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STABLE AND METASTABLE AUGITE CRYSTALLIZATION TRENDS IN A SINGLE BASALT FLOW

DOUGLAS SMITH AND D. H. LINDSLEY, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., 20008.*

ABSTRACT

Compositions of augite in the chilled basal margin and more slowly cooled interior of a thick flow of Picture Gorge basalt from Oregon form trends with contrasting directions in the pyroxene quadrilateral. Whereas compositions of augite from the interior of the flow define a normal plutonic trend, those from the chilled base define a "quench trend" characterized by Fe-Ca substitution with Mg constant. Al in these quickly formed crystals systematically decreases with iron enrichment. The "quench trend" apparently reflects a metastable crystal-liquid partition caused by rapid crystallization. Some of the less calcic pyroxene in the chilled margin probably formed metastably within a two-pyroxene field. The results provide unusually good evidence on how crystallization rate can influence the type of chemical variation in an igneous phase.

A diversity of compositional variations found for Apollo 11 lunar pyroxenes (Weill *et al.*, 1970; Ware and Lovering, 1970; Ross *et al.*, 1970; Mason *et al.*, 1970; Kushiro *et al.*, 1970; Keil *et al.*, 1970; Frondel *et al.*, 1970; Douglas *et al.*, 1970; Brown *et al.*, 1970; Bailey *et al.*, 1970; Arrhenius *et al.*, 1970; Anderson *et al.*, 1970; Agrell *et al.*, 1970) has intensified the need to understand pyroxene trends in terrestrial volcanic rocks. In particular, clinopyroxenes from a number of volcanic rocks have compositions that lie in a two-pyroxene field as inferred from plutonic assemblages and phase-equilibrium studies. For example, Kuno (1955) reported a series of lavas in which the clinopyroxenes (augites and subcalcic augites) had nearly uniform magnesium contents but a wide range of calcium-iron ratios. Muir and Tilley (1964) referred to this as a "quench trend." Inasmuch as some lunar clinopyroxenes show similar trends—either among a number of crystals in a given thin section or as zoning within a single crystal—it is important to know whether trends of this sort do in fact reflect quenching conditions. Because lunar samples to date represent loose grab samples it has been impossible to infer their cooling history on the basis of their original position within the parent rock unit. Studies of pyroxene compositional trends in specimens of terrestrial lavas for which cooling rates are known or can be inferred should provide insight into the origins of these trends. Such studies also test the assumption, tacitly made in many studies of igneous rocks, that mineral composition trends reffect an equilibrium between growing crystals and a melt of changing composition.

Contrasting trends of pyroxene crystallization in the chilled basal zone and slowly cooled interior of a thick basalt flow provide unusually

TABLE 1. WHOLE-ROCK ANALYSIS OF A SAMPLE FROM THE CHILLED BASAL MARGIN OF THE FLOW, TOGETHER WITH A REPRESENTATIVE MICROPROBE ANALYSIS OF AUGITE IN EACH OF THE TWO ROCK TYPES

	1		2	3
SiO_2	47.4	SiO_2	50.1	50.5
TiO_2	1.7	TiO_2	1.4	1.3
Al_2O_3	16.0	Al_2O_3	2.0	2.2
Fe_2O_3	3.3			
FeO	8.5	Fe as FeO	11.8	10.5
MnO	0.19	MnO	0.26	
MgO	7.6	MgO	13.8	14.5
CaO	10.0	CaO	20.5	20.1
Na_2O	2.6	Na_2O	0.39	
K_2O	0.40			
P_2O_5	0.32			
H_2O	2.4			
Total	100.4		100.3	99.1

1. Chilled margin of flow (sample 727-1). U. S. Geological Survey rapid rock analysis by P. L. D. Elmore, S. D. Botts, I. H. Barlow, and G. Chloe (Lindsley, 1960).

