

Oscillatory zoning in clinopyroxenes from the Guide Copper Mine, Phalaborwa, South Africa

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Abstract

The feldspathic pyroxenite of the Guide Copper Mine, Phalaborwa, South Africa, contains cumulus clinopyroxenes poikilitically enclosed in microcline and chalcopyrite. The clinopyroxenes range in composition from diopside to aegirine-augite within a single crystal. Superimposed on this normal zoning are fine-scale laminations, on the order of 12–30 μm , which oscillate in Na and Fe^{3+} versus Ca and Mg. This oscillatory zoning of acmite versus diopside components is unique among reported cases of oscillatory zoning in pyroxenes. The greater number of oscillations, parallel to faces that have grown faster, points to diffusion-controlled growth of these pyroxenes, possibly due to differential diffusion rate of coupled Na and Fe^{3+} in the melt.

Introduction

The oscillatory zoning common in plagioclases (Smith, 1974, p. 212–214) has been attributed to differences in diffusion and nucleation rates or to major changes in physical or chemical conditions within the magma. Phe-mister (1937) suggested that finer-scale oscillations result from local disequilibrium and coarser ones from more extensive chemical or physical changes within the magma as a whole.

Oscillatory zoning is less common in pyroxenes, but it has been recognized in terrestrial (Boesen, 1964; Smith and Carmichael, 1969; Nash and Wilkinson, 1970; Downes, 1974, Grapes, 1975) and lunar rocks (Boyd and Smith, 1971, Weill et al., 1971). Clinopyroxenes from the Guide Copper Mine, Phalaborwa, South Africa, are strongly zoned from diopside to aegirine-augite. Superimposed on this normal zonation are fine-scale laminations of pale green to dark green pyroxene. This paper describes the pyroxenes from this unique locality and proposes a mechanism for the oscillatory zoning based on its distribution in the pyroxene crystals.

Geologic relations and petrography

The feldspathic pyroxenite of the Guide Copper Mine is one of numerous syenite and pyroxenite pipes surrounding the Phalaborwa Complex, northeastern South Africa (Fig. 1). The Phalaborwa Complex is 2047 ± 22 m.y. in age (Eriksson, 1984) and is comprised predominantly of py-

roxenites with various proportions of diopside, phlogopite, apatite and microcline. Eriksson (1982) interpreted these pyroxenites to have formed by cumulus processes from a peralkaline, ultrabasic melt. Carbonatite and phosphorite, which make up only a small percentage of the rocks of the complex, formed from a distinctly different magma.

The presence of pyroxenite pipes in this area was noted by Shand (1931). The locations of the three pyroxenite pipes are shown on the map of Hanekom et al. (1965). Two pipes occur to the east of the main complex; one is at the site of the Palabora Mining Company magnetite dump, and the other is too deeply weathered to yield any petrologic information. The third pyroxenite pipe at the Guide Copper Mine property (Fig. 1) is the only one that has been described in any detail (Shand, 1931). Based on initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, mineral chemistry and trace element chemistry, Eriksson (1982) interpreted the feldspathic pyroxenite of the Guide Copper Mine to have formed from the magma producing the pyroxenites of the main complex.

The Guide Copper Mine pyroxenite is pipe-like in form with a U-shaped outcrop covering approximately 15,000 square meters (Hanekom et al., 1965). The feldspathic pyroxenite, which resembles that of the main complex, is closely associated with the syenite of the adjoining Kitchener's Kop; carbonatite dykes have been mapped in the area (Shand, 1931).

The pyroxenite was described by Shand (1931) as containing idiomorphic clinopyroxenes poikilitically enclosed in microcline and sulfide. Clinopyroxenes are occasionally zoned from clear cores to bottle green rims and range in length from <1 mm to >3 cm, commonly a

