Pyroxene Crystallization Trends and Contrasting Augite Zoning in the Sudbury Nickel Irruptive

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Abstract

Intercumulus augite at the base of the noritic cumulates in the Sudbury Irruptive has WO₉₅ En₅₈ Fs₅₈ cores grading to WO₉₄ En₄₄ Fs₅₆ rims. Despite the Ca enrichment and lower Fe/Mg ratio in the rims, augite cores show a normal iron enrichment with height in the cumulates reaching WO₉₇ En₄₄ Fs₃₇, but the rims remain WO₉₄ En₅₈ Fs₅₈. The augite rims do not coexist with orthopyroxene but with late magnetite and biotite, and their calcium enrichment is interpreted as movement of the augite composition off the solvus and into the augite field. Their reverse Fe/Mg zoning may be a primary result of increasing oxygen fugacity in the intercumulus liquid or a secondary result involving loss of orthopyroxene component to late liquid.

Introduction

In layered tholeiitic intrusions, such as Skaergaard (Wager and Brown, 1967), pyroxenes display cryptic trends of iron enrichment with relatively constant calcium contents. Zoning of pyroxenes in specimens from these intrusions is usually minor, and the zoning trends follow the overall crystallization trends. Individual specimens of volcanic rocks commonly show very strong zoning in pyroxenes, in some cases following a normal plutonic trend and in others a quench trend (e.g., Smith and Lindsley, 1971). In this paper an unusual zoning of augite involving increase in Ca and decrease in Fe/Mg in rims, accompanying a normal augite crystallization trend from rock to rock, is reported. It is interpreted as the result of equilibration between the liquid and the outer zone of the crystals.

The Sudbury Nickel Irruptive consists of noritic and gabbroic cumulates overlain by a granophyric rock, the micropegmatite. The minerals display normal cryptic trends with continuous iron enrichment in augite from the base of the main noritic unit (felsic norite) through an oxide-rich gabbro to a point high in the micropegmatite (Naldrett et al, 1970). An additional unit, mafic norite, has been shown to be part of the Irruptive (Hewins, 1970, 1971). It consists of a rapidly crystallized border group overlain by cumulates which grade into felsic norite. The pyroxenes discussed in this paper were collected in the mafic norite (border group and cumulates) and the lowest felsic norite (cumulates) at the adjacent Strathcona, Fraser, and North mines. Work in the Strathcona mine area has suggested that this part of the Irruptive is sill-like (Naldrett et al, 1970). Contacts between the border group and cumulates, and contacts within the cumulates, are parallel to the outer margin of the Irruptive and now dip about 30° inwards.

Orthopyroxene, the first phase to crystallize in these rocks, is enclosed poikilitically by plagioclase in orthopyroxene cumulates which grade upwards into orthopyroxene-plagioclase cumulates. The intercumulus material consists of ophitic augite, the third phase to crystallize, and quartz intergrown with perthite. Other phases occurring in minor amounts are biotite, magnetite, and ilmenite. Augite, magnetite, and ilmenite are cumulus phases at higher levels in the Irruptive.

Pyroxene Analyses

The analyses were made with an ARL EMX microprobe at 15 kV and 0.5 μA beam current, using a beam about 10 microns in diameter. The standards were synthetic diopside, ferrosilite, anorthite, rutile, tephroite, and chromium. The data were corrected with Empadr VII (Rucklidge and Gasparini, 1969). Every second set of analyses obtained on augite from Strathcona mine, where the most complete sampling cross section was obtained, is summarized in Table 1.

Average compositions, each associated with stan-
Table 1. Augite Analyses

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Notes: Specimen number indicates height in feet above base of Irruptive, whether cores (C) or rims (R), and digit in parentheses indicates number of analyses in the reported averages. Totals include average values for elements not determined but used in data reduction.


dard deviations of about 1 percent Wo and 0.5 percent En and Fs, are plotted in Figure 1. The mean compositions of the pyroxene cores in the Sudbury cumulates show normal plutonic trends with iron enrichment upwards. Thus iron content of these points is proportional to the distance of the specimens above the base of the Irruptive. The new points for the mafic norite fit smoothly on the trends established by Naldrett et al (1970) for the higher rocks. In the case of the border group, however, there is a reverse trend. The mean core compositions become less iron-rich upwards, as the specimens grade from rocks crystallized rapidly in situ to cumulates. The Skaergaard trends (SK in Figure 1) are shown here for reference. Note that some augites unaccompanied by calcium-poor pyroxene have slightly higher calcium contents than Skaergaard pyroxenes.

