Ti-phlogopites of the Shaw's Cove minette: a comparison with micas of other lamprophyres, potassic rocks, kimberlites, and mantle xenoliths

SHARON W. BACHINSKI AND EVANNA L. SIMPSON
Department of Geology, University of New Brunswick
Fredericton, New Brunswick, E3B 5A3 Canada

Abstract

The two generations of micas in the Shaw’s Cove minette (mica-potash feldspar lamprophyre) of northern New Brunswick, Canada, are TiO₂-rich phlogopites with variable but low silica and potash contents, low soda, and effectively all their aluminum in tetrahedral sites. A majority of the micas have an excess of Y cations and a deficiency of X cations; there are positive correlations between excess Y ions and number of Al ions in Z sites, between K₂O and SiO₂ contents, and between K₂O and volatile-free totals; yet the micas optically appear fresh, do not respond to hydration or glycolation, and X-ray diffraction patterns show none of the peaks of talc, montmorillonites, vermiculite, or 7- or 14-Å chlorites. This suggests that some normally octahedrally coordinated cations and water or hydronium ions are located in the interlayer X sites. Phenocryst micas are sharply zoned. Cores are paler colored and have high mg [atomic ratio Mg/(Mg + Fe²⁺)] (0.81-0.88), Cr₂O₃ (x = 0.88 wt.%), and NiO (x = 0.08 wt.%), but relatively low TiO₂ (x = 2.93 wt.%), and negligible BaO. Phenocryst rims and groundmass micas are darker reddish brown and have lower mg (0.68-0.79), nil Cr₂O₃ and NiO, but high TiO₂ (x = 5.40 wt.%), and BaO (x = 0.38 wt.%). Micas in minettes from other localities (62 analyses) are frequently richer in silica and potash than the Shaw’s Cove samples but otherwise are generally chemically comparable. Chemical zoning or bimodalism is nearly universal in minette micas, though the boundary between high-mg-low-TiO₂ (phenocryst) and low-mg-high-TiO₂ (groundmass) groups varies from province to province and even from minette to minette within a swarm.

Comparison of analyses of minette micas with 353 analyses of micas from other mafic (largely potassic) rocks indicates that micas chemically indistinguishable from those of minettes can be found within some other lamprophyres, (ultra)potassic rocks, kimberlites, and high-pressure xenoliths in alkaline volcanic rocks and kimberlites, though each of these groups also contains micas unlike those in minettes. Those kimberlite phlogopites that match minette micas are predominantly secondary rims of phenocrysts (or megacrysts) or groundmass crystals (mainly “Type II”), but some are unzoned pre-fluidization phenocrysts. While primary, primary-metasomatic, and MARID-suite phlogopites of mantle xenoliths are unlike minette micas (higher mg and SiO₂, lower TiO₂ and Al₂O₃), some of the secondary-metasomatic phlogopites in sheared garnetiferous mantle xenoliths are wholly minettelike.

The chemical identity of minette-mica phenocryst cores and some phenocrysts of diverse mantle-derived rocks implies crystallization under similar conditions. By analogy with the chemistry of phlogopites produced experimentally in potassic systems at high pressures and studies of equilibration conditions of natural phlogopites, it is concluded that phenocrystic phlogopites in minettes may form at temperatures and pressures up to at least ~1250°C and ~40 kbar and probably under fO₂ conditions between the NNO and HM buffers: higher fO₂ than for primary, primary-metasomatic, and MARID-suite micas in kimberlites and their included xenoliths.

Introduction

Magnesium-rich trioctahedral micas are critical phases in most lamprophyres but especially in minettes (biotite–K-feldspar lamprophyres) and kersantites (biotite–plagioclase lamprophyres) in which they are the dominant ferromagnesian mineral. Studies of the mineral chemistry of lamprophyres are relatively few in number; this undoubtedly contributes to the present lack of agreement on their petrogenesis. If minettes are in fact mantle-derived...
(Bachinski and Scott, 1979, 1980), then detailed examination of the chemistry of their micas plus a comparison with the micas of other potassic mantle-derived rocks may yield useful information relating to the distribution and movement of water and large lithophile ions in the subcontinental upper mantle as well as the chemical and/or genetic relationships, if any, between minette magma and other potassic magmas.

Micas of minettes and other lamprophyres are nearly universally zoned discontinuously (see, e.g., Velde, 1969): phenocrysts have lighter-colored cores surrounded by darker rims generally equivalent in color to the groundmass micas. Méliais et al. (1962) were the first to confirm that this color zonation is indeed due to differing chemical composition. They semi-quantitatively demonstrated that in the micas of a minette (and a kersantite) the paler cores are richer in magnesium and chromium and are poorer in iron, titanium, manganese, and cerium than the darker rims. Similar zoning has since been observed in the micas of ultrapotassic rocks and lamproites (e.g., Emeleus and Andrews, 1975; Rich, 1969; Velde, 1969, 1975; Mitchell, 1981), carbonatites (e.g., Heinrich, 1966; Rimsaita, 1969; Gaspar and Wyllie, 1982), kimberlites (e.g., Emeleus and Andrews, 1975; Boettcher et al., 1977, 1979; Smith et al., 1978; Mitchell and Meyer, 1980; Boctor and Boyd, 1982), and ultramafic mantle xenoliths in both basaltic rocks (e.g., Dawson et al., 1970) and kimberlites (e.g., Boettcher et al., 1977, 1979; Rawlinson and Dawson, 1979; Jones et al., 1982).

