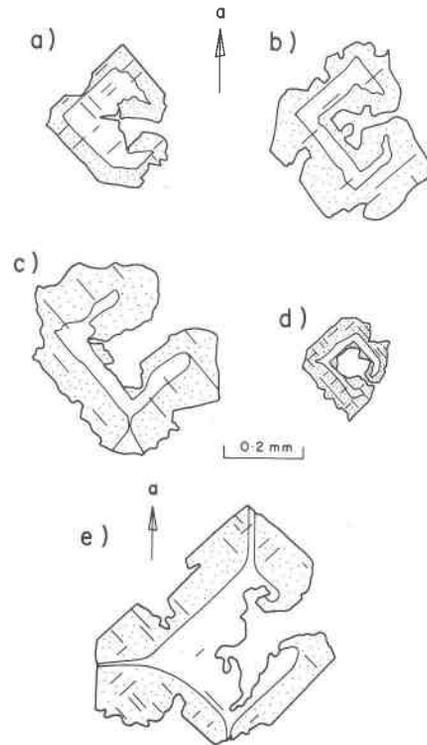


Fig. 3. Typical appearance of individual composite clinopyroxene megacrysts from pyroxene spinifex rock sectioned normal and subnormal to *c* axis in (a) and (d) Ax 11d; (b) and (c) Ax 13; (e) Ax 11c: clear, pigeonite; stippled, augite.

tor zoning. Thus, these composite clinopyroxene crystals are morphologically similar, and clearly genetically equivalent, to the composite pyroxene phenocrysts in Apollo 12 basalts (Hollister *et al.*, 1971). However, because they are much more elongated than their lunar counterparts, they are characteristically tubular in appearance. A few grains are markedly elongated along [100]\* and polysynthetically twinned on (100). In the megacrysts, parallel rows of composite clinopyroxene needles extend in the [100]\* direction (Fleet, 1975).

Fresh pigeonite in the composite needles is optically homogeneous: all the sections examined have the optic axial plane parallel to (010) and a  $2V$  near  $5^\circ$ . X-ray diffraction precession analysis of fragments of the composite needles removed from thin sections (Fig. 4) confirmed that the Ca-poor clinopyroxene cores are pigeonite, with  $P2_1/c$  symmetry. Measurements on precession photographs of several grains from Ax 11d give  $\beta$  parameters of  $108^\circ 15'$  for pigeonite and  $106^\circ 35'$  for augite. Pigeonite and augite reciprocal lattices have a preferred orientation which is equivalent to  $a_{\text{pig}}$  inclined to  $a_{\text{aug}}$ , with  $(a_{\text{pig}} \wedge a_{\text{aug}})$

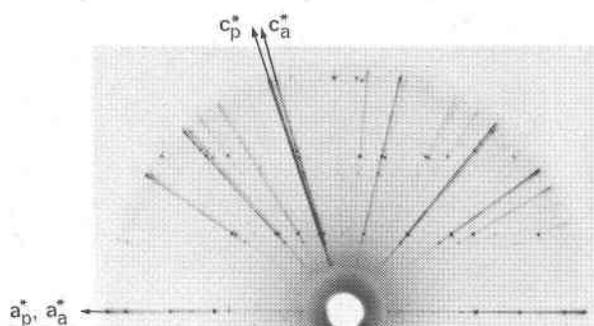


Fig. 4. X-ray diffraction precession photograph of a fragment of composite clinopyroxene needle from 11d, showing preferred orientation of pigeonite ( $a^*p$ ,  $c^*p$ ) and epitaxially overgrown subcalcic augite ( $a^*a$ ,  $c^*a$ ); zero level,  $b$  axis,  $\mu = 25^\circ$ , MoK $\alpha$  radiation, 35kV, 20mA, 3-day exposure.