The zoning in orthopyroxenes is a normal iron enrichment with negligible calcium enrichment. A plot of all points analyzed defines a narrow band less than one mole percent wide about the mean trend for orthopyroxene cores in Figure 1.

In highly ophitic augite grains, zoning is less easy to define than in euhedral orthopyroxenes. Where an augite grain is bounded by earlier plagioclase grains (as in Figure 2), it is not possible to tell where it nucleated nor which was the last part to crystallize. Rims have been positively identified, however, in the case of subhedral terminations against quartz and perthite and show up as fairly clear areas. The parting evident in the rest of the grain consists of exsolution lamellae ranging from less than 2 microns thick down to immeasurably thin. Rims poor in lamellae on similar augite crystals from the Duluth Gabbro have been noted by Robinson et al (1971). Note that most of the grain shown in Figure 2 is fresh despite alteration elsewhere. Element profiles across this grain are shown in Figure 3.

The counts for Mg, Ca, and Fe plotted against distance were collected simultaneously by step-scanning. The lack of apparent change in magnesium concentration from core to rim (Figure 3) is not entirely typical of these augite crystals. Most show a decrease in magnesium concentration towards the rim although, for example, the two most magnesian points in the 380 foot specimen in Figure 4 consi-
tute a core-rim pair with the same En content. On the other hand, there is strong and continuous enrichment in calcium and depletion in iron from core to rim, the Fe/Mg ratio thus decreasing towards the rim. Chromium similarly decreases from about 0.6 to 0.1 wt percent from core to rim, this low concentration indicating that the augite rim crystallized very late.

In Figure 4 individual augite analyses from the same sequence of rocks as in Figure 1 are plotted on a segment of the pyroxene quadrilateral. The precision for each point plotted, determined by replicate analyses, is 0.5 percent for Wo and 0.003 for Fe/(Fe + Mg); i.e., the analyses are reproducible within the size of the symbol used to plot them. The calcium enrichment from cores to rims contrasts strongly to the relatively constant calcium content of the cores in all the rocks. As indicated in Figure 1, the average Fe/Mg ratios decrease from rock to rock immediately above the base and then increase through the cumulates in the normal way. Notice the variation in Fe/Mg ratio associated with the calcium zoning. The rims in almost all cases have lower Fe/Mg ratios than the cores. A notable exception to this is the lowest specimen whose rims show a distinct iron enrichment accompanied by a slight calcium enrichment. This, the most rapidly cooled rock, has an almost normal trend; the other rocks have almost the opposite of a quench trend (compare Smith and Lindsley, 1971). The presence in the augite rims of the cores in all the rocks. As indicated in Figure 1, the average Fe/Mg ratios decrease from rock to rock immediately above the base and then increase through the cumulates in the normal way. Notice the variation in Fe/Mg ratio associated with the calcium zoning. The rims in almost all cases have lower Fe/Mg ratios than the cores. A notable exception to this is the lowest specimen whose rims show a distinct iron enrichment accompanied by a slight calcium enrichment. This, the most rapidly cooled rock, has an almost normal trend; the other rocks have almost the opposite of a quench trend (compare Smith and Lindsley, 1971). The presence in the augite rims of
lower amounts of calcium-poor pyroxene lamellae is consistent with the general trend. Whether the variation in abundance of lamellae is a result of the chemical trend, or vice-versa, is discussed below.

**Calcium Enrichment in Augite**

The zoning of augite to calcium-rich rims has been reported before. Smith and Lindsley (1971) described such a trend in one crystal from the light pegmatoid of the Picture Gorge basalt, and it is common in the Cargill ultramafic complex (Allen, 1972, p. 133). Cryptic variation in augite commonly entails constant or decreasing calcium contents with increasing iron content. However, in some ultramafic and alkaline intrusions there is a trend of increasing calcium with increasing iron in augites (Irvine, 1967; Nash and Wilkinson, 1970; Allen, 1972). These pyroxenes fall above the pyroxene solvus and, as indicated by Irvine, are undersaturated in orthopyroxene.

