Ion microprobe analyses of exsolution lamellae in peristerites and cryptoperthites

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Abstract

Combined data from electron microscope, electron microprobe, and ion microprobe analyzers can be used to determine the composition and thickness of lamellae in peristerite and cryptoperthite feldspars. Blue iridescent peristerite from Hybla, Ontario has a bulk composition of An₃0Or₁ and lamellae compositions of An₃0Or₁, and An₃0Or₁ₐ. Orange-red iridescent peristerite from the same location has a bulk composition of An₃0Or₁, and lamellae of An₃0Or₁ and An₃0Or₁ₐ. Two pale blue iridescent cryptoperthites from Quebec and Johana, Japan have the following compositions: An₃6Or₃ (bulk) and An₃6Or₃, An₃6Or₅₁ for lamellae; An₃0Or₅₀ (bulk) and An₃0Or₃₆, An₃0Or₇₂ for lamellae. The irregular nature of the lamellae in peristerites and cryptoperthites precludes ion microprobe depth profiling, such as has been applied to more regular labradorite lamellae. Point analysis must be performed instead, which may result in possible overlap onto adjacent lamellae and compositional values that do not reflect the extreme limits.

Introduction

Exsolution lamellae in peristerite and cryptoperthite are usually well under 0.1 μm in thickness. As this is below the spatial resolution of conventional electron probe microanalysis (EPMA), and the detection of minor contents of alkali ions is not reliable using analytical electron microscopy, the surface analysis and sputtering properties of the ion microprobe analyzer (IMA) can be used to make depth profiles through the lamellae.

Miura and Tomisaka (1978) reported results of an ion microprobe study of exsolution lamellae in labradorite. They determined the An and Or contents from working curves only in the compositional range of Bøggild intergrowths (An₃₅ to An₆₀). Calibration curves were obtained by analyzing independently well-characterized standard specimens of feldspar by both EPMA and IMA. In this way a relationship between secondary ion emission intensity and element concentration in feldspars was established. It should be noted that secondary ion intensity is a function of crystal orientation as well as concentration, such that calibration curves must be constructed for secondary ion intensity ratios. While the absolute intensities of ions from two elements may vary, the ratios do not. Each lamella in labradorite is more than 50 nm in thickness, and the boundaries between lamellae are almost uniformly parallel to each other, at a particular composition (Miura et al., 1974, 1975). Consequently it was not necessary to use a small spot when depth profiling; in fact it was preferable to use a wide beam to minimize edge effects in the eroded crater. In peristerite and cryptoperthite lamellae, however, the thickness of one of the two lamella types is below 50 nm and the lamellar boundaries are usually irregular. It is thus necessary to use a finely-focussed ion beam to avoid overlap of the spot onto adjacent lamellae. Therefore, the compositions of peristerite and cryptoperthite lamellae can be determined mainly by using “point analysis” with a very small diameter primary ion beam in the ion microprobe analyzer (see Fig. 1).

Two-phase fields of peristerite and Bøggild intergrowths may be formed either by a two-phase binary “loop” or by solvus (Smith, 1975; Barron, 1972; Nord et al., 1978). The question of whether the precursors to peristerite or Bøggild lamellae are spinodally controlled can be addressed by exploring the compositions of the two phases, because compositional fluctuations are the precursors to spinodal decomposition. The ion microprobe analyzer has the resolution to resolve such compositional fluctuations, and

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the problem can be tested on coarse (>75 nm) ex-
solution lamellae.

Analytical procedure

The specimens used in this study are peristerites
from Ontario (precise locality unknown; shown as
P-1, 2) and Hybla, Ontario (H-1, 2, 3) (cf. Ribbe,
1962), and cryptoperthites from Quebec, Canada
(CC-1), Larvik, Norway (CND-1, 2), and Johana, Ja-
pan (CJ-1). These specimens were polished with 0.25
µm diamond paste so that the polished surface would
be closely parallel to lamellar planes whose orienta-
tion had been determined by previous TEM study of
surface replicas. The specimens were then analyzed
by EPMA (JXA-50A) at 15kV prior to performing
the IMA analysis (see Table 1). The mean bulk com-
positions determined by EPMA are accurate to ap-
proximately 4 mole percent of the Or content in peri-
sterite or 0.6 percent in cryptoperthite. The Ab
contents are accurate to 0.4 percent in cryptoperthite,
and 0.3 percent in peristerite. A Hitachi ion micro-
probe analyzer, IMA-2, incorporating an electron
spray gun (cf. Nakamura et al., 1976; Miura and
Tomisaka, 1978) was used to collect the secondary
ion intensities from the surfaces of these specimens.
The specimens were bombarded with a positively-
charged primary beam of oxygen (¹⁸O⁺) at 12kV, us-
ing a beam diameter of approximately 5 µm, a beam
current of 5 x 10⁻⁸A, and an electron spray gun cur-
rent of 4 µA.