2. Representative microprobe analysis of augite from the interior of the flow (sample 351-69).

3. Representative microprobe analysis of augite from the chilled basal margin (sample 346-69).

clearcut evidence of how crystallization rate can influence the "direction" of a compositional trend. The flow, about 95 meters thick, is part of the Miocene Picture Gorge basalt, a subdivision of the Columbia River basalt (Waters, 1961). It is the uppermost of three unusually thick flows cropping out along the John Day River valley in the Spray 15' quadrangle in north-central Oregon. The electron microprobe analyses presented here were obtained from two samples, one representing the lower chill zone collected from 1.5 meters above the flow base, and the other representing the host basalt in a zone containing pegmatoid lenses in the upper central part of the flow, approximately 45 meters above the base. An analysis of a sample of the chill zone of the flow is given in Table 1. Studies by Lindsley (1960) demonstrated that there are only minor chemical differences between the chilled margins and the interiors of similar thick flows in the area.

Both rocks contain the same primary mineral assemblage—plagioclase, augite, olivine, oxides, and a trace of late-stage pigeonite. The sample from the flow interior is distinctly coarser grained than that from the chill zone, primarily because of a difference in plagioclase grain size.

Augite crystals in the interior sample have only slightly greater average diameters than in the chilled-margin sample, but in the latter augite forms intricate ophitic crystals whereas ophitic textures are only poorly developed in the former. No visible exsolution lamellae are present in the pyroxenes. Augite was the only pyroxene to crystallize in both rocks during most of their crystallization histories, as pigeonite occurs only in trace amounts associated with pockets of residuum.

Compositions[1] of augite in both rock types are plotted in the pyroxene quadrilateral in Figure 1, and a representative analysis of augite in each rock is shown in Table 1. Compositions from the more slowly crystallized sample from the interior of the flow form a trend in the quadrilateral roughly parallel to that defined by pyroxenes in the Skaergaard intrusion and other differentiated intrusions of basaltic magma. The augites are more calcic than the Skaergaard trend, as is consistent with the fact that they did not coprecipitate with a calcium-poor pyroxene. The trend in the chilled basalt is at a high angle to the other and reflects Ca-Fe substitution with a nearly constant proportion of Mg. Trends defined by compositional zoning in individual crystals in each rock type are compatible with those defined by the analyses from many different crystals plotted in Figure 1.

Since both basalt samples are from the same flow and are distinguished primarily by their different crystallization and cooling rates, the difference in pyroxene trends between them verifies the concept of a quench trend and illustrates the importance that crystallization rate, or kinetics, can have on crystallization trends. Augite trends in plutonic igneous rocks are due to changes in liquid composition caused by crystal-liquid fractionation and are presumed to reflect stable equilibrium partitioning of Ca, Fe, and Mg between the precipitating material and melt. The quench trend might be due to either a nonequilibrium or a metastable partitioning between crystals and liquid, or it might reflect the presence of a zone of liquid depleted in pyroxene components adjacent to rapidly growing pyroxene crystals. Such compositional zoning in the liquid might arise if diffusion in the liquid were slow compared to the growth rate of pyroxene in the chilled basalt.

Two arguments suggest that the direction of the quench trend is not caused by such depleted zones in the magma. First, aluminum and