$\approx \Delta\beta$ ;  $b_{\text{pig}}$  approximately parallel to  $b_{\text{aug}}$ ;  $c_{\text{pig}}$  approximately parallel to  $c_{\text{aug}}$  (Fig. 4). This orientation relationship is different from that of the composite pyroxene phenocrysts of Apollo 12 basalts (Ross *et al.*, 1973), which have  $(a_{\text{pig}} \wedge a_{\text{aug}}) \approx (c_{\text{pig}} \approx c_{\text{aug}}) \approx \Delta\beta/2$ , and in fact is similar to that for (100) pigeonite and augite exsolution lamellae in, respectively, augite and pigeonite. However, for each fragment X-rayed, the intensities of the two superimposed diffraction patterns were consistent with the observed proportions of core pigeonite and mantle augite, and exsolution lamellae could not have made a significant contribu-

tion to these diffraction patterns. In the composite needles of Ax 13 the pigeonite and augite  $c$  axes are slightly misaligned, and a single grain from Ax 12, in which most of the core pigeonite has been altered, gave the 'opposite' preferred orientation to that observed in Ax 11d with  $a_{\text{pig}}$  approximately parallel to  $a_{\text{aug}}$ ;  $(c_{\text{pig}} \wedge c_{\text{aug}}) \approx \Delta\beta$ .

Finely laminated striations, subparallel to (001), are observed in the mantle augite of Ax 11c clinopyroxene megacrysts. These could be (001) pigeonite exsolution lamellae, since the latter were identified optically in one grain of a double-polished thin section. However, pigeonite reflections were not detected in long-exposure precession photographs of these pyroxenes, and it is possible that some of these striations may be crystal growth features.

The pigeonite in the composite needles has unusually high magnesium-iron ratios [Table 1, Mg/(Mg + Fe) = 0.81 to 0.85] and high alumina contents (2.0 to 2.7 weight percent). The composition is fairly uniform, although there is, from a point close to the inner margin to the outer margins of the pigeonite areas, a slight increase in CaO, a gradual decrease in MgO/FeO, and a marked decrease in Cr (Fig. 5).

The clinopyroxene surrounding the pigeonite cores of the composite needles is aluminous, subcalcic augite (Table 1). In many grains, CaO remains essentially constant from the inside to the outside of the

Table 1. Representative electron microprobe analyses for pyroxenes in layered flows

	1	2	3	4	5	6	7	8	9
SrO <sub>2</sub>	55.2	53.6	51.9	50.6	51.9	51.3	51.3	57.1	52.5
TiO <sub>2</sub>	0.11	n.d.	.37	n.d.	n.d.	.51	.46	0.04	0.20
Al <sub>2</sub> O <sub>3</sub>	2.02	2.32	4.6	5.1	3.14	2.67	2.56	0.91	2.53
Cr <sub>2</sub> O <sub>3</sub>	0.63	0.76	.23	.16	.39	.13	0.04	0.50	0.81
FeO (tot)	9.4	9.7	7.7	8.4	7.6	10.6	13.8	7.9	5.91
MnO	0.26	n.d.	.25	n.d.	n.d.	.26	.37	0.21	0.15
MgO	28.9	26.7	17.8	17.6	18.3	14.8	16.2	32.0	18.4
CaO	4.02	6.76	17.3	17.0	17.8	19.4	15.1	1.18	19.7
Na <sub>2</sub> O	0.04	n.d.	.14	n.d.	n.d.	.17	0.14	0.01	0.11
Total	100.6	99.8	100.2	98.9	99.1	99.8	100.4	99.8	100.5
Ca	7.7	12.9	36.0	35.4	36.2	40.2	31.2	2.2	39.5
Mg	78.1	72.3	51.5	50.9	51.8	42.7	46.6	86.0	51.3
Fe	14.2	14.8	12.4	13.6	12.0	17.1	22.2	11.8	9.2
Mg/(Mg+Fe)	0.85	0.83	.81	0.79	0.81	0.71	0.68	0.88	0.85