Phlogopites of the Shaw’s Cove minette

A 15-meter-thick minette sill crops out on the southern shore of the Restigouche River at Shaw’s Cove, west of the town of Dalhousie, in northernmost New Brunswick, Canada, where it has been emplaced along a conglomerate-sandstone bedding plane of the lowermost Middle Devonian Campbellton Formation. On stratigraphic grounds the minette is presumed to be no younger than Late Devonian in age. Within the minette, phenocrysts of sanidine. Accessory phases include apatite, titanomagnetite, Ni metal, Ilm 96189, and Opx R62.

Representative analyses of these titaniferous phlogopites (‘‘titanphlogopites’’ in the terminology recommended by Rock, 1982) are presented in Table 1a. All the micas are trioctahedral and have mg = (atomic ratio Mg/(Mg + Fe3+)) values equal to or greater than 0.68, high titania, low silica, and moderate alumina. Structural formulae calculated on the basis of 22 oxygens (Simpson, 1980) show that the number of Si ions ranges from 4.824 to 5.624 and Al from 2.999 to 2.987 per formula unit. Aluminum is essentially confined to tetrahedrally coordinated, or Z, sites: only three of the 51 micas contain any octahedrally coordinated Al. As Si + Al is less than 8.000 for nearly all the micas, the Z sites must be completed by either titanium or ferric iron. Since the Shaw’s Cove minette contains important amounts of Fe2O3 (Simpson, 1980), it is possible that its micas have a ‘‘tetraferriphlogopite’’ component. However, ferric iron in the Z sites of phlogopites is believed to produce reverse pleochroism (Hogarth et al., 1970; Farmer and Boettcher, 1981) which we did not observe; also, tetraferriphlogopites have only been reported from rocks with very low alumina contents (e.g., Wendlandt, 1977), much lower than those of minettes. Farmer and Boettcher (1981) have suggested that the sequence of tetrahedral site preference in phlogopites is Si > Al > Ti > Fe3+, since all known normal phlogopites have Si + Al + Ti greater than 8 while all known reverse phlogopites have this sum less than 8. The Shaw’s Cove micas all have Si + Al + Ti greater than 8. Therefore conclude that Ti rather than Fe3+ occupies the tetrahedral sites unfilled by Si and Al.

The range of values for any given oxide in the mica analyses is relatively broad but similar to literature values for micas in other minettes (see below). Several points concerning the data, however, warrant special comment.

TiO2, mg, and trace elements

The analytical results for TiO2, MgO, FeO, and the trace elements in the micas are markedly bimodal (Table 1b and Figure 1a,b,c). A plot of wt.% TiO2 against mg defines two chemically distinct groups of micas: Group 1, with high mg, low TiO2, and significant concentrations of Cr and Ni but negligible Ba, and Group 2, with low mg, high TiO2, no Cr or Ni but important amounts of Ba. The micas of Group 2, in fact, are the major carrier of Ba in the minette as the maximum amount of BaO in the feldspar is 0.20 wt.% (Simpson, 1980).

With few exceptions, light-colored phenocryst cores comprise Group 1, darker phenocryst rims and groundmass crystals Group 2. (We did not detect any reversely zoned micas as are occasionally seen in minettes else-
Table 1a. Representative analyses of phlogopites from the Shaw’s Cove minette (oxides in wt.%)

