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ELECTRON-PROBE STUDY OF PYROXENE EXSOLUTION

FRANCIS R. BOYD

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20008

AND

G. MALCOLM BROWN

Department of Geology, The University, Durham, England

ABSTRACT

Electron-probe scans of pyroxenes from large mafic intrusions such as the Bushveld, Skaergaard, and Stillwater show exsolution features ranging from 1 μm up to 100 μm or more in thickness. In the augites, Ca-poor pyroxene has exsolved in the form of regularly repeated patterns of clinohypersthene lamellae oriented parallel to (001). Exsolution in the Ca-poor pyroxenes is more complex inasmuch as inverted pigeonites sometimes contain multiple sets of augite lamellae.

Quantitative analyses of an augite host-lamella set and an inverted pigeonite host-lamella set from separate crystals in a thin section of the Bushveld gabbro show that both major and minor elements have fractionated in the exsolution process. The composition of the augite lamella in the inverted pigeonite is almost identical to that of the separate augite host, and the composition of the clinohypersthene lamella in augite is very close to that of the separate rhombic hypersthene (inverted pigeonite) host. This relationship shows that subsolidus equilibrium was maintained over a substantial period during cooling.

INTRODUCTION

Progress in understanding the crystal chemistry of the pyroxenes has developed equally through study of natural crystallization products and through laboratory determination of phase relations. For example, the essential form of the two-pyroxene field separating augites from Ca-poor pyroxenes was deduced by Hess (1941) through petrographic study of pyroxenes from mafic rocks. However, experimental studies (Boyd and Schairer, 1964; Davis and Boyd, 1966; Kushiro, 1969) have been required to give a quantitative picture of the solid solution relations. Experimental work has also provided insights into the inversion relations among the Ca-poor pyroxenes that were not evident from petrographic studies (*e.g.* Atlas, 1952; Munoz, 1968; Brown, 1968). Many problems in understanding phase relations in the pyroxene quadrilateral remain, and their resolution will require a continuing blend of petrographic study and experiment.

Electron-probe techniques have provided fresh impetus to the study of natural pyroxenes, particularly through the study of pyroxene exsolution features. Binns, Long, and Reed (1963) showed the importance and practicality of this approach when they demonstrated that monoclinic lamellae in two augite crystals were clinohypersthene, rather than pigeonite as had previously been supposed.

Exsolution features are particularly well developed in pyroxenes from slowly cooled, large, mafic intrusions such as the Skaergaard, Bushveld, and Stillwater. The textures and optical characteristics of these pyroxenes have been described in particular by Poldervaart and Hess (1951) and Brown (1957). Bown and Gay (1960) have made X-ray studies of the Skaergaard pyroxenes, confirming many of the details established by the optical work.

The aim of the present study was to make a qualitative survey of a variety of exsolution features in certain pyroxenes from gabbroic rocks and then to make quantitative analyses where practicable. Practicability is here entirely a matter of resolution. The scale of exsolution features in these pyroxene crystals ranges widely from 1 μm or less, up to 100 μm or more. The resolution that can be attained with an electron probe depends on the nature of the target, the elements sought, and the degree of accuracy desired. Our experience suggests that it would be extremely difficult to obtain analytical data accurate within ± 5 relative percent for pyroxene lamellae thinner than 6–8 μm. However, it is practical to make analyses for as many as ten elements on lamellae as thin as 10–12 μm. Unfortunately, many exsolution features of interest are smaller than 6μm.

ANALYTICAL PROCEDURE

The electron probe[1] used in this study is a Materials Analysis Company model 400, equipped with three spectrometers and simultaneous readout on an automatic typewriter and a card punch. The analyses were carried out on polished thin sections of pyroxene separates or whole rocks. Use of transmitted light with cross polarization was found essential to locate grains suitable for analysis. Quantitative analyses were made at 20 kv for Fe, Cr, and Mn and at 15 kV for other elements. The specimen current was held below 0.04 μA with an X-ray spot size in the range 2–3 μm. A glass prepared by H. G. Huckenholz was used as a standard for Ca, Mg, Fe, and Si. Other standards and the analytical techniques used have been described by Boyd (1969). Progress in the development of correction procedures for atomic number effects (Duncumb and Reed, 1968) now makes it practicable to use pure elements in the range Cr to Ni as standards for silicate analysis, and this was done for Cr and Mn. The data were reduced with the use of computer programs described by Boyd, Finger, and Chayes (1969).