1. Pigeonite from core of needle in pyroxene spinifex-textured lava (Ax 11d)
2. Pigeonite from core of needle in pyroxene spinifex-textured lava (Ax 14)
3. Augite adjacent to pigeonite in composite needle (Ax 11d)
4. Augite at margin of composite needle (Ax 11d)
5. Augite from centre of mantle surrounding pigeonite; composite needle in spinifex-textured lava (Ax 14)
6. Augite interstitial to composite needles in spinifex-textured lava (FC-1)
7. Augite interstitial to composite needles in spinifex-textured lava (FC-1)
8. Bronzite from cumulate layer, Alexo Flow
9. Augite from cumulate layer, Fred's Flow

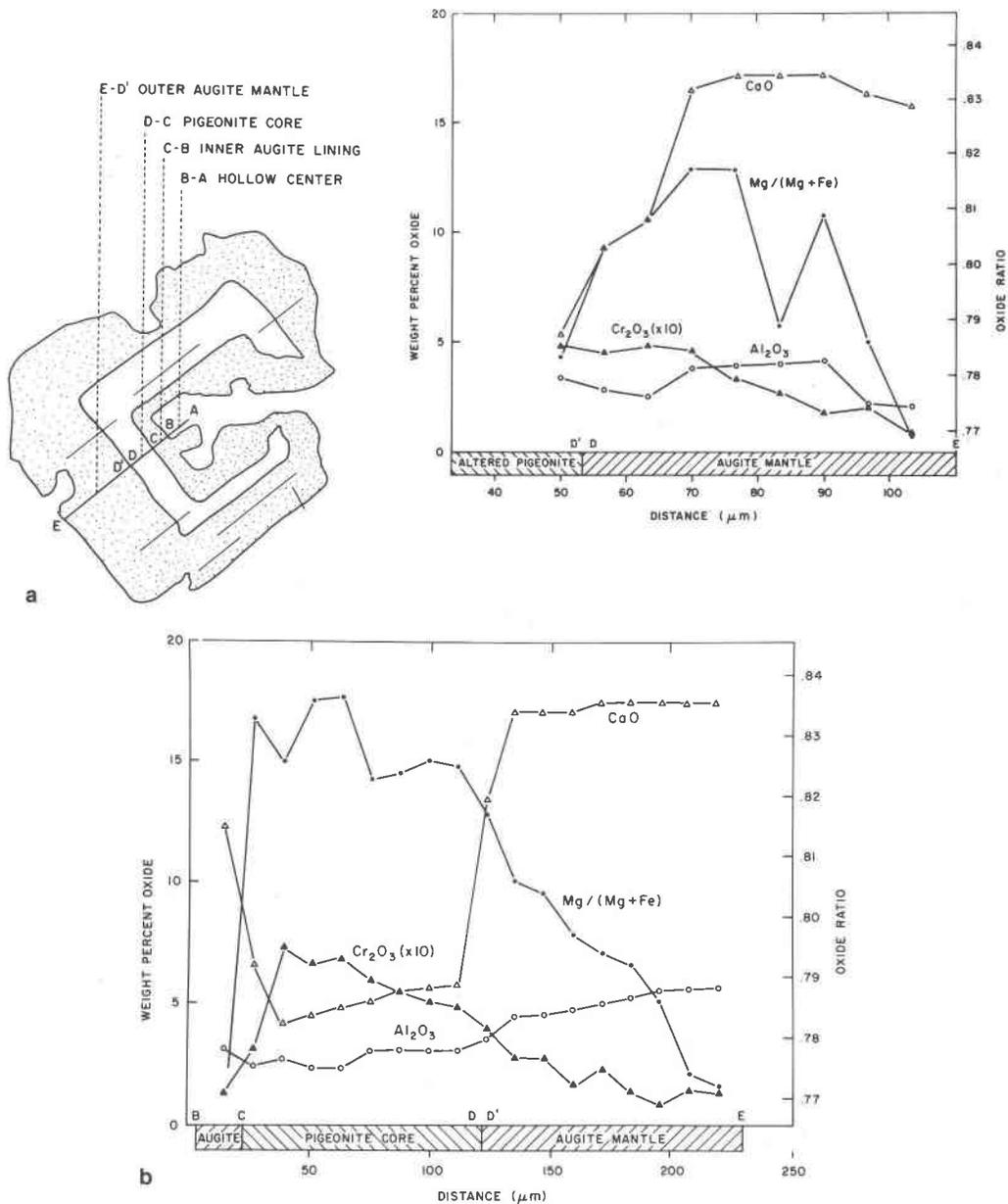


Fig. 5. Chemical profiles across composite pigeonite-augite needles from (a) Fred's Flow and (b) the Alexo Flow.