<table>
<thead>
<tr>
<th>Type*</th>
<th>SC25c-9</th>
<th>SC25c-10</th>
<th>SC26-1</th>
<th>SC26-5</th>
<th>SC26-13</th>
<th>SC27b-1</th>
<th>SC27b-12a</th>
<th>SC30-11</th>
<th>SC30-17</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PR</td>
<td>MC</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>PR</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>SiO₂</td>
<td>35.18</td>
<td>38.32</td>
<td>32.13</td>
<td>33.88</td>
<td>35.11</td>
<td>34.30</td>
<td>36.69</td>
<td>34.89</td>
<td>36.19</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.82</td>
<td>3.18</td>
<td>6.39</td>
<td>4.90</td>
<td>5.00</td>
<td>5.01</td>
<td>5.55</td>
<td>6.43</td>
<td>5.76</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.50</td>
<td>0.06</td>
<td>0.19</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>9.93</td>
<td>5.78</td>
<td>11.90</td>
<td>13.39</td>
<td>10.78</td>
<td>10.94</td>
<td>10.41</td>
<td>11.75</td>
<td>11.96</td>
</tr>
<tr>
<td>CaO</td>
<td>20.49</td>
<td>22.77</td>
<td>19.41</td>
<td>16.63</td>
<td>19.74</td>
<td>18.82</td>
<td>17.87</td>
<td>16.58</td>
<td>17.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.23</td>
<td>0.24</td>
<td>0.30</td>
<td>0.20</td>
<td>1.03</td>
<td>0.47</td>
<td>0.51</td>
<td>0.37</td>
<td>0.39</td>
</tr>
<tr>
<td>K₂O</td>
<td>7.02</td>
<td>8.33</td>
<td>3.41</td>
<td>5.82</td>
<td>6.16</td>
<td>5.74</td>
<td>8.70</td>
<td>7.56</td>
<td>7.65</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.00</td>
<td>0.60</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.04</td>
<td>0.16</td>
<td>0.42</td>
<td>0.61</td>
<td>0.65</td>
<td>0.32</td>
<td>0.80</td>
<td>0.25</td>
<td>0.57</td>
</tr>
<tr>
<td>H₂O</td>
<td>79.67</td>
<td>93.69</td>
<td>90.74</td>
<td>89.73</td>
<td>93.48</td>
<td>91.18</td>
<td>94.42</td>
<td>91.95</td>
<td>94.24</td>
</tr>
<tr>
<td>mg</td>
<td>0.79</td>
<td>0.88</td>
<td>0.74</td>
<td>0.69</td>
<td>0.77</td>
<td>0.75</td>
<td>0.75</td>
<td>0.72</td>
<td>0.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type*</th>
<th>SC36-2</th>
<th>SC36-4</th>
<th>SC37-2</th>
<th>SC37-4</th>
<th>SC38-7</th>
<th>SC38-10</th>
<th>SC38-12</th>
<th>SC46-8</th>
<th>SC46-10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC</td>
<td>PR</td>
<td>PC</td>
<td>MC</td>
<td>PC</td>
<td>M</td>
<td>G</td>
<td>MC</td>
<td>PC</td>
</tr>
<tr>
<td>SiO₂</td>
<td>35.56</td>
<td>35.18</td>
<td>36.82</td>
<td>35.12</td>
<td>39.30</td>
<td>36.86</td>
<td>36.14</td>
<td>36.14</td>
<td>36.02</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6.25</td>
<td>5.32</td>
<td>2.95</td>
<td>5.82</td>
<td>3.20</td>
<td>6.21</td>
<td>4.75</td>
<td>2.85</td>
<td>3.07</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.71</td>
<td>15.63</td>
<td>15.09</td>
<td>14.59</td>
<td>14.18</td>
<td>14.57</td>
<td>15.14</td>
<td>15.08</td>
<td>14.77</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>FeO</td>
<td>11.29</td>
<td>13.08</td>
<td>7.87</td>
<td>10.66</td>
<td>5.60</td>
<td>11.22</td>
<td>12.70</td>
<td>7.45</td>
<td>7.11</td>
</tr>
<tr>
<td>CaO</td>
<td>18.12</td>
<td>18.55</td>
<td>22.81</td>
<td>18.10</td>
<td>21.89</td>
<td>17.55</td>
<td>16.44</td>
<td>22.83</td>
<td>22.93</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.10</td>
<td>0.11</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.25</td>
<td>0.39</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.65</td>
<td>0.48</td>
<td>0.41</td>
<td>0.40</td>
<td>0.29</td>
<td>0.62</td>
<td>0.78</td>
<td>0.14</td>
<td>0.29</td>
</tr>
<tr>
<td>MgO</td>
<td>6.20</td>
<td>5.81</td>
<td>5.67</td>
<td>7.62</td>
<td>9.48</td>
<td>8.62</td>
<td>8.28</td>
<td>5.17</td>
<td>6.28</td>
</tr>
<tr>
<td>NiO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.05</td>
<td>0.54</td>
<td>0.00</td>
<td>0.99</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>BaO</td>
<td>0.39</td>
<td>0.52</td>
<td>0.09</td>
<td>0.49</td>
<td>0.00</td>
<td>0.50</td>
<td>0.34</td>
<td>0.00</td>
<td>0.13</td>
</tr>
<tr>
<td>total</td>
<td>93.67</td>
<td>94.33</td>
<td>92.32</td>
<td>92.31</td>
<td>94.95</td>
<td>95.65</td>
<td>94.23</td>
<td>91.89</td>
<td>91.44</td>
</tr>
<tr>
<td>mg</td>
<td>0.74</td>
<td>0.72</td>
<td>0.84</td>
<td>0.75</td>
<td>0.87</td>
<td>0.74</td>
<td>0.70</td>
<td>0.85</td>
<td>0.85</td>
</tr>
</tbody>
</table>

* P = phenocryst, M = microphenocryst, G = groundmass, C = core, R = rim
** P₂O₅ and MgO are below the limits of detection
Table 1b. Chemical characteristics of the two groups of micas in the Shaw’s Cove minette

<table>
<thead>
<tr>
<th>Range</th>
<th>wt.% TiO₂</th>
<th>mg</th>
<th>wt.% Na₂O</th>
<th>wt.% Cr₂O₃</th>
<th>wt.% TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-low TiO₂</td>
<td>2.26-3.20</td>
<td>2.93</td>
<td>0.00-0.28</td>
<td>0.28-1.86</td>
<td>0.00-0.19</td>
</tr>
<tr>
<td>Low-high TiO₂</td>
<td>4.03-7.96</td>
<td>5.40</td>
<td>0.00-0.80</td>
<td>0.00-0.05</td>
<td>0.00-0.05</td>
</tr>
</tbody>
</table>

Overall mean values for K₂O (5.59 wt.%) and SiO₂ (34.18 wt.%) are not balanced by correspondingly higher Na₂O (0.36 wt.%) and Al₂O₃ (15.23 wt.%) and are significantly lower than previously published values for micas in lamprophyres. For analyses of minette micas in the literature of the last two decades for which both potash

K₂O and SiO₂

K₂O and SiO₂ contents of most of the micas, both phenocrysts and groundmass, are lower than normal for phlogopites and are positively correlated. The mean K₂O content of groundmass micas is lower than the mean for phenocrysts, although individual groundmass crystals cover virtually the entire range of K₂O values, from the lowest to the second highest. For a given silica content, the phenocrysts tend to have less K₂O than do ground-

mass micas; such a relationship is displayed by, e.g., Velde’s (1969) analyses of phenocrysts and groundmass micas in a French minette (Table II, anal. 12 &13), but the reverse can also apply in other minettes (cf. anal. 18 & 19 of her Table II).