Secondary ion intensities of the ³⁹K⁺, ²⁵Na⁺, and
³⁷Al⁺ isotopes were used to determine the Or, Ab,
and An contents, because ³⁷Al⁺ has the highest rela-
tive yield of all the elements in the feldspars and be-'
cause ³⁷Al⁺ and ²⁵Na⁺ are unique isobars for which
interference by other ion species is very small. The
Or and Ab (or An) contents in peristerite and crypto-
perthite lamellae could be calculated from the ion in-
tensity ratios K⁺/Al⁺ and Na⁺/Al⁺, just as for the ra-
tios in labradorite (Miura and Tomisaka, 1978).

The measured secondary ion intensity ratio of bulk
standard specimens determined with IMA can be re-
lated to the atomic ratio determed with EPMA by using
correction factors fOr and fAb (or fAn). These corre-
lations are shown by the working curves which
determine the compositions of the exsolution la-
rellae.

In attempting to obtain depth profiles of these ma-
terials, no regular variation in the ratios Iₖ⁺/Iₐ⁺ and
Iₙa⁺/Iₐ⁺ could be found as erosion proceeded
through the layers. This is due in part to smaller or
larger lamellae intervening between host lamellae,
and also to irregular curved boundaries of the lamel-
lar texture. The average sputtering rate was usually
about 30 nm/min. Electronic aperturing, which dis-
criminates against ions from the crater walls, was
used when appropriate in raster mode. An alterna-
tive approach was made using point (5 µm diameter)
analyses on a grid pattern, with grid meshes of 10, 50,
and 100 µm.

The working curves for estimating Or and Ab (or
An) contents of the lamellae were determined on a
standard specimen, which was chosen from the speci-
mens of each intergrowth type so as to make the
measured and corrected ion intensity ratios equal; i.e.
the values of the correction factors fOr and fAb (or fAn)
Table 2. Observed and corrected ion intensity ratios and Or and Ab (or An) correction factors for the establishment of working curves to determine Or and Ab (or An) contents in peristerite and cryptoperthite lamellae

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Iridescence Color</th>
<th>( \frac{I_{Na^+}/I_{Al^+}}{obs} )</th>
<th>( f_{Ab} )</th>
<th>( \frac{I_{Na^+}/I_{Al^+}}{corr} )</th>
<th>( \frac{I_{K^+}/I_{Al^+}}{obs} )</th>
<th>( K_{100} )</th>
<th>( f_{Or} )</th>
<th>( \frac{I_{K^+}/I_{Al^+}}{corr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>Blue</td>
<td>0.69</td>
<td>1.22</td>
<td>0.84</td>
<td>0.009</td>
<td>0.010</td>
<td>2.11</td>
<td>0.020</td>
</tr>
<tr>
<td>P-2</td>
<td>Whitish blue</td>
<td>0.64</td>
<td>1.27</td>
<td>0.81</td>
<td>0.008</td>
<td>0.009</td>
<td>2.13</td>
<td>0.018</td>
</tr>
<tr>
<td>H-1</td>
<td>Orange-red</td>
<td>0.81</td>
<td>1.11</td>
<td>0.90</td>
<td>0.003</td>
<td>0.003</td>
<td>2.33</td>
<td>0.008</td>
</tr>
<tr>
<td>H-3</td>
<td>Whitish blue</td>
<td>0.92</td>
<td>1.00</td>
<td>0.92</td>
<td>0.038</td>
<td>0.041</td>
<td>1.00</td>
<td>0.041</td>
</tr>
<tr>
<td>CC-1</td>
<td>Whitish blue</td>
<td>0.54</td>
<td>0.90</td>
<td>0.49</td>
<td>0.29</td>
<td>0.31</td>
<td>1.02</td>
<td>0.32</td>
</tr>
<tr>
<td>CND-1</td>
<td>Whitish blue</td>
<td>0.48</td>
<td>0.95</td>
<td>0.46</td>
<td>0.38</td>
<td>0.41</td>
<td>1.01</td>
<td>0.41</td>
</tr>
<tr>
<td>CND-2</td>
<td>Whitish blue</td>
<td>0.44</td>
<td>1.00</td>
<td>0.44</td>
<td>0.46</td>
<td>0.49</td>
<td>1.00</td>
<td>0.49</td>
</tr>
<tr>
<td>CJ-1</td>
<td>Whitish blue</td>
<td>0.39</td>
<td>1.05</td>
<td>0.41</td>
<td>0.55</td>
<td>0.59</td>
<td>0.99</td>
<td>0.58</td>
</tr>
</tbody>
</table>

* For cryptoperthite the factor is \( f_{Ab} \).