Qualitative scans of host-lamella relations are most easily accomplished by monitoring CaKα. Good intensity is obtained for this peak with a PET crystal, and it is possible to keep the specimen current down to 0.01 μA or less, which enhances resolution. Most of the qualitative scans described in this paper were made at 30 kV. Subsequent experience has shown that better resolution is obtained at 15 kV because of the boundary fluorescence of CaKα

[1] We gratefully acknowledge the assistance of the National Science Foundation under grant GP 4384 in the purchase of this instrument.

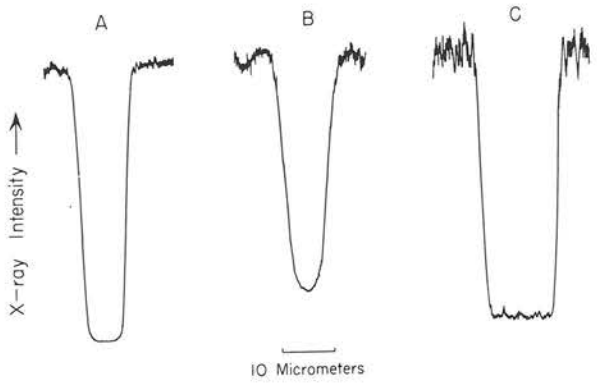

FIG. 1. Effects of boundary fluorescence and beam voltage on probe resolution. A. FeKα scan of silver lamella in steel, 30kV. B. CaKα scan of clinohypersthene lamella in augite, 30kV. C. CaKα scan of another clinohypersthene lamella in augite, 15 kV.

by FeKα, an effect that has been discussed and analyzed by Reed and Long (1963). Its influence can be seen by comparing the scans in Figure 1. Scan A is a traverse across an artificial lamella of silver in steel, monitoring FeKα radiation at 30 kV. Scan B (Fig. 1) is a traverse across a clinohypersthene lamella in augite at the same voltage and essentially the same beam diameter as for scan A. In scan B, FeKα radiation from the lamella fluoresces CaKα in the enclosing augite, and the resolution is greatly reduced. The intensity of this boundary fluorescence is dependent on the voltage of the electron beam and is diminished by reducing this voltage. Scan C is also for CaKα across a clinohypersthene lamella, but this scan was made at 15 kV. The lamella in scan C is considerably wider than the lamella in scan B, but even so the improvement in resolution achieved by reducing the voltage is striking.

In a preliminary report on these scans (Boyd and Brown, 1968) we suggested that the reduced resolution observed in scans on the pyroxene lamellae at 30 kV was due to compositional zoning. In the light of subsequent results obtained at 15 kV, this suggestion seems to have been in error.

QUALITATIVE RESULTS

A group of scans of Ca-rich and Ca-poor pyroxenes in Figure 2 illustrates the wide range in size of pyroxene exsolution features. The very fine lamellae in bronzite (Fig. 2, A) from a Stillwater harzburgite range down to 1 μm in thickness, whereas in the Bushveld gabbros the inverted pigeonites, now hypersthenes (Fig. 2, C), contain coarse blebs of augite up to 100 μm across. Characteristically the augite lamellae in inverted pigeonite from the Skaergaard gabbros (Fig. 2, B) are less coarse than those from the Bushveld.

The nature of the exsolution in the Stillwater bronzite is rather a puzzle. Under the microscope this pyroxene is seen to contain very fine, closely spaced lamellae. Some crystals are rimmed with a zone in which there are fewer lamellae (Boyd and Brown, 1968, Plate 1). The CaKα scan (Fig. 2, A) shows that the bronzite has a Ca-poor phase interlaminated with a more calcic phase. The scan clearly indicates exsolution rather than the twinning or deformation lamellae suggested by Henry (1942). The slightly more abundant Ca-poor phase is barely resolved, whereas the thinner and slightly less abundant lamellae of more calcic pyroxene are incompletely resolved. The lack of resolution makes it impossible to estimate the composition of the more calcic phase with any certainty. Nevertheless this phase must be much less calcic than augite because it is abundant and yet the bulk Ca content of the bronzite is low (about 2 percent CaO; Hess, 1960, Table 3). The scan confirms the evidence from optical data that the low birefringent, orthorhombic host is the Ca-poor phase.