subcalcic augite mantle, although in others it varies in an irregular manner, usually to produce a CaO-depleted outer rim (Figs. 5 and 6). Magnesium-iron ratios and Cr contents decrease from the inside to the outside of the mantles, and Al<sub>2</sub>O<sub>3</sub> increases markedly in the same interval, continuing trends present in the pigeonite cores. The composition of the augite at the outermost rims resembles that of smaller interstitial augite grains.

The pyroxene lining the hollow cores of the pi-

geonite grains has a subcalcic augite composition with somewhat lower CaO and Al<sub>2</sub>O<sub>3</sub> contents, much lower Cr<sub>2</sub>O<sub>3</sub> contents, and conspicuously higher FeO(tot) contents than the subcalcic augite in the outer mantles. The inner linings are too thin to permit detailed measurement of their chemical zonation.

#### *Clinopyroxenes in gabbro and cumulate layers*

The clinopyroxenes in the gabbroic and cumulate layers of Fred's Flow have been described previously

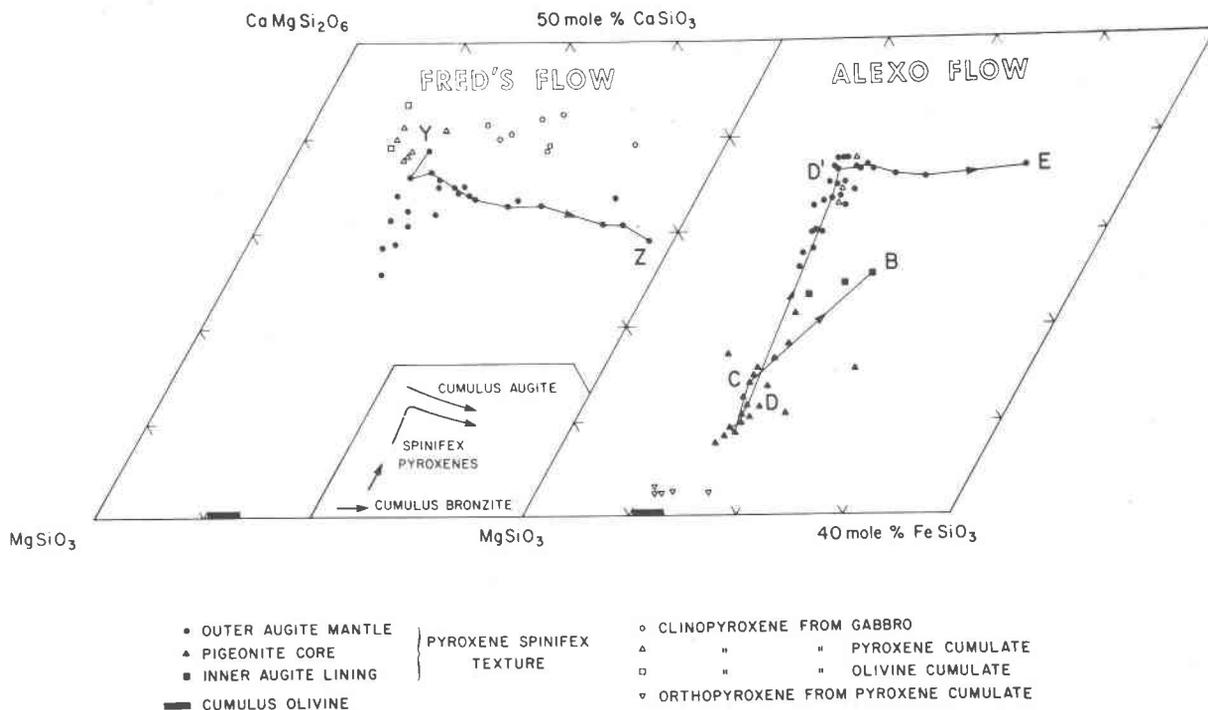


Fig. 6. Compositions and principal chemical variations of spinifex and cumulus pyroxenes in both layered flows. The line *BCDE* shows the compositional variation in the spinifex needle from the Alexo Flow illustrated in profile b, Fig. 5; the line *YZ* shows variation within a spinifex needle from Fred's Flow.

(Arndt, 1977a), and only aspects pertinent to the following discussion will be reviewed here.

Toward the base of the spinifex layers, the pyroxene grains lose their skeletal habit and become shorter and stubbier. They characteristically have unusual curved outlines [bent about the *b* crystallographic axis, (Figure 10, Arndt, 1977a)], are twinned on (100), and show evidence of (*h0l*) and (100) laminated growth features. A few grains have chlorite cores, presumably after Ca-poor pyroxene. In the gabbroic layer, augite makes up 30–40 percent of the rock, and occurs as subhedral prismatic grains, and as intergrowths with plagioclase. Sector zoning produces characteristic hourglass patterns in some samples, particularly those from coarser-grained pegmatoid patches. Throughout the gabbroic layer, the pyroxene is augite. Zonation in individual grains and compositional variation between samples results in a normal "plutonic" trend of Fe-enrichment with slightly decreasing CaO content (Fig. 6).