Fig. 1. Chemistry of phlogopites in the Shaw’s Cove minette. (a) Covariation of mg and wt.% TiO₂. (b) Covariation of mg and wt.% Al₂O₃. (c) Atomic proportions of Ti, Al, and (Mg+Fe²⁺).
and silica values are given, means are 9.2 wt.% and 38.6 wt.% respectively (N = 58); for micas in lamprophyres other than minettes (50 analyses, a little less than half of which are of micas from kersansites) K₂O = 8.4 wt.%, SiO₂ = 36.8 wt.%. Of the Shaw's Cove micas, 71% have K₂O < 7.0 wt.% and 73% have SiO₂ < 36.0 wt.%, while of the 112 literature values for micas in other lamprophyres including minettes, only 8 have less than 7.0 wt.% potash and 21 have less than 36.0 wt.% silica. Thirty of our 51 analyses are of groundmass micas. In distinction, only 10% of the published mica analyses for lamprophyres are microprobe analyses of groundmass crystals. Because of the differing proportions of groundmass mica analyses in our data set and in the lamprophyre literature, it may not be appropriate to compare mean values. It should be noted, though, that 7 of the 8 literature analyses of lamprophyric micas that show K₂O < 7.0 wt.% do not represent microprobe analyses of groundmass micas but are wet analyses of bulk mica samples; low potash values in these samples certainly cannot be attributed to loss of potassium from the sample under the electron beam of the microprobe. Volatilization of potassium during analysis of our micas is unlike since only some micas have low K₂O and identical microprobe conditions prevailed during all mica analyses. Also, under similar conditions there was no loss of sodium, an even more volatile element, from other minerals.

Micas with K₂O < 7.0 wt.% and/or SiO₂ < 36.0 wt.% have been observed in igneous rocks other than lamprophyres, including granitic rocks (e.g., Barrière and Cotton, 1979), leucite-bearing lavas (e.g., Cundari, 1973; Birch, 1978; Thompson, 1978), high-pressure cognate megacrysts (Ellis, 1976), monticellite peridotite and tur-jaite (Wendlandt, 1977), carbonatites (Gaspar and Wyllie, 1978), ultramafic complexes (Skinner, 1969; Grapes, 1975; Donaldson, 1975), and as phencrysts and groundmass phases in kimberlites (e.g., Dawson et al., 1970; Giardini et al., 1974; Mitchell, 1978; Smith et al., 1978; Clement et al., 1979; Boctor and Boyd, 1982), as well as in xenoliths in alkaline basalts (Ryabchikov et al., 1982). Some of these micas are especially rich in TiO₂ or BaO. But the existence in minettes of equally titanium- or barium-rich phlogopites with normal amounts of K₂O and SiO₂ (e.g., Nicholls, 1969) indicates that the enrichment in titanium and barium is not necessarily complemented by an impoverishment in potassium and silicon.

It could be hypothesized that there is either a physical mixture with, layering, or an alteration of our mica to an essentially K₂O-free, more hydrous phyllosilicate. The requirement that the second phase, relative to phlogopite, be poorer in SiO₂, richer in Al₂O₃, and not drastically different in MgO, FeO, CaO, and Na₂O contents and mg ratio eliminates serpentine, talc, and smectites (including saponitic ones) from consideration. Minerals of appropriate composition include chlorites (−clinochlore), sepechlorites (−amesite), and vermiculite; all have been reported as weathering or alteration products of phlogopitic micas elsewhere (Deer et al., 1962, p. 48 & 156; Velde, 1969; McCallum et al., 1975; Mitchell, 1978): for example, Skinner (1969) records that K₂O-poor micas in an ultramafic rock contain up to 15% vermiculite.

Several arguments, however, nullify the proposition that a mixture of phlogopite and some other phyllosilicate exists on anything but a negligible level in the Shaw's Cove micas. First, the micas of this minette microscopically appear fresh and unaltered. Indeed, this is a general characteristic of most micas in lamprophyres (e.g., Velde, 1969). Second, if one uses the analysis of one of our phlogopites whose potash and silica contents correspond to the mean values for these oxides in minettes in general as one end-member and the analysis of a Ti-bearing clinohlore (Deer et al., 1962, Table 25, anal. 28) as the other, approximately 40 wt.% SiO₂ would have to be mixed with the phlogopite in order to produce the mean, not the lowest, potash and silica values of the Shaw's Cove phlogopites! It is inconceivable that such a quantity of chlorite or any similar phase could not be detected optically. Third, X-ray diffraction patterns of Shaw's Cove micas show none of the peaks of either 7-Å or 14-Å chlorites, montmorillonites, talc, or vermiculite; the micas do not respond to either hydration or glycolation. We conclude, therefore, that the low potash and silica contents of many of our micas are real and are not an artifact of analytical technique, alteration, or admixture.

Structural formulæ of our micas indicate that nearly two-thirds of the analyses—including phenocrysts and groundmass crystals—have Y parameters in excess of 6.000, the maximum number of octahedral sites (our highest Y value is 6.949, the mean is 6.220), and there is a strong negative correlation between Y and X site occupancies, the latter of which is always less than 2.000 (0.473 to 1.827; x = 1.261). This suggests that some normally octahedrally-coordinated cations are in the interlayer position. The positive correlation between excess Y ions and the number of tetrahedrally-coordinated aluminum ions provides further support for this and an explanation for the positive correlation between wt.% K₂O and SiO₂: low amounts of silicon require high amounts of tetrahedrally-coordinated aluminum to complete the sheet structure, but this leads to a charge imbalance that may be offset by substitution of divalent cations (e.g., Mg²⁺, Fe²⁺) for K⁺ in the X site. Interestingly, Group I micas (high mg, MgO, and FeO) show a greater number of tetrahedrally-coordinated aluminum ions than do Group 2 micas. Of the potash- and silica-poor mica analyses in the literature, only one a “platy phlogopite replacing hornblende” (Deer et al., 1962, anal. 6), combines the excess of Y cations with the X-site deficiency that characterizes the majority of the Shaw's Cove micas.