** \( K_{100} = 1.074 \times \frac{I_{K^+}/I_{Al^+}}{obs} \) to correct for natural isotopic abundance.

Fig. 2. Schematic procedure of quantitative ion microprobe analysis of exsolution lamellae in this study.
were arranged to equal unity in one of the standard specimens, as listed in Table 2.

The compositions of the exsolution lamellae were determined from the working curves based on measured ion intensity ratios. These ratios sometimes included data from adjacent lamellae, or inclusions, or both. The ion intensity ratios, therefore, had to be screened from the raw data. The analytical procedure of the quantitative IMA analysis is shown in Figure 2.

**Working curves for determining Or and Ab (or An) contents**

The correction factors $f_{Or}$ and $f_{Ab}$ for cryptoperthite, and $f_{Na}$ for peristerite, which are dependent on the average atomic fraction of Al, are determined from the ratios of the corrected and measured ion intensity ratios $(I_{K+/I_{Al}})_{corr}/1.074(I_{K+/I_{Al}})_{obs}$ and $(I_{Na+/I_{Al}})_{corr}/(I_{Na+/I_{Al}})_{obs}$ respectively. These values are listed in Table 2 and plotted against the known bulk Or and Ab (or An) contents in Figures 3 and 4, where Ab (mole percent) = 100 - An - Or in each intergrowth. The equations for the regression lines relating $(I_{K+/I_{Al}})_{corr}$ and $(I_{Na+/I_{Al}})_{corr}$ to Or and Ab (or An) contents, respectively, are given in Tables 3 and 4.

The working curves for estimating the Or and Ab (or An) contents of cryptoperthite and peristerite lamellae show good correlations between the values of Or and Ab (or An) contents as determined by EPMA and the normalized $^{40}K^+$ and $^{23}Na^+$ intensities as measured on standards with the IMA. Thus the composition of exsolution lamellae can be determined from the working curves listed in Table 3.

The results of spot analyses of cryptoperthites and peristerites are plotted in Figure 5 and listed in Table 3.

![Fig. 3. Working curves for mole percent An (in plagioclase) or Ab (in cryptoperthite). Ab(mol.%) = 100 - An - Or. Ratios $I_{Na+/I_{Al}}$ in standard specimens are obtained from EPMA data (cf. Table 1) which are shown by filled circles, and from IMA data (cf. Table 2) shown by open circles. The values of the correction factors $f_{An}$ (or $f_{Ab}$) were arranged to equal unity in one of the standard specimens.](image)

**Table 3. Equations for regression lines relating the observed and corrected ion intensity ratios to An and Or contents in peristerite lamellae**

<table>
<thead>
<tr>
<th>Equation for least-squares regression line</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$An = 49.6 - 49.1 (I_{Na+/I_{Al}})_{corr}$</td>
<td>-0.99</td>
</tr>
<tr>
<td>$(6.1)^a (6.6)$</td>
<td></td>
</tr>
<tr>
<td>$f_{An} = 0.94 (I_{Na+/I_{Al}})_{obs}$</td>
<td>-0.99</td>
</tr>
<tr>
<td>$(0.02) (0.02)$</td>
<td></td>
</tr>
<tr>
<td>$Or = -0.06 + 0.06 I_{Al+/I_{Al}}$</td>
<td>0.99</td>
</tr>
<tr>
<td>$(0.22) (8.4)$</td>
<td></td>
</tr>
<tr>
<td>$f_{Or} = 2.49 - 39.7 (I_{Al+/I_{Al}})_{obs}$</td>
<td>-0.99</td>
</tr>
<tr>
<td>$(0.03) (2.8)$</td>
<td></td>
</tr>
</tbody>
</table>

*The numbers in parentheses below the regression coefficients are estimated standard deviations.*
Table 4. Equations for regression lines relating the observed and corrected ion intensity ratios to Or and Ab contents in cryptoperthite lamellae

<table>
<thead>
<tr>
<th>Equation for least-square regression line</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Or (mol.%)} = 3.0 + 81.0(\text{I}<em>K^{+}/\text{I}</em>{\text{Al}}^{+})$ corr</td>
<td>0.99</td>
</tr>
<tr>
<td>$\text{Ab (mol.%)} = 0.82 + 19.2(\text{I}<em>{\text{Na}}^{+}/\text{I}</em>{\text{Al}}^{+})$ corr</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig. 5. Results of point analysis of two kinds of lamellae in peristerite and cryptoperthite, together with those in labradorite.