The augite in augite cumulate layers occurs as euhedral or more or less equant grains, although in some cases adcumulus growth has produced anhedral outlines and the augite partially or completely encloses grains of other cumulus minerals. In addi-

tion, augite is found as epitaxial overgrowths on cumulus bronzite grains, in the form of {100} platelets and more irregular protrusions on {101} faces. Where present in two-pyroxene cumulates, augite grains are smaller (0.3–0.5 mm) than pseudomorphs after bronzite grains (0.5–0.8 mm). Augite in cumulate rocks is more magnesian than that in gabbro, and its compositional variation within the pyroxene quadrilateral follows the high-temperature end of the normal "plutonic" trend (Fig. 6).

#### *Bronzite in the cumulate layer of the Alexo flow*

The bronzite cumulate is composed of 70 to 80 modal percent prismatic bronzite grains and scattered euhedral grains of olivine and chromite in a fine-grained (devitrified glass) groundmass. The bronzite grains are elongated parallel to *c* axis with length:width ratios of about 2:1 to 6:1 (Fig. 7) and are bounded by the crystallographic forms {010}, {100}, {101} and minor {210}. Although the grains are euhedral in outline, the grain boundaries are markedly crenellate (Fig. 7); this texture may be characteristic of Mg-rich orthopyroxene grown under a high cooling rate. The bronzite grains have a discontinuous rim of epitaxially overgrown augite.

which is principally in the form of {100} platelets, and contain ragged augite exsolution lamellae oriented parallel to (100). Long-exposure X-ray precession photographs confirmed the common orthopyroxene space group *Pbca*. Compositional data are reported in Table 1 and Figure 5.

## Discussion

### Magnesian pigeonite

Pigeonite in the spinifex units of the layered komatiite flows is significantly more magnesian than any pigeonite that has been reported from terrestrial rocks (for example, Kuno and Nagashima, 1952; Ishii, 1975). In tholeiitic lavas and differentiated intrusions, magnesian pigeonite has  $Mg/(Mg + Fe)$  of about 0.7, which is considerably lower than the values of 0.81 to 0.85 for komatiite pigeonite. Pigeonite of similar composition to komatiite pigeonite may exist in Apollo 17 spinel troctolites (Smith and Steele, 1976). Smith and Steele (1976) also suggest that Ca-poor pyroxene from an Apollo 17 dunitic rock with composition  $En_{81}Fs_{11}Wo_8$  (Albee *et al.*, 1974) may be a clinopyroxene. However, there are no supporting crystallographic data for any of these pyroxenes.