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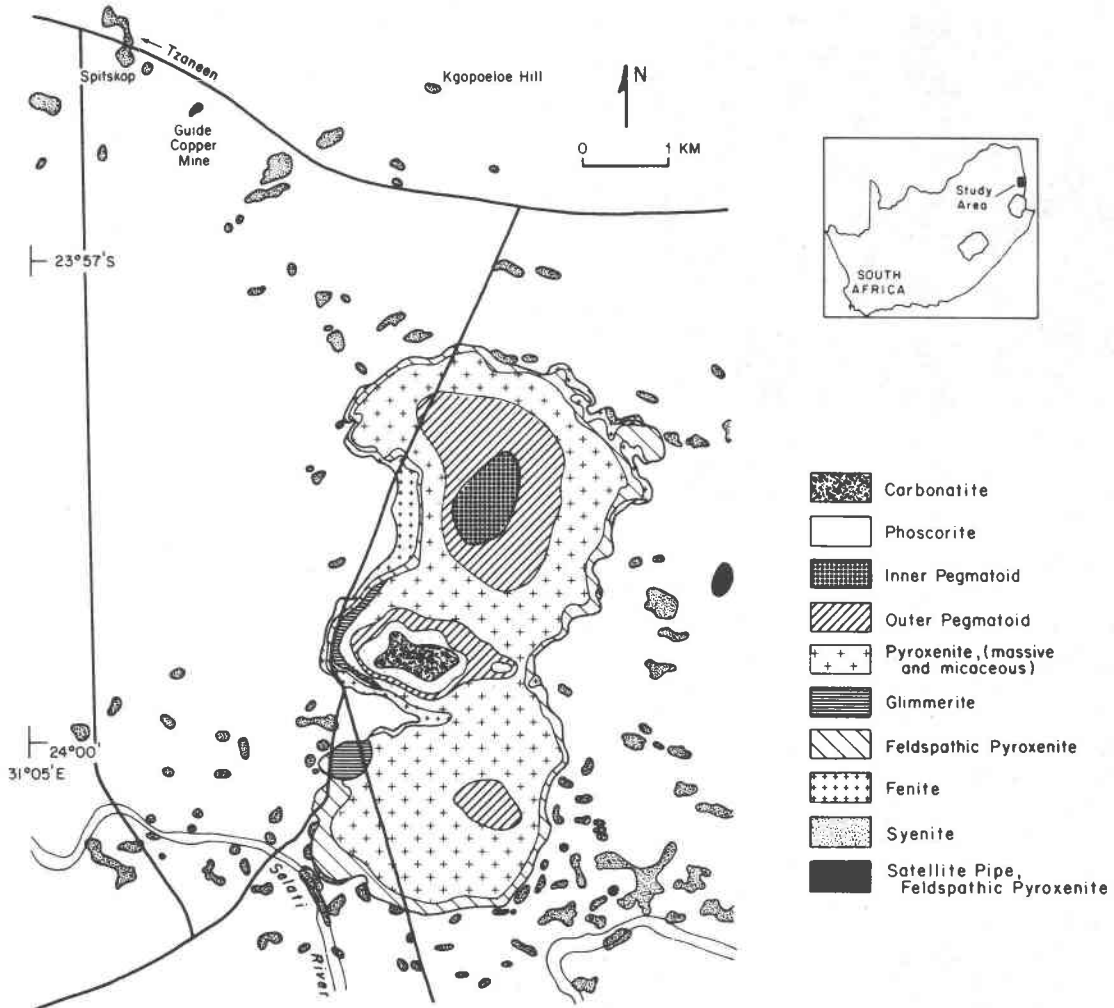


Fig. 1. The generalized geology of the Phalaborwa Complex. Later dolerite dikes which cut across the complex have been omitted for clarity (after Hanekom et al., 1965).

single hand specimen. Figure 2 shows idiomorphic, bottle green clinopyroxene crystals poikilitically enclosed in microcline closely associated with finer-grained, monomineralic clinopyroxenite. Changes in rate of crystal growth and/or accumulation or mechanism of trapping intercumulus liquid may account for changes in texture over a short distance.

Locally, biotite and chalcopyrite with bornite form irregular patches and constitute a major proportion of the rock. The biotite is altered in all of the samples studied, thus its chemistry is not reported here. Chalcopyrite with exsolution lamellae of bornite poikilitically encloses clinopyroxene and occurs in patches up to 5 cm across. Accessory apatite and sphene occur as minute, idiomorphic crystals. Aldous (1980) found that sulfides replace the feldspar, but not the pyroxene, and used this texture to suggest that the replacement of feldspar occurred as a remobilization of sulfide liquid.

A distinctive feature of this rock is the oscillatory banding in the pyroxenes. Alternating bands of pale green and bottle green clinopyroxene are concentrically arranged with oscillatory zoning more pronounced at ends of elongate crystals (Fig. 3). Rarely, fragments of pyroxene crystals occur where oscillatory banding abutts and is truncated by the pyroxene-feldspar contact.