Table 5. Results of point analysis in iridescent peristerites from Hybla. The estimated standard deviations are given in parentheses

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Major lamellae</th>
<th>Minor lamellae</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{An (mol.%)}$</td>
<td>$\text{Or (mol.%)}$</td>
</tr>
<tr>
<td>H-1</td>
<td>2.4 (1.9)</td>
<td>1.2 (1.2)</td>
</tr>
<tr>
<td>H-2*</td>
<td>2.5 (1.9)</td>
<td>1.1 (1.1)</td>
</tr>
<tr>
<td>Mean</td>
<td>2.4 (1.9)</td>
<td>1.2 (1.2)</td>
</tr>
</tbody>
</table>

* The composition of H-2 peristerite is An$_7.0^{0.9}$.

The numbers in parentheses below the regression coefficients are estimated standard deviations.

calculated from the IMA data are within 6 or 14 percent of the An content as determined by EPMA for H-1 and H-2 peristerites, respectively; and within 8 or 3 percent in Or content and 1 or 9 percent in Ab content of CC-1 and CJ-1 cryptoperthites, respectively (Table 7).

Discussion

IMA analysis problem

The secondary ion mass spectrum of feldspar is complicated (see Meyer et al., 1974; Shimizu et al., 1978), due to mass overlapping of various ion species at the same nominal mass numbers. The $^{27}\text{Al}^+$ and $^{23}\text{Na}^+$ signals used in this study should be free from overlaps, but Ca and Si ions are overlapped by several complex molecular ions. While there may be minor interference with $^{39}\text{K}^+$, we assumed this to be small or constant, and the consistency of the results vindicates this assumption. Hence only Al, Na, and K ions were used to determine the feldspar compositions.

The distribution of lamellae on the analysis surface can be determined by taking an electron micrograph of replicas of the side faces of a cube-shaped specimen. Depth-profiling ion microprobe analysis of the slightly irregular lamellae of the cryptoperthites...
and peristerites may give an irregularly varying signal, while for the regular lamellae of labradorites a regularly varying signal, which oscillates between two extremes, is obtained. In the latter case the compositions of the two lamellar phases are thus easily measured, and the thicknesses correlated with the electron micrograph data (see Miura and Tomisaka, 1978). In the point analysis approach on the less regular lamellae, there are many data points which reflect overlap of the ion beam on to more than one lamella, or the presence of inclusions. If a large number of measurements is taken at many points, usually selected on a grid pattern, those data showing the extreme compositional values can be selected as being representative of the lamellae, and the remainder discarded.

**Compositions of exsolution lamellae**

The working curve method for determining feldspar compositions by ion probe is a valuable and reliable technique providing certain precautions are observed. Firstly, there must be at least three similar ‘standard’ specimens to establish a linear regression line. Secondly, discontinuities may be expected across a solid-solution series (Steele et al., 1977), which may arise because of varying complex microstructure, structural state, or the presence of inclusions (cf. Miura, 1978a). For this reason the working curves must not be extrapolated beyond the range of the standards used.

The bulk compositions as determined by ion probe (calculated from lamellae data) and electron probe (measured directly) deserve some comment. For specimen H-1 the results agree within the limit of error. For H-2 there is a difference of 1 percent An absolute at a level of 6 percent An, implying perhaps that complete resolution of the two phases was not achieved with the ion probe. This could possibly be due to the presence of smaller lamellae about 30 nm in thickness, or markedly irregular lamellar boundaries (see Miura, 1978b). A further small error may arise if there are substitutions such as Fe³⁺ for Al, or if there are vacancies in the alkali site, but no attempt has been made to allow for this.

Orthoclase contents in cryptoperthites CC-1 and CJ-1 show deviations of 2.5 and 1.3 percent absolute, respectively, when compared with those from EPMA, and the An contents show larger deviations. This may be partly because of the rapid change of the relative lamellar thicknesses in a small region, and partly because of incomplete resolution where the smaller thickness is less than 60 to 70 nm (see Miura, 1978c). Nevertheless, the IMA analyses give sufficiently good agreement that the results may be considered valid.