Highly magnesian pigeonites have been produced experimentally. When Huebner *et al.* (1973) partially melted pigeonite from a lunar basalt, certain samples lost iron to their platinum-iron containers, resulting in pigeonites with compositions that extended from natural compositions to the Di-En join.

### Compositional zoning and crystal growth

The stratigraphic position of the pyroxene spinifex rocks suggests that the clinopyroxene megacrysts grew downwards with continued crystallization of the komatiite flows. The morphology and chemical zonation of the clinopyroxene needles (Figs. 5, 6) is consistent with initial crystallization of the pigeonite cores as hollow skeletal crystals and later epitaxial overgrowth of subcalcic augite. The subcalcic augite lining the interior of the needles crystallized from the residual liquid that was trapped within the hollow cores and effectively isolated from the bulk of the remaining liquid. Chromium and Mg/Fe zonation (Fig. 5b) indicate that crystal growth proceeded outwards and inwards from a point close to the inner margin of the present pigeonite core.

The compositional zoning trend of the composite clinopyroxene needles has many counterparts in less



Fig. 7. (010) section of bronzite grain from bronzite cumulate rock (Ax 27), showing crenellate outline and epitaxial augite overgrowth (stippled).

mafic rocks and appears to be characteristically developed in volcanic (rapidly-cooled) rocks in which Ca-poor pyroxene appears early in the crystallization sequence; examples include zoned clinoenstatite from Cape Vogel, Papua (Dallwitz *et al.*, 1966), zoned pyroxene phenocrysts from Apollo 12 basalts (Hollister *et al.*, 1971), and zoned phenocrysts and groundmass grains from Oshima, Japan (Ishii, 1975). Although the compositions of the liquids that crystallized these composite clinopyroxene grains vary markedly, the only essential difference in the resulting zoning trends is a displacement to higher Fs values.

The composition of the clinopyroxene in the Fred's Flow gabbro defines a trend of FeO enrichment largely at the expense of MgO. The trend follows the  $900 \pm ^\circ C$  isotherm for the augite limb of the pyroxene solvus (Fleet, 1974, Fig. 1). However, this clinopyroxene does not coexist with Ca-poor pyroxene and probably crystallized within the augite stability field, above the corresponding solvus temperature. In contrast, the composition of the cumulus augite, which frequently coexists with bronzite, is more subcalcic and corresponds to an apparent crystallization temperature near  $1100^\circ C$  relative to the simple geothermometer of Fleet (1974). Correction for the high CaTs content would raise the calculated crystallization temperature somewhat, and it appears that the cumulus augite has probably crystallized on or near the pyroxene solvus.

*Stable and metastable pyroxene crystallization*

The petrologic importance of Archean komatiite flow rocks is not limited to their high MgO character. The rapid crystallization permitted by highly magnesian magma exaggerates the effect produced by the two contrasted thermal regimes, a slowly-cooled interior and a rapidly-cooled upper margin. Hence, the chemical and mineralogical compositions of the cumulus rocks and gabbros resemble those ordinarily associated with layered intrusions. Only the presence of hopper olivine and the skeletal and dendritic interstitial areas would indicate a different environment of formation on superficial examination. The chemistry of the pyroxenes crystallized in the two thermal regimes is clearly quite distinct and, in part, corresponds to that observed for pyroxene in a thick basalt flow from Picture Gorge, Oregon (Smith and Lindsley, 1971). The composition of augite from the interior of the Picture Gorge flow, where it is presumed to have crystallized in stable equilibrium, is very similar to that of the Fred's Flow gabbro and defines a "normal plutonic trend." In contrast, the composition of augite from the chilled basal margin defines a trend of FeO enrichment at the expense of CaO, very similar to the initial FeO enrichment of the zoned phenocrysts from Apollo 12 basalts. Smith and Lindsley have identified this as a "quench trend" and ascribe it to metastable crystal-liquid equilibration through rapid crystallization.