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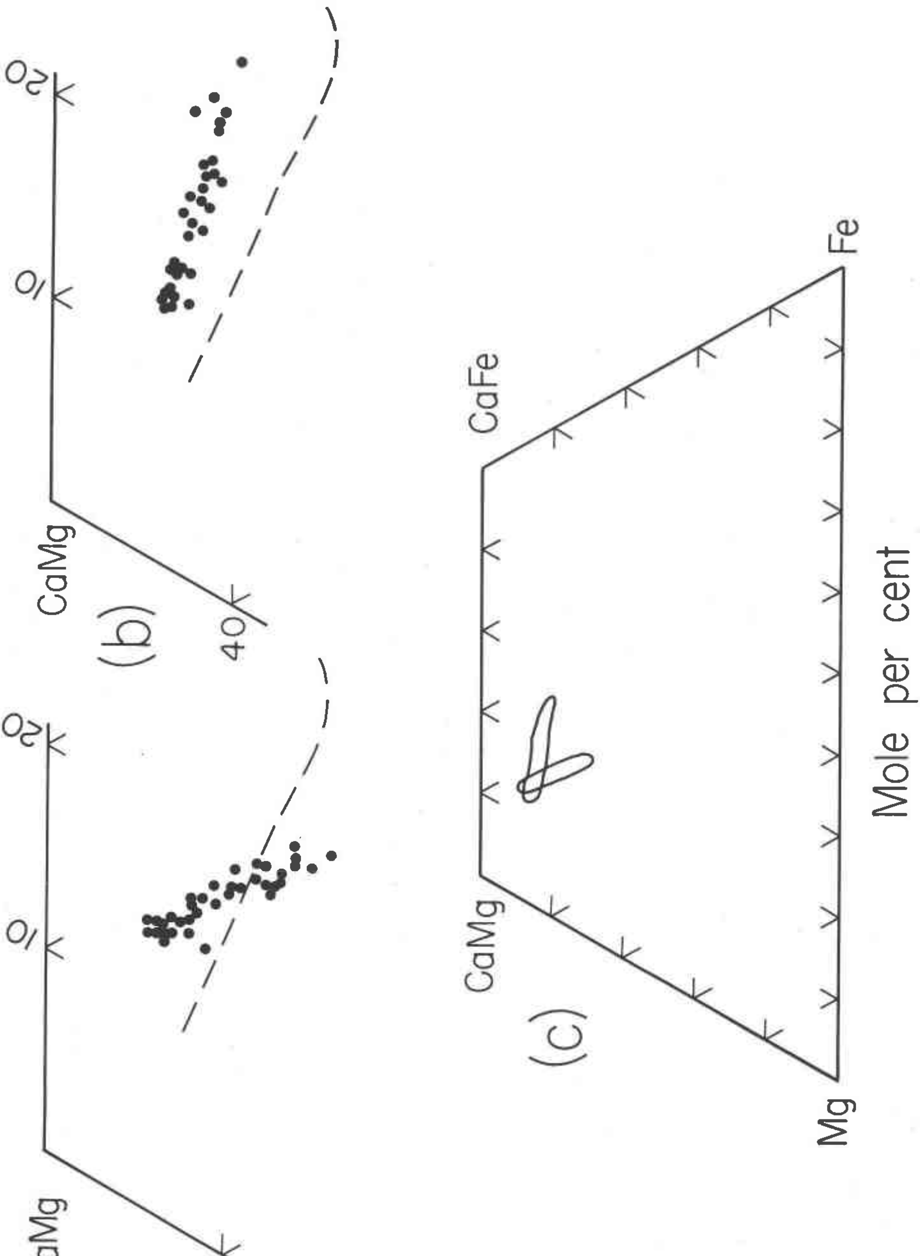
[1] Pyroxene compositions were determined with a Materials Analysis Company electron microprobe on polished thin sections using the smallest spot size attainable, about a micrometer in diameter. Each point in Figure 1 represents the composition at one spot. Ca, Fe, and Mg were obtained simultaneously at each spot; a number of these spots were also analyzed for three to five other elements. The programs of Boyd *et al.* (1969) as modified by Hadidiacos *et al.* (1970) were used for data reduction.


(a)
CaMg
40
10
20
(b)
CaMg
40
10
20
(c)
CaMg
CaFe
Fe
Mg
Mole per cent

titanium in augite are similar in the two rock types (Fig. 2), aluminum decreasing with iron enrichment in the pyroxene. Individual crystals in the chilled margin are zoned from iron-poor, calcium-rich centers high in aluminum to iron-rich, calcium-poor extremities lower in aluminum. The pyroxene-melt fractionation of Al favors the melt; if there were a diffusion zone around the growing crystal, it should be enriched in Al over normal magma, and Al might be expected to increase rather than decrease with iron enrichment in the rapidly growing crystals. Second, plagioclase formed from the quenched liquid as well as pyroxene, and if diffusion in the liquid were slow relative to crystal growth, the liquid should have irregular concentration gradients due to locally different proportion of crystallizing pyroxene and plagioclase. In this case, one might expect a scatter of pyroxene compositions and not a distinct trend. Evans and Moore (1968) noted that pyroxene compositions in quenched samples of a Hawaiian lava lake and flow formed irregular patterns in the quadrilateral rather than well defined trends; these patterns might be due either to local small-scale variations in melt composition or to a disequilibrium crystal-liquid partitioning. In contrast, the quench trend shown here represents a more systematic chemical variation, and we suggest that it reflects an equilibrium partition between crystals and melt that is metastable with respect to plutonic trends (as well as the "normal" trend for the interior sample).