Mineral chemistry

Microprobe analyses of representative pyroxenes are listed in Table I together with analytical conditions. Given the general formula for clinopyroxene $X^{viii}Y^{vi}Z_2^{iv}O_6$, the Z site contains from 1.947 to 1.995 Si, with Al^{iv} varying from 0.005 to 0.023. The important feature of the tetrahedral site occupancy is the low Al content. The Y site is primarily occupied by Fe and Mg, with 0.000 to 0.008 Al^{vi} , a low, constant amount of Mn and little or no Ti. Ca and Na occupy the X site.

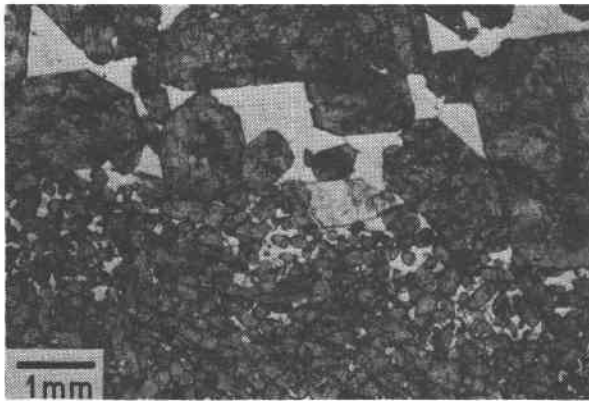


Fig. 2. Photomicrograph (plane light) of feldspathic pyroxenite from the Guide Copper Mine. One grain of microcline poikilitically encloses the larger grains of euhedral clinopyroxene.

Ferric iron was estimated by two methods. Cawthorn and Collerson (1974) calculated Fe^{3+} by assuming stoichiometry, i.e., four cations and six oxygens, but this method is heavily dependent on the quality of the analysis. Alternatively, Fe^{3+} may be assumed to balance the Na content, "forming" an acmite component. Tyler and King (1967), Stephenson (1972) and Larsen (1976) show that this is the case in pyroxenes from alkaline rocks. Analyses in Table 1 are calculated by allotting an equal portion of Fe cations to Na, giving Fe_2O_3 , with the remaining iron reported as FeO. Clinopyroxenes from the Guide Copper Mine range from diopside through Na-rich augite to aegirine-augite ($\text{Fe}^{3+} > 0.2$ cations). The majority of the clinopyroxene compositions are sodic augite (Deer et al., 1978). The clinopyroxenes are highly zoned and commonly exhibit the entire compositional range in one crystal.

Optical oscillatory zoning described above is a result of compositional fluctuations. These are illustrated in Figure 4, which shows reversals in the normal zonation from diopside- to acmite-rich pyroxene, and in Figure 5, which shows variations in various oxide chemistry plotted against distance. A plot for Fe^{3+} would be identical to the plot for Na because of the calculation procedure. Figure 5 shows that total Fe varies sympathetically with Na and inversely with Mg and Ca. This implies enrichment of acmite over diopside components in the dark- as opposed to the light-green bands.

The scale of zoning, obtained from over 250 spot analyses by electron microprobe, has a range in composition of $\text{Na}_2\text{O} = 1.5\text{--}3.0$ wt.%, $\text{FeO} = 7.76\text{--}11.3$ wt.% and $\text{MgO} = 11.9\text{--}14.1$ wt.% representing a maximum range in acmite component of 8–22 mol% and a characteristic chemical variation of approximately 15 mol% acmite. Microprobe analyses were taken every 6 μm , and the wavelength of oscillations ranges from 12–30 μm . Be-

cause of the spacings of analyses, oscillations with widths less than 12 μm cannot be detected, although these are much more common than the longer ones. In one traverse of 600 μm , 19 oscillations were detected with bands of constant composition up to 54 μm thick. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is dramatically different between areas of constant composition ($\text{Fe}^{3+}/\text{Fe}^{2+} = 0.15\text{--}0.19$) and areas with oscillatory zoning ($\text{Fe}^{3+}/\text{Fe}^{2+} = 0.25\text{--}2.2$).