However, as even those micas that do not have an excess of Y cations still have less than 2.000 X cations, many of the mica analyses in Table 1a have low totals, and there is a rough positive correlation between wt.% K₂O and volatile-free totals, it is possible that there is
Table 2. Mean composition of micas in minettes, excluding Shaw's Cove micas (N=62)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt.%</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.6</td>
<td>38.4 – 41.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.5</td>
<td>1.4 – 11.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.4</td>
<td>9.7 – 18.0</td>
</tr>
<tr>
<td>FeO</td>
<td>7.9*</td>
<td>4.8 – 13.1*</td>
</tr>
<tr>
<td>Na₂O</td>
<td>9.2</td>
<td>4.4 – 10.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.5</td>
<td>0.0 – 1.1</td>
</tr>
</tbody>
</table>

*M whisked micas from the Pendennis minette (see text)

some water or hydronium ion substitution in the interlayer position.

We believe that these variations in the potash and silica contents of the Shaw's Cove micas are predominantly primary and reflect the relative activities of these and other components that may enter the phlogopite at the time of its crystallization. That the activities can vary widely in minette liquids is illustrated especially well by the groundmass phlogopites for which the availability of components is complicated by the simultaneous crystallization of other groundmass phases.

**Comparison with micas from other minettes**

Ranges and mean values of the important oxides in analyses of 62 micas of minettes in the literature are presented in Table 2 (see Appendix for sources of data) and the covariation of the major atoms that may occur in octahedrally coordinated sites—Mg, Fe, Ti, and Al—is shown in Figure 2a,b,c. Like the Shaw's Cove micas, micas in other minettes are phlogopites of moderate aluminum and high titanium contents but are richer in silica and potash; the lack of a correlation between mg and Al₂O₃ (Fig. 2b) presumably reflects an absence of Al ions in octahedrally-coordinated sites. One of these micas (phenocryst core, mafic minette ring dike, Buell Park, Navajo Indian Reservation, Arizona; Roden and Smith, 1979, Table 3, rock BPR-5) is among the most Ti-rich micas (TiO₂ = 11.3 wt.%) known to us regardless of rock type! This specimen also has the lowest SiO₂ concentration (33.9 wt.%) of any minette mica but has a normal alumina content.

Analyses of five minette micas are chemically identical in all respects to those of Shaw's Cove micas; these micas occur in minettes from southernmost East Germany (Kramer, 1976, Table 8, anal. 152, bulk sample), eastern France (Velde, 1969, Table II, anal. 5, bulk analysis of phenocrysts), southwestern Scotland (Gallagher, 1963, Table II, anal. 2, bulk sample), and the Navajo Indian Reservation of southwestern U.S.A. (Velde, 1969, Table III, anal. 6-A-5, bulk sample; Nicholls, 1969, Table 6, anal. 666-P, microprobe analysis of a phenocryst). Interestingly, the analyses of the German and Scottish specimens, like many of those from Shaw's Cove, have low K₂O and SiO₂ values.

Although color zoning and the associated chemical bimodalism is observed in virtually all those micas analyzed by microprobe, the boundaries of the two chemical groups vary from geographical area to area and even from minette to minette within a swarm. Considering the
entirety of the minette mica analyses, it is not possible to predict whether a given mica sample will have a relatively high or low TiO$_2$ content merely by knowing whether it is a phenocryst core or a groundmass crystal (or phenocryst rim); the same applies to prediction of the mg value. For example, in one minette from the Navajo area a groundmass mica contains 4.84 wt.% TiO$_2$ while a mica phenocryst from another minette in the same volcanic field has 7.69% (Nicholls, 1969, Table 6, anal. 672-GM and 649FP). Nonetheless, for microprobe analyses of single crystals or portions thereof, the following generalizations may be stated: from core to rim to groundmass, mg decreases while TiO$_2$ increases (except in rare cases of reverse zoning of core and rim) and groundmass micas nearly always have mg < 0.80 and TiO$_2$ > 4.00 wt.%.

Sodium, a minor but ever-present constituent of minette micas, is slightly less abundant in the Shaw’s Cove micas than in those of other minettes (X = 0.36 and 0.5 wt.% respectively) though the range of values is nearly identical. The overall mean Na$_2$O content in all minette micas is 0.43 wt.%.

Only rarely have minette micas been analyzed for trace elements. NiO and, in particular, Cr$_2$O$_3$ may reach sizeable concentrations in phenocryst cores while in phenocryst rims and groundmass crystals BaO commonly exceeds 0.1 wt.% and may be more than an order of magnitude greater. Overall means, including Shaw’s Cove analyses, are NiO = 0.02 wt.% (N = 76), Cr$_2$O$_3$ = 0.30 wt.% (N = 82), BaO = 0.48 wt.% (N = 86). We have not analyzed our phlogopites for fluorine, though minette micas are known to contain significant amounts; literature values (Némec, 1968; Nicholls, 1969; Kramer, 1976; Luhr and Carmichael, 1981) have a mean of 1.11 wt.% F (N = 24) and fluorine contents may increase or decrease from phenocryst core to rim to groundmass (see also Jones and Smith, 1982). Luhr and Carmichael (1981) report fluorine contents of ≤1.52 wt.% in phlogopite phenocryst rims, F/(F + OH) = 0.1 – 0.2 for phenocryst phlogopites in general, and 4.85 wt.% F in a groundmass phlogopite in the minettes of Colima, Mexico. Because of the marked variations of all these trace elements (or oxides) between phenocryst cores and rims and groundmass crystals, mean values are of negligible use.