Kuno (1955) suggested an alternative explanation for the formation of subcalcic augites in chilled volcanic rocks. He proposed that during rapid crystallization ferric iron might substitute for silicon in tetrahedral sites in pyroxene, and that the resulting lattice distortions might favor substitution of Fe and Mg for Ca. Iron oxidation states were not determined in our microprobe analyses, and Kuno's hypothesis cannot be discarded as a conceivable explanation of this "quench trend." However, we consider it an unlikely cause for the difference between the contrasting pyroxene trends in these two samples. Kuno proposed his explanation because of several analyses of subcalcic augites which apparently lacked sufficient Al+Ti+Si to fill tetrahedral positions. However, suf-

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FIG. 1. (a) Compositions of augite in a sample of the chilled basal margin of the flow plotted in part of the pyroxene quadrilateral. (b) Compositions of augite in a sample from the central portion of the flow, 45 meters above the base. (c) The complete pyroxene quadrilateral, showing the locations of the two trends.

The dashed line in parts (a) and (b) represents the early part of the Skaergaard augite trend (Wager and Brown, 1968). Pyroxene compositions were determined with an electron microprobe.

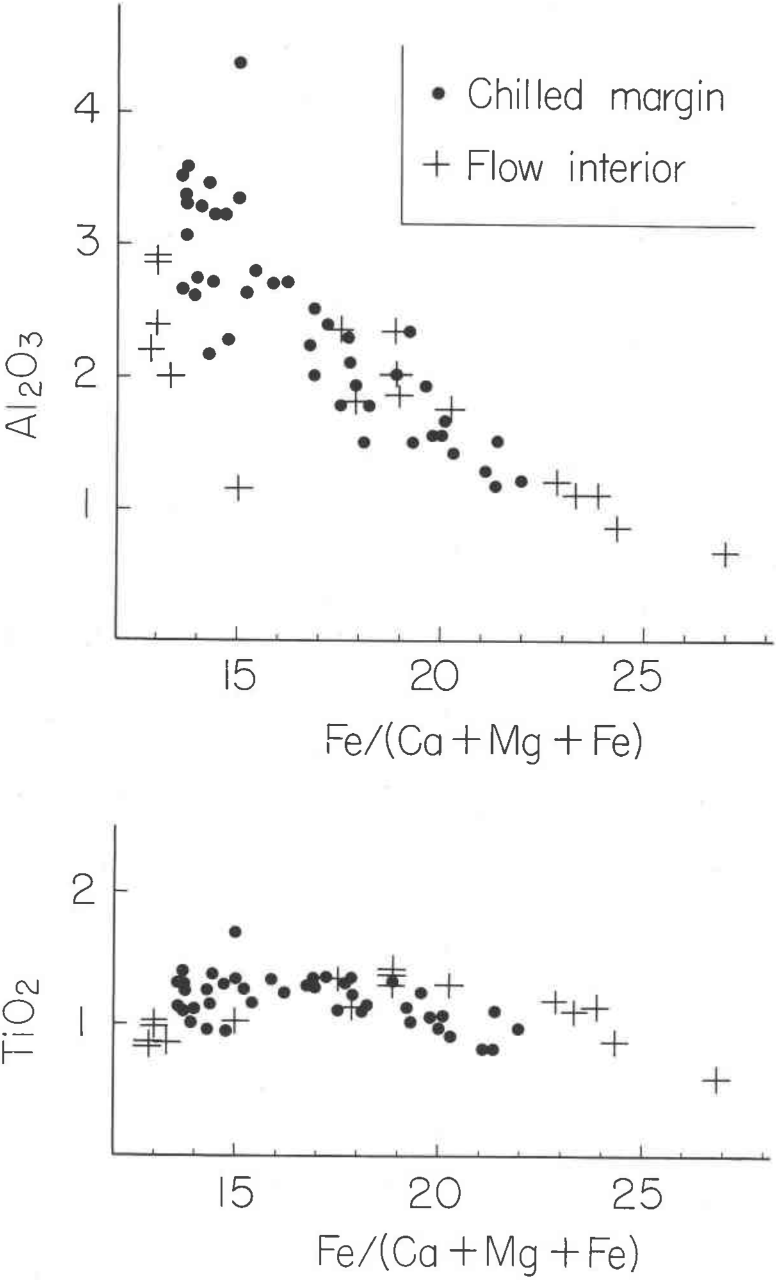

FIG. 2. Weight percentage of Al_2O_3 and TiO_2 in augite in the two samples of the flow, as determined with an electron microprobe on spots also analyzed for Fe, Ca, and Mg.

ficient Al+Si to essentially fill tetrahedral positions is present in augite in each of the two samples of Picture Gorge basalt, and there is no necessity to postulate the existence of tetrahedral ferric iron in these pyroxenes. Furthermore, the existence of subcalcic augite in Apollo 11 volcanic rocks containing metallic iron (e.g. Agrell *et al.*, 1970) suggests that the formation of such calcium-poor augite compositions need not depend on ferric iron. The possibility of minor trivalent iron in lunar pyroxene cannot be excluded, since melts containing Fe_2O_3 can coexist with metallic iron (Bowen and Schairer, 1932). It seems most unlikely, however, that augite formed in the reducing environment typical of Apollo 11 volcanic rocks contains enough tetrahedrally coordinated ferric iron to be responsible for the unusual type of Fe-Mg-Ca substitution producing lunar subcalcic augties.