It is tempting to speculate that the exsolution shown by this bronzite may have been produced by cooling across a transition loop in the Mg-rich portion of the quadrilateral. Nevertheless Brown (1968, p. 352) has conducted some heating experiments on similar natural bronzites and failed to produce inversion to either proto or clino forms at 1230°C under conditions where natural hypersthenes with augite lamellae invert readily to monoclinic pigeonites at much lower temperatures. Hence the origin of the exsolution in this and similar bronzites is presently enigmatic.

A scan of inverted pigeonite from a Bushveld gabbro (Fig. 2, C) shows the development of secondary, less calcic lamellae in an exsolved bleb of augite. Secondary lamellae of "augite" also develop in the Ca-poor host (not shown here), and in the inverted pigeonites they are typically oriented at an angle to the primary set. In some cases there are two sets of secondary lamellae oriented at angles to each other and to the primary set (Boyd and Brown, 1968, Plate 1). The coarse, primary set of augite lamellae and blebs in inverted pigeonite is believed to have formed while the host was monoclinic. With further cooling the host inverted to orthorhombic form and the secondary, augite lamellae exsolved. Apparently at the same stage the primary set exsolved the Ca-poor lamellae shown in Figure 2, C. Quantitative comparison of the compositions of primary and secondary lamellae has not been made because the secondary lamellae examined thus far have always been less than 5 μm thick.

CaKα scans of augites from Bushveld gabbros (Fig. 2, D, E) show remarkably regular patterns of exsolution on (001). Commonly the intervals between regularly spaced, relatively coarse lamellae show the development of finer lamellae which are less completely resolved by the probe. The coarser lamellae are monoclinic, Ca-poor pyroxene, like that studied by Bown and Gay (1960) in Skaergaard specimens with similar optical properties. Binns, Long, and Reed (1963) showed that lamellae similar to these are very poor in CaO and are clinohypersthene rather than pigeonite. Our quantitative results confirm their finding. Coexisting crystals of pigeonite have attained clinohypersthene composition by augite exsolution, but the host has since inverted to the orthorhombic form. Presumably, energy relations along the host-lamellae interfaces have acted to inhibit inversion of the clinohypersthene lamellae within augite crystals.