The unusual peralkaline but silica-oversaturated Pendennis minette at Falmouth, Cornwall, England (Hall, 1982) contains titaniferous phlogopites whose iron-rich rims (Table III, anal. 7–12) are unlike micas in all other minettes and all other mafic rocks considered here (see below). We have designated them as “anomalous” because they have lower mg values than “normal” minette micas and Al$_2$O$_3$ contents matching those of the most Al-poor minette micas, but have TiO$_2$ contents that are high but in the minette-mica range (see Fig. 2a,b). For five of these six analyses, mg = 0.48–0.57, Al$_2$O$_3$ = 10.20–11.97 wt.% and TiO$_2$ = 6.36–7.23 wt.%; the sixth (anal. 7); mg = 0.63, Al$_2$O$_3$ = 11.39, TiO$_2$ = 4.57) is transitional to normal minette micas.

Although Hall (1982), Barton (1979), and Arima and Edgar (1981) suggest that the composition, especially the alumina content, of micas in mafic potassic rocks is a reflection of the composition of the magma from which they crystallized, the nature of this relationship is not clear for minettes. For the Pendennis minette, molecular proportions [(K + Na)/Al] = 1.11, mg = 0.64, Al$_2$O$_3$ = 10.4 wt.% (after correcting for CO$_2$); yet a metaluminous and silica-undersaturated minette in the Navajo volcanic field with mg value similar to that of the Pendennis minette (mol. prop. [(K + Na)/Al] = 0.78, mg = 0.67, Al$_2$O$_3$ = 10.7 wt.%; Nicholls, 1969, Table 10, rock 649F) carries groundmass phlogopite with mg = 0.76 and Al$_2$O$_3$ = 10.5 wt.% (op. cit., Table 6)—much higher mg but the same Al$_2$O$_3$ as in the anomalous rims of the Pendennis micas—while the peralkaline but more magnesian Sisco minette of Corsica (mol. prop. [(K + Na)/Al] = 1.04, mg = 0.73, Al$_2$O$_3$ = 12.1 wt.%; Velde, 1965) is host to relatively aluminum-rich phlogopites with high mg values (Al$_2$O$_3$ = 13.8 and 15.0 wt.%, mg = 0.90 and 0.88; Velde, 1969, Table II, anal. 2 & 3). The Holsteinsborg minettes are silica-saturated to –oversaturated but more magnesian and even more Al-poor than the Pendennis minette and are remarkably peralkaline (average mol. prop. [(K + Na)/Al] = 1.39, mg = 0.74, Al$_2$O$_3$ = 7.8 wt.% after correcting for CO$_2$; Scott, 1979, Table 4); their phlogopites have high mg values (0.87 and 0.83) and one of them (op. cit., Table 3, anal. 137) has the lowest Al$_2$O$_3$ (9.70 wt.%) of any minette mica. On the other hand, one of the Colima minettes, which have mg values similar to those of the Holsteinsborg dikes but more Al$_2$O$_3$ and are metaluminous rather than peralkaline (mol. prop. [(K + Na)/Al] = 0.69–0.80, mg = 0.70 – 0.75, Al$_2$O$_3$ = 11.1–12.5 wt.%; Luhr and Carmichael, 1981, Table 3), contains groundmass phlogopite (Al$_2$O$_3$ = 10.8 wt.%, mg = 0.82; op. cit., Table 9, anal. 100B) that has a much higher mg value but Al$_2$O$_3$ as low as that of the anomalous micas in the peralkaline Pendennis minette. Furthermore, as the minette magma evolves and the mica’s mg value decreases from phenocryst core to rim and/or groundmass, the Al$_2$O$_3$ content of the mica may decrease (e.g., Hall, 1982; Roden and Smith, 1979, Table 3, micas in rocks BPR-5 and BP-51; Luhr and Carmichael, 1981, Table 9, micas in rock 104; Nicholls, 1969, Table 6, micas in rocks 672 and 681), stay the same (Nicholls, 1969, Table 6, micas in rock 649F), increase (this work, Table 1, anal. 30-11.17 and 36-2.4; Roden and Smith, 1979, Table 3, micas in rock BP-35), or even first decrease then increase (Nicholls, 1969, Table 6, micas in rock 649C).

Comparison with micas in other igneous rocks

Minette micas are unlike those of common granitoids, their extrusive equivalents, pegmatites, or metamorphic rocks (e.g., Velde, 1969; Kramer, 1976) and none of these rocks is likely to be directly connected to minettes genetically. Although the petrogenesis of lamprophyres
sensu lato is still controversial, recent studies increasingly indicate that the liquids from which minettes and at least some other lamprophyres have crystallized are from the mantle and may be generated by processes, under conditions, and/or from source rocks related (to varying degrees) to those responsible for (ultra)potassic rocks and kimberlites (e.g., Bachinski and Scott, 1979, 1980; Ehrenberg, 1979, 1982; Roden and Smith, 1979; Luhr and Carmichael, 1981; Mitchell, 1981; Paul and Potts, 1981; Roden, 1981; Hall, 1982; Platt and Mitchell, 1982; Rogers et al., 1982). It is therefore of interest to compare the phlogopites of minettes with the micas of these rocks and xenoliths from the mantle and lower crust.

For this comparison 353 mica analyses from rocks other than minettes were collected from the literature of 1966-1982 and a few older papers. Subdivided by rock type into five groups, these analyses include the following: 50 from lamprophyres other than minettes; 68 from a variety of ultramafic to intermediate, intrusive and extrusive, potassic and ultrapotassic rocks (madupites, orenrites, woyomingites, fitzroyites, cedricites, woldingites, jumillites, verites, fortunites, leucitites, shoshonites, jumillites, verites, fortunites, leucitites, shoshonites, shonkinites, biotitites, etc.); 113 from micas of kimberlites; and 122 from high-pressure xenoliths (51 of these are in minettes, nephelinites, basanites, and other alkaline volcanic rocks, while 71 are in kimberlites and diamonds). Combined with the 113 minette phlogopites, including those of Shaw's Cove, 466 mica analyses are considered here.