Oscillations among grains within a single thin section are not constant. Based on optical examination, equant or nearly equant grains have similar zonation parallel to each crystal face. In contrast, elongate crystals have many more oscillations parallel to the smaller faces than to the long, prismatic faces (Fig. 3). In addition, amplitude and wavelength of the various oscillations are not stratigraphically equivalent among grains; i.e., grains vary in both number and width of oscillations. This phenomenon has been observed in certain plagioclases with oscillatory zoning (Weibe, 1968).

Pyroxenes from the Guide Copper Mine contain <0.5 wt.% Al_2O_3 and are similar to the low-Al clinopyroxenes of the main Phalaborwa Complex. This low Al content of the latter has been attributed to the peralkaline nature of the magma (Eriksson, 1982). The pyroxenes from the Guide Copper Mine are considered to have crystallized from a magma that is cogenetic with that forming the pyroxenites of the main complex.

Discussion

Mechanisms previously proposed for oscillatory zoning include varying rates of growth and diffusion (Boesen, 1964; Downes, 1974; Boyd and Smith, 1971; Sibley et al., 1976; Haase et al., 1980), growth kinetics (Bottinga et al., 1966; Boyd and Smith, 1971), crystallization above and below a peritectic (Boyd and Smith, 1971), movement of magma (Boesen, 1964; Boyd and Smith, 1971) and fluctuations of volatile composition (Boesen, 1964).

These oscillations or rapid changes in composition may

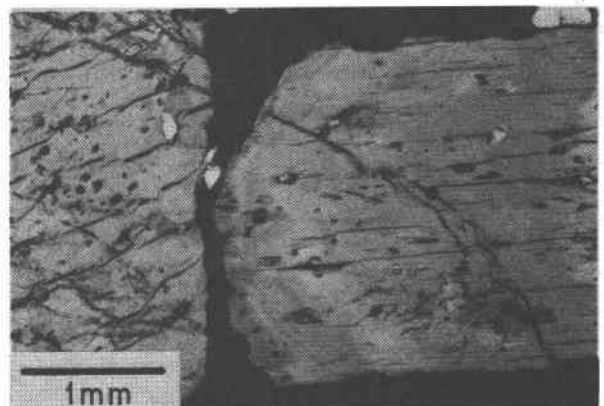


Fig. 3. Euhedral clinopyroxene surrounded by chalcopyrite exhibits parallel bands of pale green and dark green pyroxene at edge of grain.

Table 1. Representative electron microprobe analyses for clinopyroxenes from feldspathic pyroxenite, Guide Copper Mine

| | Weight percent oxide | | | No. of cations based on 6 oxygens | | | |
|---|----------------------|--------|-------|-----------------------------------|-------|-------|-------|
| | (1) | (2) | (3) | (1) | (2) | (3) | |
| | core | | rim | | | | |
| SiO ₂ | 53.70 | 53.50 | 52.00 | Si | 1.975 | 1.973 | 1.976 |
| TiO ₂ | 0.23 | 0.35 | 0.22 | Al | 0.023 | 0.013 | 0.015 |
| Al ₂ O ₃ | 0.52 | 0.29 | 0.33 | Tet. Total | 1.997 | 1.986 | 1.991 |
| FeO | 7.76 | 10.30 | 11.30 | Al | 0.000 | 0.000 | 0.000 |
| MnO | 0.16 | 0.29 | 0.18 | Ti | 0.006 | 0.010 | 0.006 |
| MgO | 14.10 | 13.00 | 11.90 | Fe ³⁺ | 0.082 | 0.129 | 0.224 |
| CaO | 23.20 | 21.80 | 19.30 | Fe ²⁺ | 0.148 | 0.175 | 0.102 |
| Na ₂ O | 1.15 | 1.80 | 3.03 | Mn | 0.005 | 0.009 | 0.006 |
| Total | 100.82 | 101.33 | 98.26 | Mg | 0.773 | 0.712 | 0.672 |
| | | | | Ca | 0.915 | 0.862 | 0.786 |
| Fe ²⁺ /(Fe ²⁺ + Mg) | .16 | .20 | .13 | Na | 0.082 | 0.129 | 0.223 |
| Fe ³⁺ /Fe ²⁺ | .55 | .74 | 2.2 | Oct. Total | 2.010 | 2.025 | 2.019 |

Microprobe analyses were obtained on an ARL microprobe, model SEMQ, at the University of the Witwatersrand. Analytical conditions included 15 kV accelerating potential, 150 μ A beam current and finely focused beam size (1-2 μ m). Replicate analyses of clinopyroxene standard yielded accuracy considerably smaller than measured precisions of around 1% for major elements and 5% for minor elements.