In calc-alkaline volcanic rocks containing from 50 to 66 percent SiO₂, Fodor (1971) showed a variation of only 5 mole percent Fs but of 8 mole percent Wo between phenocryst and matrix augites. The principal variation in the augite composition is in calcium content, as in individual specimens from Sudbury. Fodor argued that high oxygen fugacity promoted crystallization of magnetite which depleted the magma in iron and prevented iron enrichment of the silicates. Similar conditions may have prevailed during crystallization of intercumulus melt at Sudbury. The cause of the calcium variation in the volcanic augites, conspicuous as a result of the relatively constant iron content, is not clear.

**Decrease in Fe/Mg Ratio in Augite**

Enrichment in iron at the expense of magnesium is the normal crystallization trend with falling temperature in silicates. It has been shown experimentally that, if oxygen fugacity increases as temperature falls, a reverse trend, namely decrease in Fe/Mg ratio, occurs in biotite (Wones and Eugster, 1965) and in olivine and pyroxene (Spiedel and Osborn, 1967). Field examples of fractionation trends of this type were reported from the Oslo (Czamanske, 1965) and Ben Nevis (Haslam, 1968) igneous complexes. Basalts are known in which olivine phenocrysts are very magnesian near a top chill zone, in which liquidus compositions are preserved, but underwent reequilibration to progressively higher iron contents in the lower, more slowly cooled parts of the body (Moore and Evans, 1967). This, of course, is not a true reverse trend. However, experimental crystallization of basaltic liquid at constant oxygen fugacity has shown that olivine becomes more magnesian if magnetite crystallization lowers the Fe content of the liquid (Gibb, 1971, pp. 113–115). Carmichael (1967) described the occurrence of Mg-rich rims on biotite in three Lassen dacites as evidence, rare at that time, of magma crystallizing with constant (or increasing) oxygen fugacity.

A number of examples of reverse Fe-Mg zoning in augite have been reported since the advent of the microprobe, e.g., Nicholls and Carmichael (1969, p. 56). Decrease in Fe/Mg ratio in the margins of both augite and coexisting orthopyroxene grains was discovered in the case of the contaminated quartz-basalts of Lassen, California (Smith and Carmichael, 1968, p. 222). This was attributed to silica contamination of the olivine-normative magma, an effect predicted by Bowen (1928, p. 206).

Where augitic pyroxene occurs without Ca-poor pyroxene and shows Mg-rich rims—for example, in the Roque Nublo basalts, Canary Islands (Frisch and Schminke, 1969, pp. 1081–1084; 1971) and in Vesuvius phonolite glass (Thompson, Lovenbury, and Wadsworth, 1971)—the trend has been attributed to increasing oxygen fugacity. In both cases it was argued that oxidation caused crystallization of magnetite and subsequent magnesium enrichment of the magma. At Vesuvius the rims are thought to have formed when the magma entered the scoriaceous superstructure of the volcano. In the Roque Nublo basalts the rise in oxygen fugacity is considered to result from resorption of inclusions of kaersutite cumulates. In similar xenoliths from Tenerife, Canary Islands, there is reverse zoning in augite and in kaersutite. Borley, Suddaby, and Scott (1971) stated that this might be caused by a rise in oxygen fugacity or alternatively to movement of crystals to different parts of the magma chamber.

**Discussion of Zoning in Sudbury Augite**

The trend to Ca-rich rims with lower Fe/Mg ratios for the Sudbury augites parallels a decrease in the abundance of Ca-poor pyroxene exsolution lamellae. The difference in composition between the cores and rims of these crystals may have arisen in one of the following ways.

1. Primary zonation: the cores and rims may have crystallized from the magma with precisely the compositions they have now.
(2) Magmatic reaction: the crystals may have been relatively homogeneous originally but some orthopyroxene component may have been lost from the rim by reaction with late liquid (as proposed for Duluth augite by Robinson et al, 1971, p. 932).

(3) Sub-solidus reaction: as (2) but orthopyroxene component lost by reaction with crystalline phases.

(4) Post-exsolution reaction: relatively homogeneous crystals exsolved Ca-poor pyroxene lamellae which were subsequently lost from the rims by reaction with the late liquid or solid phases.

In (1), (2), and (3) exsolution in the cores followed the development of rims too calcic to permit exsolution of Ca-poor pyroxene lamellae.