The analyses are presented in a series of mg vs. wt.% TiO2 diagrams (Figs. 3 to 7) like those used above for the minette micas. On each of the diagrams the superimposed long curved lines indicate the field in which plot micas from all minettes (N = 107) including the Shaw's Cove but excluding the anomalous Pendennis micas of Figures 1a and 2a: the broken line encloses the field containing 93% of the solid line encloses 100% of these; the field of the five anomalous and one transitional Pendennis micas is indicated separately. To be conservative, the following comparisons are presented with reference to the broken lines (main minette mica field) unless explicitly stated otherwise. Diagrams of mg vs. wt.% Al2O3 and atomic proportions of (Mg + Fe2+) Ti-Al were also constructed for all the sets of analyses. Although these latter two sets of figures are not presented here for the sake of economy, when we say below that certain micas fall "within the minette field" or make equivalent statements we are referring to the minette field on all three diagrams. In terms of the four components encompassed by these sets of diagrams as well as wt.% SiO2, K2O, Na2O, and trace element concentrations, it is important to note that none of the five groups of micas is wholly distinct from minette micas. (Considering the errors associated with analyzing for Na2O by electron microprobe, especially when it is present in such minimal amounts as in phlogopites, differences in Na2O contents may not be significant). It must be stressed, though, that each of the five groups of rocks also contains micas that differ from those of minettes and/or have differing trends of compositional evolution (see also Mitchell, 1981, and Arima and Edgar, 1982).

**Lamprophyres other than minettes (Fig. 3)**

The micas of other lamprophyres tend to have lower mg values, the same or slightly lower TiO2, the same Na2O (although micas of kersantites as a distinct subgroup have slightly higher), and somewhat higher Al2O3. Of those analyses (26) that plot within the minette field on all three diagrams, about half are of micas from kersantites (Métais, et al., 1962, Table 2, anal. 1; Velde, 1969, Table 4, anal. 4, 7, 8, 9, 12, 15; Strong and Harris, 1974, Table 2, anal. 3; Kramer, 1976, Table 8, anal. 205, 217, 271). The others are from monchiquites and camptonites (Nicholls, 1969, Table 6, anal. 618-P; McHone, 1978, Table III-4, anal. BU-1, BU-2; Rock, 1978, Table 9, anal. 2; Cooper, 1979, Table 1, anal. LG-core and O-core); kersantites (monchiquite?); (Griffin and Taylor, 1975, Table 3, anal. 7), three un-named lamprophyres (Rimsaite, 1971, Table 1, anal. 8-PH, 9-PH; Janse, 1977, Table 1, anal. 4), and Precambrian alnöitic ultrabasic lamprophyres (Platt and Mitchell, 1982, Table 3, anal. 1, 2, 3, 6).

Approximately half of these minette-like micas have the low SiO2 and K2O contents commonly seen in minette micas. Three minette-like micas, however, do not truly match minette micas if Na2O and trace element contents are taken into consideration: the two camptonite specimens from New Zealand (Cooper, 1979) contain significantly more Na2O than any minette mica while the mica of the biotite monchiquite from Arizona (Nicholls, 1969) has a BaO content (6.20 wt.%) over twice as great as the

---

2 For convenience this group will be referred to hereinafter as "potassic rocks".
maximum reported for a mica from a minette. The highest value known to us is 10.3 wt. % BaO in the core of a phlogopite from the Jacupiranga carbonatite's sôvite facies; Gaspar and Wyllie, 1982).

Potassic rocks (Fig. 4)
Because of the diversity of this group of rocks, general comparisons between their micas and those of minettes are not possible; instead reference must be made to subgroups. Two of these, biotites (2 analyses; Boettcher, 1967, Table 3) and shonkinites (5 analyses; Nash and Wilkinson, 1970, Table 5; Langworthy and Black, 1978, Table 1) carry micas that are not at all like those of minettes. The micas of the other subgroups are minette-like to varying degrees. Of the 13 mica analyses that fall within the minette field, one shows higher BaO than the phlogopites of minettes and another higher Na2O.

Ultrapotassic rocks (lamproites) (40 analyses). The micas of ultrapotassic volcanic rocks or lamproites are of particular interest because these rocks are geochemically much like minettes (e.g., Carmichael et al., 1974; Mitchell, 1981). The micas of two of the ultrapotassic lavas of southeastern Spain (verite and fortuneite; Velde, 1969, Table 3, anal. 12-A-5 and 14-A-7) are identical to minette micas, but the jumillite micas (Borley, 1967, Table II; Carmichael, 1967, Table 6), although as rich in TiO2 as the most titaniferous minette micas, are Al-deficient. In contrast, the micas from the famous Leucite Hills, Wyoming (U.S.A.) locality (Cross, 1897; Carmichael, 1967, Table 6; see also Barton, 1979) are wholly distinct from minette micas though similar in Na2O and trace element contents: orendite and wyomingite micas have higher mg values and lower TiO2 while the madupite mica has lower Al2O3. In the equally famous West Kimberley province of Australia (Carmichael, 1967, Table 6; Mitchell, 1981) the micas are very TiO2-rich, have higher mg values than most minette micas of equivalent TiO2 content, and plot within or above the borders of the minette field of Figure 4; they all, however, have Al2O3 contents lower than or equal to the most Al-poor minette micas, and trace elements in the same concentrations as in minette micas. (Nearly three-quarters of the analyses of micas from ultrapotassic rocks plotted on Fig. 4 are from West Kimberley).