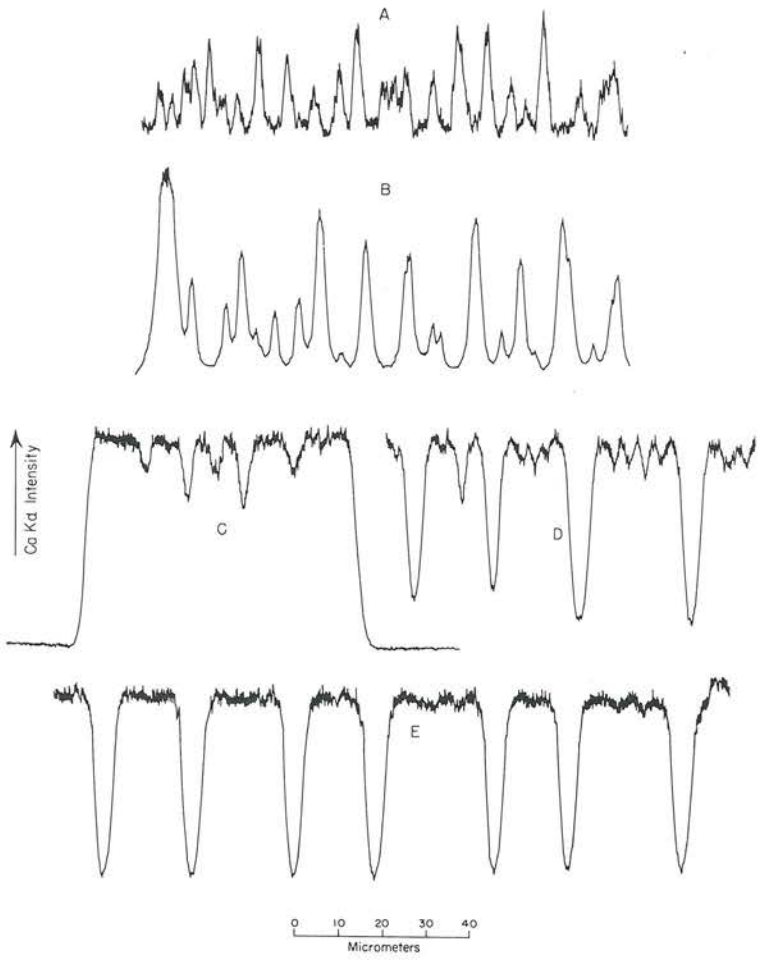

FIG. 2. Electron probe scans, monitoring CaKα across pyroxene crystals that have undergone exsolution. A. Bronzite (W80), Stillwater. B and C. Inverted pigeonites (hypersthene + coarse augite lamellae) from Skaergaard (EG 4330) and Bushveld (SA 1019), respectively. D and E. Augites from Bushveld containing clinohypersthene lamellae (SA 1139 and 616, respectively). Specimen numbers cross-refer to Brown (1957) and Atkins (1965), except for W80 from a bronzitite collected by Brown from the Ultramafic Zone of the Stillwater intrusion.

QUANTITATIVE ANALYSES

Exsolution features are particularly coarse and well developed in the pyroxenes of the Bushveld Main Zone gabbros, and a typical specimen (SA 1019) was selected for detailed study. The pyroxenes in this rock consist of monoclinic augite with (001) lamellae of clinohypersthene ranging up to about 15 μm in thickness, coexisting with inverted pigeonite containing blebs and secondary lamellae of exsolved augite in a rhombic hypersthene host. The analyses were carried out on a polished thin section.

A grain of inverted pigeonite and a grain of augite lying about 2 cm apart in this thin section were chosen for analysis. Selection of the augite grain was based on favorable thickness and orientation of the clinohypersthene lamellae. The pigeonite grain was selected primarily because secondary lamellae, which would have interfered with the analysis, were sparse. However, other grains of inverted pigeonite in this gabbro have well developed, multiple sets of lamellae.

The analyzed clinohypersthene lamella is doubly terminated within the augite crystal, and its original form was evidently that of a thin lens oriented normal to the slide. The thin section has cut a segment from the edge of this lens. The analyses had to be confined to the central portion of the lamella because the beam penetrated into the underlying augite toward the ends. A CaKα scan across this augite grain is shown in Figure 3, and the intersections of the scan with the narrow zones of host and lamella that were analyzed are indicated by points A, B, and B′. Those areas of augite host, adjacent to the lamella, that are free of finer lamellae, are quite restricted, and it was necessary to repolish the slide midway through the study to remove contamination spots.

In the inverted pigeonite grain the elongate bleb of ex-

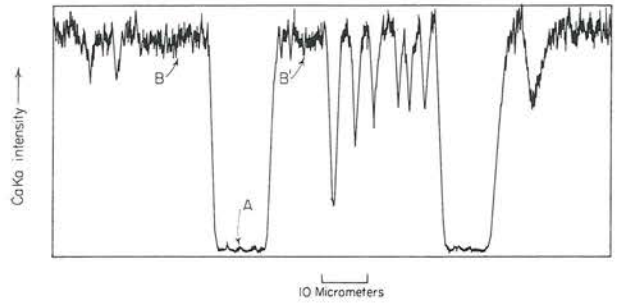

FIG. 3. Electron-probe scan, monitoring CaKα across the augite crystal for which analytical data are given in Table 1. Analyses for the clinohypersthene lamella were made in the vicinity of point A, and those for the augite host were made in the vicinities of points B and B'.

solved augite ranges up to 50 μm in width, and the area available for analysis was much greater than needed.