It is noteworthy that a number of pyroxene compositions comprising the Spray quench trend reported here fall on the calcium-poor side of the Skaergaard augite trend (Fig. 1), that is, in the two-pyroxene field for that intrusion. Two possible explanations are: (1) these low-calcium pyroxenes may have precipitated metastably with respect to a two-pyroxene assemblage, or (2) different physical conditions prevailing in this basalt flow may have caused the boundary of the two-pyroxene field to be shifted to less calcic compositions. Although the second explanation cannot be categorically rejected, it is unlikely for the following reasons. Differences in pressure have little effect on the boundaries of the two-pyroxene field for the iron-free system diopside-enstatite (Boyd and Schairer, 1964; Davis and Boyd, 1966) in the temperature range of interest. These experimental studies also show that although the two-pyroxene field does indeed narrow with increasing temperature, the Spray basalt would have had to be some 100°C or more hotter than was the Skaergaard magma to precipitate the pyroxenes of the quench trend as stable phases. (This estimate is made on the assumption that the *slope* of the calcium-rich boundary of the two-pyroxene field is relatively unchanged by the addition of approximately 18–20 mole percent $FeSiO_3$). There is, however, no independent evidence for any significant difference in temperature between the Spray basalt and the Skaergaard magma: when the Skaergaard magma was crystallizing augite of $Wo_{39}En_{42}Fs_{19}$ composition (the approximate composition at which the two trends cross), olivine (Fo_{66}) and plagioclase (An_{66}) were coprecipitating (Wager and Brown, 1968). In the groundmass of the chilled Spray basalt, these minerals show a range of Fo_{62-55} for olivine and An_{70-60} for plagioclase. Inasmuch as these three minerals comprise the bulk of the samples from both bodies, it seems unlikely that there was a significant temperature difference between them. We conclude, therefore, that the most calcium-poor pyroxenes of the Spray quench trend crystallized metastably with respect to a two-pyroxene assemblage. This metastability is *in addition to* the presumed metastable partitioning of Ca, Mg, and Fe between melt and crystals that gave rise to the quench trend.

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