The concentrations of Cr, Ti, and Al decrease markedly from the augite cores to the extreme rims, a trend that is not obscured in the average core and average rim analyses (Table 1). This is consistent with crystallization from a late liquid depleted in these components. Cr, Ti, and Al are preferentially partitioned into augite as opposed to orthopyroxene, the distribution coefficients being approximately 2 at Sudbury assuming that core augite was in equilibrium with rim orthopyroxene (Hewins, 1971). If originally homogeneous augite crystals had lost orthopyroxene lamellae, the rims would have been slightly enriched in Cr, Ti, and Al relative to the cores. The depletion in these components indicates that the rims are an early feature; therefore, alternative (4) may be discarded.

Considering alternatives (2) and (3), the rims occur almost exclusively against micrographic intergrowth. Any reaction of the augite crystals would therefore most probably have been with late liquid; therefore alternative (2) is next compared with alternative (1).

The late decrease in Fe/Mg ratio is found at Sudbury in the augite but not in the orthopyroxene. The augite crystallized later than the orthopyroxene, in part along with magnetite and biotite. Alternative (2) suggests that after orthopyroxene ceased to crystallize from the melt, the augite (still crystallizing with relatively low Ca) would have begun to react with the melt. Augite rims would have lost orthopyroxene component, becoming more calcic as the liquid became increasingly undersaturated in orthopyroxene. Alternative (1) suggests rather that the liquid crystallized a more calcic augite as the augite composition, no longer restricted to the solvus, moved into the one pyroxene field.

This may seem a fine distinction as far as the Ca content of the rim augite is concerned, but it has important implications for the decrease in Fe/Mg ratio in the rim. If the rim composition developed by loss of orthopyroxene component to the liquid, the lower Fe/Mg ratio in the rims simply reflects the absence of Ca-poor pyroxene lamellae. Tie lines joining the rim- and core-compositions extend towards a composition of hypersthene appropriate for the lamellae. The similarity of these hypothetical tie lines to tie lines joining host augite and analyzed orthopyroxene lamellae in augite from the Bushveld (Boyd and Brown, 1969) appears to support alternative (2).

Alternatively, if the rim composition was the result of primary zonation, the cause of the decrease in Fe/Mg must be sought elsewhere. In the examples quoted above, increasing oxygen fugacity is the common mechanism causing such trends. Taylor and Forester (1971) concluded from oxygen isotope data that the presence of granophytic textures, as in Sudbury intercumulus material, "requires the coexistence of an aqueous gas phase." The water content of Sudbury norites (Collins, 1934), the estimated pressure of 1.2 to 0.5 kbar due to overlying Irruptive and Onaping Formation, and the saturation data for granitic melts (Burnham, 1967) suggest that the intercumulus melt was saturated. Dissociation of water vapor is therefore possible and, if so, perhaps the presence of water vapor facilitated the diffusion away of hydrogen and raised the oxygen fugacity. A rise in oxygen fugacity only at the late stages in each level is consistent with decrease in Fe/Mg ratio in augite from cores to rims but not from rock to rock.

Conclusion

Augite crystals near the base of the Sudbury Irruptive display enrichment in calcium and decrease in Fe/Mg ratio towards rims, despite normal (upward) iron enrichment in cores through the overlying rocks. The Ca-rich rims are a consequence of the disappearance of orthopyroxene. As the late liquid became more undersaturated in orthopyroxene component, augite further inside the solvus became stable. Either (1) late calcic augite crystallized from the liquid as the augite composition moved into the
one pyroxene field, or (2) early augite became more calcic by loss of orthopyroxene component to the liquid. The decrease in Fe/Mg ratio is caused by either (1) increasing oxygen fugacity in the late liquid, or (2) the absence of co-existing Ca-poor pyroxene lamellae in the rim augite.

Calcium enrichment has not accompanied decrease in Fe/Mg ratio in augite at other localities, perhaps because these augites did not generally co-exist with orthopyroxene. The augite composition did not initially fall on the solvus and therefore has not been shown to be a very common phenomenon. The relationship between augite composition and ces- sation of orthopyroxene proposed here clearly has a limited application because in many systems augite crystallizes much earlier than at Sudbury. However, decrease in Fe/Mg ratio of cores of ferromagnesian minerals is to be expected towards the later stages of crystallization of large intrusions, if loss of hydrogen occurs after the formation of vapor.

Acknowledgments

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