Analyses for ten elements on these two host-lamella sets are given in Table 1. Values for the ratio $\sigma/\sqrt{N}$, where σ is the standard deviation and $\sqrt{N}$ is the mean count, are included. This ratio is used as a homogeneity index, and a value in excess of 3 indicates significant inhomogeneity. In the inverted pigeonite grain, inhomogeneities for Ca and Fe are pronounced in the augite bleb, and there is considerable inhomogeneity for Ca in the hypersthene host. These inhomogeneities are probably due to fine, secondary lamellae, which could not be seen and avoided. Otherwise these pyroxenes are relatively homogeneous.

The analyses show that all the cations except silicon have participated in the unmixing process. This is true for the minor elements as well as for Ca, Fe, and Mg. Even Cr, which is present at concentration levels of 150 ppm and less, has clearly fractionated. Mn has been concentrated in the Ca-poor phases, and Ti, Al, Cr, and Na are concentrated in the Ca-rich phases. The composition of the calcic augite host in the original augite grain is almost identical to that of the exsolved augite bleb in the original pigeonite grain, and the composition of the hypersthene host in the original pigeonite grain is close to that of the exsolved clinohypersthene lamella in the original augite grain.

TABLE 1. ELECTRON-PROBE ANALYSES OF COEXISTING PYROXENES FROM THE BUSHVELD INTRUSION[a]

	Inverted Pigeonite				Augite			
	Host (hypersthene)		Lamella (augite)		Host (augite)		Lamella (clinohypersthene)	
SiO_2	53.0	*2*	52.4	*2*	51.8	*3*	52.2	*6*
TiO_2	0.3	—	0.5	—	0.5	—	0.2	—
Al_2O_3	0.73	*1*	1.34	*6*	1.52	*3*	0.85	*2*
Cr_2O_3	<0.01	—	0.02	—	0.02	—	<0.01	—
FeO[b]	23.6	*2*	11.2	19	10.8	*6*	25.6	*3*
MnO	0.5	—	0.3	—	0.3	—	0.6	—
CaO	1.36	*15*	21.0	*21*	21.2	*6*	0.8	*3*
MgO	20.7	*2*	13.6	*3*	13.3	*1*	19.6	*3*
Na_2O	0.05	—	0.2	—	0.2	—	0.05	—
K_2O	<0.005	—	<0.01	—	<0.005	—	<0.01	—
Totals	100.3		100.5		99.5		99.9	
Atomic Proportions for 6 Oxygen Atoms								
Si	1.98		1.96		1.95		1.98	
Ti	0.008	2.000	0.01	2.000	0.01	2.000	0.006	2.000
Al	0.012		0.03		0.04		0.014	
Al	0.020		0.029		0.028		0.024	
Fe	0.740		0.349		0.340		0.812	
Mn	0.02		0.009		0.01		0.02	
Ca	0.055	1.998	0.842	2.009	0.857	2.000	0.031	2.001
Mg	1.16		0.760		0.748		1.11	
Na	0.003		0.02		0.02		0.004	
Atomic Percentage								
Ca	2.8		43.2		44.1		1.6	
Mg	59.2		38.9		38.4		56.8	
Fe	38.0		17.9		17.5		41.6	

[a] Numbers in italics are for the ratio $\sigma/\sqrt{N}$, where σ is the standard deviation and N is the mean count.
[b] Total Fe as FeO.

These relations are further demonstrated by a plot of the four analyses in the pyroxene quadrilateral (Fig. 4). Also shown are the pigeonite and augite trend lines for the Bushveld intrusion which have been established from wet-chemical analyses of bulk pyroxene separates by F. B. Atkins (Wager and Brown, 1968). The particular pyroxenes from the gabbro studied in this investigation (SA 1019)