be attributed generally to changes in the bulk composition of the magma or to differences in growth rate versus diffusion in the melt. In plagioclase, Bottinga et al. (1966) and Sibley et al. (1976) propose that these two mechanisms may be distinguished by the nature of zoning. They argue that changes in bulk chemistry within the magma will produce oscillations that are symmetrical with respect to crystallographic orientation. In contrast, oscillations

resulting from rapid growth of crystal faces relative to slow diffusion of ions through the melt will be non-uniform in both amplitude and wavelength with respect to more slowly growing crystallographic directions. This results in the fastest growing faces of a crystal having a larger number of oscillations with greater amplitude and wavelength than faces growing more slowly.

Variations in composition due to changes in bulk composition of a liquid should be stratigraphically equivalent among grains within one sample. Weibe (1968) and Sibley et al. (1976) attribute large-scale variations in plagioclase to changes in bulk magma composition and the smaller, more uniform variations to diffusion-controlled processes. The smaller, uniform variations are considered to have formed isothermally (Sibley et al., 1976) because the average composition of neighboring zones is relatively constant.

The pyroxenes from Guide Coper Mine have characteristics diagnostic of diffusion-related processes. Most of the oscillations have small, uniform amplitude (7 mol% aegirine) and wavelength (12 μ m) and are numerous (up to 19 oscillations per grain). Oscillations are more pronounced at the ends of elongate crystals and do not correlate among grains within one thin section. Although zones of oscillations with larger amplitude exist, they also do not correlate among grains. As with plagioclase oscillations attributed to diffusion-related growth (Sibley et al., 1976), the smaller-scale oscillations in the pyroxenes have relatively uniform composition (Fig. 5), which may be attributed to isothermal crystallization.

Oscillatory zoning in pyroxenes most commonly results from variation in Al and Ti contents (Downes, 1974;

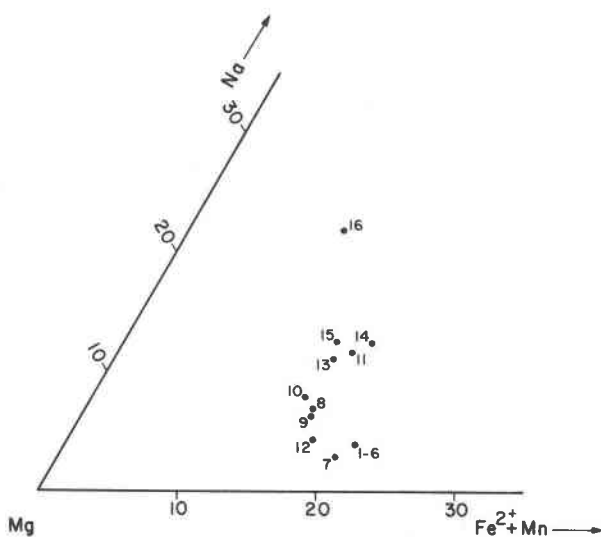


Fig. 4. Representative analyses for one pyroxene grain plotted Na-Mg-Fe²⁺ + Mn for analyses from core (analysis 1) to rim (analysis 16).