The data in Table 7 are consistent with the composition of the lamellar pairs being different by at least 17 percent An in H-1 and 21 percent An in H-2. The difference in Or content, however, is at most 1 mole percent in H-1 but greater in H-2, which may be richer in minor lamellae. However, the Or standard deviations do not appear to be related to lamellar

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**Table 7. Calculated bulk compositions from IMA data in Tables 5 and 6, compared with the bulk compositions determined by EPMA listed in Table 1. Equation (2) is used to obtain this comparison between IMA and EPMA data**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>IMA data</th>
<th>E M data</th>
<th>EPMA data</th>
<th>Calculated data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Or (mol.%)</td>
<td>Ab (mol.%)</td>
<td>An (mol.%)</td>
<td>Or (mol.%)</td>
</tr>
<tr>
<td>H-1</td>
<td>1(1)</td>
<td>97(2)</td>
<td>2(2)</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>3(1)</td>
<td>80(2)</td>
<td>19(2)</td>
<td>26</td>
</tr>
<tr>
<td>H-2</td>
<td>1(1)</td>
<td>97(2)</td>
<td>2(2)</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>3(1)</td>
<td>74(2)</td>
<td>23(2)</td>
<td>31</td>
</tr>
<tr>
<td>CC-1</td>
<td>15(8)</td>
<td>66(5)</td>
<td>19(6)</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>51(3)</td>
<td>49(6)</td>
<td>0(0)</td>
<td>38</td>
</tr>
<tr>
<td>CJ-1</td>
<td>35(2)</td>
<td>59(7)</td>
<td>6(4)</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>72(7)</td>
<td>28(5)</td>
<td>0(0)</td>
<td>60</td>
</tr>
</tbody>
</table>

*Another composition of two lamellae in IMA data is listed below. The estimated standard deviations in IMA data are given in parentheses.*
Fig. 6. Schematic diagram of IMA analytical results together with lamellar thicknesses. Bulk compositions for each specimen are shown on the upper surfaces. Labradorite from a previous study (Miura and Tomisaka, 1978) is shown for comparison. The lamellar compositions of the labradorite examples change as a function of bulk composition, rather than from thickness variation in lamellae of constant compositions. The same phenomenon can be seen for peristerite and cryptoperthite. The angle between surface and lamellar boundaries in point analysis is exaggerated.

composition. These data are close to the results of Cliff et al. (1975) obtained from electron microscopy, and of McLaren (1974). The results in this study show that the peristerite region ranges from An<sub>28</sub> to An<sub>31</sub>.

Ion probe analysis of fine feldspar lamellae has the advantage over other methods used previously, in that data for all three components are obtained. This permits examination of the Or content of plagioclase lamellae, and this study has shown that peristerite lamellae vary slightly in this respect. Similarly, Böggild lamellae show variations in Or at the one sigma level (Miura, 1977; Miura and Tomisaka, 1978). Rather than speculate on the precise meaning of these observations, we will merely point out that future discussions on the mechanisms by which plagioclase exsolutions take place should take account of this third component.

In CC-1 the difference in composition (Δ) of the lamellae are ΔOr<sub>36</sub> and ΔAn<sub>19</sub>, and for CJ-1 ΔOr<sub>27</sub> and ΔAn<sub>7</sub>. Cryptoperthite lamellae compositions have been reported by Brown et al. (1974) and by Sipling and Yund (1976), but their data did not include the third An component. Figure 5 shows that this third component is in fact important, particularly in specimen CC-1 where the extension into the ternary system is large. This specimen should perhaps be more correctly assigned the name 'cryptoantiperthite.'

Acknowledgments

We thank Mr. I. Nakamura of the Central Research Laboratory, Hitachi Ltd., for facilities and collaborating in the IMA study, and Professor I. Sunagawa of Tohoku University for his interest in this study. We are also grateful to Drs. D. Stewart and G. Nord, Jr. of the U.S. Geological Survey, Professor R. Yund and Dr. Tullis of Brown University, and Dr. C. Meyer, Jr. of NASA, Houston for discussion. Professors C. Klein and A. E. Bence are thanked for critically reviewing the manuscript. An operating grant (A3549) from the National Sciences and Engineering Research Council of Canada assisted in this work.
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*Manuscript received, February 16, 1979; accepted for publication, June 29, 1979.*