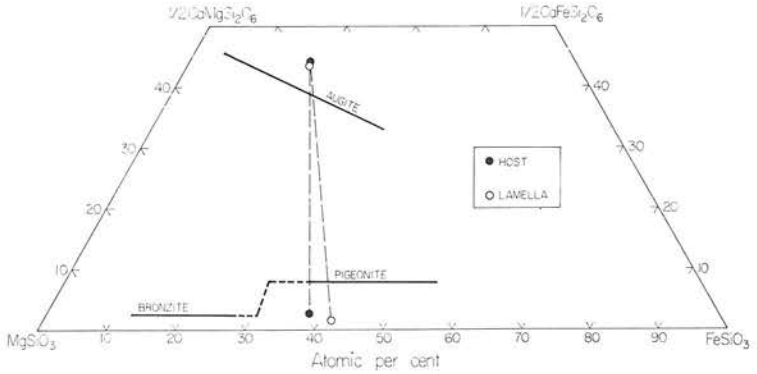

FIG. 4. Analytical data from Table 1 together with trend lines established by bulk analyses of pyroxene pairs from the Bushveld intrusion (Wager and Brown, 1968).

have not been separated and analyzed by wet-chemical methods, but to a good approximation the bulk compositions of the primary augite and pigeonite can be taken as the points of intersection of the host-lamella tie lines with the respective trend lines. A tie line formed by joining these two points of intersection has a slope compatible with those established by bulk analyses of other augite-pigeonite pairs. Exsolution shifts the compositions of the host and lamella phases on the augite side to more Ca-rich compositions and the phases on the pigeonite side are shifted to more Ca-poor compositions, as would be expected by slow cooling through an expanding two-pyroxene volume. As discussed previously (Boyd and Brown, 1968, pp. 358–359), the data confirm the hypothesis that with slow cooling, pigeonites change to clinohypersthene through exsolving augite and then (unless enclosed within augite) invert to orthorhombic hypersthene. Equilibration is maintained through an appreciable temperature range by diffusion of ions between host and lamellae within each grain.

The CaO content of the clinohypersthene lamella analyzed in this study was found to be 0.8 percent, in approximate agreement with the value of 0.7 percent found by Binns, Long, and Reed (1963) for a clinohypersthene lamella in augite from a noritic gabbro of the Bushveld Main Zone. It is a particular problem to establish the Ca content of such a lamella because FeKα radiation from the lamella fluoresces CaKα in the enclosing augite host. Reed and Long (1963) showed that the intensity of the fluorescent radiation decreases exponentially with distance of the point of impingement of the electron beam from the host-lamella boundary. Reed's calculations (pers. commun.) show that the fluorescence correction for this effect will be less than 0.1 percent Ca at the center of a clinohypersthene lamella of 13-μm width. The magnitude of the fluorescence depends also on geometric factors which differ in the analysis we have made from the set-up used by Binns, Long, and Reed. Nevertheless the fluorescence effect should be of the same order of magnitude in the two analyses. The lamella analyzed by Binns *et al.* (*op. cit.*) and the one described herein are of almost identical width, and the effective take-off angles of the probes used in the two studies are the same. The uncertainties are such that we have not attempted to correct for this boundary fluorescence, and hence the value of 0.8 percent CaO given is probably slightly high.

Discussion

The close similarity in composition between the two analyzed Ca-poor phases and between the two analyzed Ca-rich phases in the host-lamella sets indicates that these pyroxenes have maintained a state of equilibrium during cooling through a substantial temperature interval below the solidus. The compositions of the two augites are virtually identical, and the compositional differences between the two Ca-poor pyroxenes are very small and probably attributable to complications introduced by the variable development of secondary lamellae. Exsolution features in the Bushveld pyroxenes are coarser than in their counterparts from the Skaergaard and Stillwater intrusions, and it is evident that the Bushveld has cooled more slowly. Whether a comparable approach to equilibrium was present during the cooling of other large, mafic intrusions remains to be discovered.

The maintenance of subsolidus equilibrium exhibited by these pyroxenes may prove useful. The cooling history of the huge mafic intrusions, several hundred cubic kilometers in volume, cannot be known nearly so well as the history of a laboratory experiment. But it is possible that the cooling history can be understood well enough so that a study of exsolution and inversion features in the pyroxenes will provide useful information about subsolidus phase relations in the pyroxene quadrilateral.

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