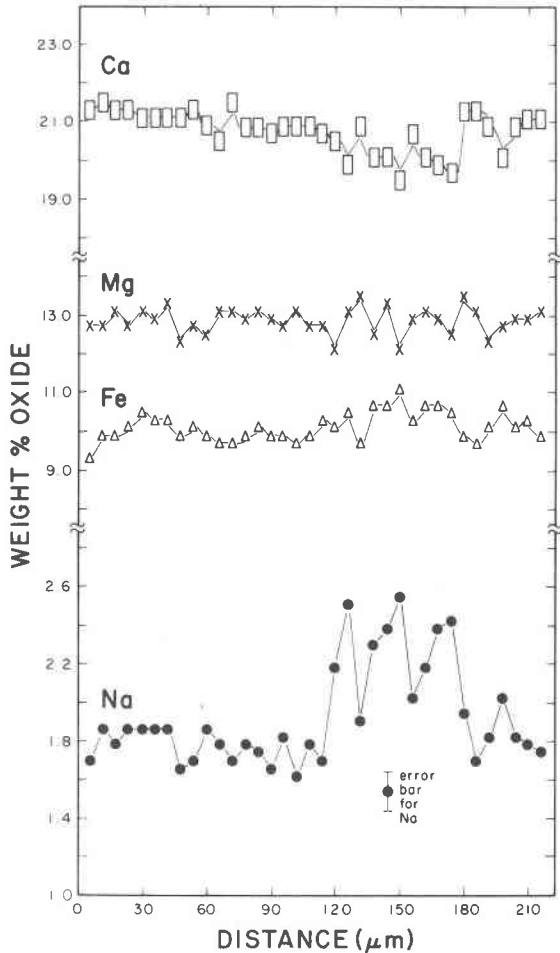


Fig. 5. Cations per unit formula are plotted against distance for a portion of one crystal. Height of symbols for Ca, Mg, and Fe represent size of error.

Smith and Carmichael, 1969; Boyd and Smith, 1971; Weill et al., 1971); other examples involve fluctuations in Al and some other cation, e.g., Fe, Si, Mg or Ca (Boesen, 1974; Grapes, 1975). There are no reported examples of regularly fluctuating diopside versus acmite components in pyroxenes. The pyroxenes from the Guide Copper Mine are low in Ti and Al and show no evidence of fluctuations in these elements. The oscillatory fluctuations in acmite component in these pyroxenes suggest that variation in Na, Fe^{3+}/Fe^{2+} or O or some combination of these elements controls the zoning.

It is interesting that all cases of oscillatory zoning in terrestrial clinopyroxenes occur in mildly to strongly alkaline rocks, e.g., feldspathic pyroxenite (this study), shonkinite (Nash and Wilkinson, 1970), monzonite (Boesen, 1964), alkali gabbro (Grapes, 1975), trachybasalt (Smith and Carmichael, 1969) and phonolite and leucitite (Barton et al., 1982). Optical examination of clinopyroxene-bearing rocks from other alkaline complexes shows

that oscillatory zoning may be more common than has generally been noted.

The entry of Na and Fe^{3+} into pyroxenes has been attributed to high oxygen fugacity by some workers (Gibb, 1973; Larsen, 1976) and, although acmite is stable over a wide range of fO_2 conditions (Bailey, 1969; Gilbert, 1969), the stability of acmite is very sensitive to fO_2 (Gilbert, 1969).

It has also been recognized (Mysen et al., 1980) that increasing alkalis in a melt stabilizes the ferric iron in tetrahedral coordination to form acmite. Gilbert (1969) found a very steep slope of dT/dP for the melting curve of acmite and attributed this to a low ΔS value, due either to the low entropy of the oxides or to similar coordination of ions in liquid and in acmite. Wones and Appleman (1963) found that Fe^{3+} -feldspar formed much more easily than Al-feldspars, suggesting that the mobility of Fe^{3+} in a melt is greater than that of Al^{3+} . Haase et al. (1980) summarized the data on ion mobility, based on metallurgical literature, e.g., $D_{Na^+} \gg D_{Ca^{++}} > D_{Al^{3+}} > D_{SiO_4^{4-}}$, where D_i is the diffusion coefficient for species i .

Thus, there is diverse evidence that Na^+ and Fe^{3+} may form a stable component in the melt and may migrate rapidly compared to other components. Differential migration is necessary for diffusion-controlled oscillatory zoning and, in the case of the pyroxenes in this study, differential movement of Na and Fe^{3+} versus Ca and Mg and/or Fe^{2+} accounts for the oscillating acmite versus diopside components. This mechanism, analogous to the common, oscillatory zoning of CaAl- and NaSi-components in plagioclase, may be easier to envisage than fluctuating fO_2 conditions controlled by diffusion. Based on the distribution and size of the oscillations in the pyroxenes from the Guide Copper Mine, fluctuating fO_2 conditions of the bulk liquid cannot account for these variations in composition.

The differential rates of migration of Na and Ca components account for oscillatory zoning in pyroxenes of this study but not for other reported cases of pyroxenes in which oscillatory zoning is a result of Al versus Fe, Si, Mg or Ca. If such oscillations are due strictly to differential migration of Al versus the other cations, then, as with plagioclase, oscillatory zoning should be more common in pyroxenes. Whatever mechanism controls this type of oscillatory zoning is common to lunar basalts and to certain types of alkaline magmas.

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