In the spinifex layers of Fred's Flow, the observed crystallization sequence is

olivine → pigeonite → subcalcic augite → augite + plagioclase

Olivine appeared as the liquidus phase only briefly at the top of the spinifex layers, pigeonite and subcalcic augite form the composite megacrysts, and augite and plagioclase crystallized as small prismatic grains interstitial to the megacrysts.

In the cumulate layers the crystallization sequence is

olivine → olivine + augite → augite + bronzite → augite + plagioclase (Fred's Flow)

or

olivine → olivine + bronzite → augite + plagioclase (Alexo Flow)

The crystallization sequences in the cumulus zones, and the variation in pyroxene compositions, are thus

very similar to sequences observed in larger layered intrusions (e.g. Muskox: Irvine, 1970).

The equilibrium crystallization sequence of komatiitic liquids has been determined experimentally (Arndt, 1977b). Samples of peridotitic komatiite crystallize olivine as the sole silicate mineral for much of the crystallization interval at 1 atm. At temperatures of about 1190°C, when the MgO content of the crystallizing liquid has been reduced to about 9 weight percent, diopsidic pyroxene joins olivine, and at about 1180°C, plagioclase appears. Orthopyroxene was not observed, but presumably appears at temperatures close to the solidus ( $\approx 1170^\circ\text{C}$ ). This sequence differs in some respects from that observed in the cumulate layers of the lava flows, where bronzite crystallized before plagioclase and augite takes the place of diopside. Possible explanations for these differences are slight alteration of the lavas following their eruption, or differences between the conditions under which the experiments were run (equilibrium crystallization, volatile-free, at  $f\text{O}_2$  close to the wüstite-magnetite buffer curve) and the conditions of more rapid cooling under which the lavas may have crystallized.

In contrast, the crystallization sequence in the flow top spinifex layers bears little resemblance to the equilibrium sequence. Pigeonite first appears in spinifex-textured lavas that contain 12–14 percent MgO. The textures of these lavas have been interpreted to indicate that (a) pigeonite was the liquidus phase, and (b) although there may have been some accumulation of pyroxene during the growth of spinifex needles, the compositions of the lavas are close to those of the liquids from which they solidified. Thus pigeonite, followed by subcalcic augite, has crystallized from liquids that under equilibrium conditions would have crystallized olivine, followed by diopside at much lower temperatures. Factors such as alteration of the lavas or accumulation of pyroxene during crystal growth may contribute to the discrepancy, but these factors cannot be the complete answer: the differences in crystallization order and in pyroxene mineralogy appear to be too large.

It is suggested, therefore, that the pigeonite and subcalcic augite are metastable products whose appearance is related to the rapid cooling conditions that would have existed in the upper parts of the flows. The following explanation is tentatively proposed. (It will be presented in more detail, and supported by experimental data, in a forthcoming paper by Arndt and I. H. Campbell, in preparation.) Dur-

ing the initial stages of rapid cooling, olivine crystallizes, but at a rate insufficient to prevent a progressive increase in the degree of supercooling of the lava. The stage is reached at which the temperature of the supercooled lava falls below the stable pyroxene liquidus. Even though the composition of the liquid has changed only slightly (because of minor olivine crystallization), the drop in temperature results in an increase in the relative stability of pyroxene. As a result, a pyroxene, pigeonite, crystallizes under these conditions of high supercooling from liquids which, under equilibrium conditions, would crystallize olivine. The crystallization of pigeonite would be followed by crystallization of augite.

If this explanation is correct, the following combination of factors is required for the crystallization of highly magnesian pigeonite in nature: (a) highly magnesian, high-temperature liquids; and (b) rapid cooling of these liquids so that a high degree of supercooling is induced. If the liquid cools slowly, only olivine would crystallize over most of the solidification interval. In less magnesian liquids, metastable pyroxenes with compositions falling within the gap between stable Ca-rich and Ca-poor pyroxenes might form under rapid cooling conditions, but these pyroxenes would have normal Mg/Fe ratios.

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