The chemistry of the lamproites at Smoky Butte, Montana (U.S.A.) is similar to that of the Australian West Kimberley rocks (Velde, 1975). A bulk analysis of Smoky Butte phlogopites from a “Type III” lamproite (op. cit., Table 3) is identical to analyses of high-TiO2 minette micas. The other two analyses are of a core and rim of extremely Ti-rich (TiO2 = 11.3 and 11.1 wt.%) phlogopite; the rim is poorer in Al2O3 (8.9 wt.%) and the core has a higher mg value (0.86) than equally titaniferous minette micas. None of these micas was analyzed for trace elements. A lamproite (called a “potash trachyte” by Nicholls, 1969, rock 643) in the Navajo area of Arizona is probably an extrusive felsic minette, so it was predictable that its phlogopite phenocryst would be identical to minette micas in all respects.

Shoshonites (2 analyses). Micas from two shoshonitic volcanic rocks (latites) are minette-like though one of them has higher Na2O than minette micas; trace element data are not given (Joplin et al., 1972, Table V).

Leucite-bearing lavas (7 analyses). All but one of these micas are rich in TiO2. Five of the 7 differ considerably from the micas of minettes (Cundari, 1973, Table V, anal. BQ-PEGM and BEH-B; Birch, 1978, Table 5; Thompson, 1978, Table 2, anal. 5), but the other two (Cundari, 1973, anal. BEH-A and CND-6) are identical to high-TiO2 minette micas and both have Na2O and trace element concentrations within the minette-mica range.

Other potassic rocks (12 analyses). Three of the six analyzed phlogopites from Precambrian hypabyssal potassic ultramafic rocks (phlogopite pyroxenites and phlogopite peridotites) in the Gardar province of south Greenland (Upton and Thomas, 1973, Table 3, anal. 1, 2, 6) match high-TiO2 minette micas in their major and minor oxides and Cr2O3 and BaO contents (there are no analyses for Na2O). The remaining three phlogopites are minette-like in all respects save that they are impoverished in FeO and consequently have marginally higher mg values (0.90 and 0.91) than minette micas of equivalent TiO2 content. Upton and Thomas believe that these rocks—which in their trace element chemistry are reminiscent of ultrapotassic rocks, minettes, and kimberlites—crystallized from magmas formed by the fractionation of olivine from kimberlitic liquids.

One of the three analyses of barian phlogopites in monticellite peridotites and turjaites at Haystack Butte, in the potassic Highwood Mountains province of Montana (Wendlandt, 1977, Table 25) plots within the minette field but contains far too much BaO (3.91 wt.%) to be minette-like; the other two micas are unlike minette micas.

**Fig. 4.** Covariation of mg and wt. % TiO2 in micas of ultramafic to intermediate potassic and ultrapotassic igneous rocks other than kimberlites and lamprophyres and xenoliths therein; see Appendix for sources of data. Curved lines indicate extent of minette-mica field as explained in caption to Fig. 3 and text.
Lastly, three representative analyses of phlogopite megacrysts (phenocrysts) from an alnditic breccia in the Solomon Islands (Dawson et al., 1978, Table 2, anal. 1, 2, 3) are chemically indistinguishable from phlogopites in minettes on the basis of all oxides for which data are presented, though their analysis #1 plots right on the border of the minette field of Figure 4.

** Kimberlites (Fig. 5) **

Generally, kimberlite phlogopites have higher mg values and SiO₂, lower TiO₂, and similar or lower Al₂O₃ contents than minette micas and many plot outside the minette field, some even off the range of the diagrams. Strictly minette-like micas, however, occur in kimberlites from Somerset Island, Northwest Territories, Canada (Clarke and Mitchell, 1975, Table 1, anal. 5; Mitchell, 1978, Table 3, anal. 2; Mitchell, 1979, Table 3, anal. 2, 3, 4, 5); Ontario, Canada (Rimsaita, 1971, Table 1, anal. 11-PH, and Table 2, anal. II, III; Smith, et al., 1978, Table 3, anal. 5, and Table 4, anal. 8a to 8f); Arkansas, U.S.A. (Giardini et al., 1974, Table 1, brown mica from light green kimberlite); western Greenland (Emeleus and Andrews, 1975, Table 2, anal. 39651/M12; Scott, 1979, Table 3, anal. 129); and various localities in South Africa (Smith, et al., 1978, Table 3, anal. 6b, 7c, and Table 4, anal. 5b, 6b, 7c, 10f, and Table 5, anal. 1b, 4a; Boettcher et al., 1977, and 1979, Table 1, anal. KB-5-1-A-rim, KB-5-1-B-rim, KB-5-1-C, KB-5-13-rim; Clement et al., 1979, Table 3, anal. 7; Doctor and Boyd, 1982, Table 2, anal. 4). Nearly all the kimberlites containing minette-like mica are micaceous kimberlites or, in the terminology recommended by Skinner and Clement (1979), phlogopite kimberlites.

Groundmass crystals (including both “Type I” and “Type II” of Smith et al., 1978) and secondary rims of large phlogopites account for approximately three-quarters of the minette-like micas in kimberlites, but unzoned pre-fluidization phenocrysts (or megacrysts) of the Canadian Arctic’s kimberlites (Clarke and Mitchell, 1975, loc. cit; Mitchell, 1978, loc. cit; Mitchell, 1979, loc. cit.) and one from the South African DeBeers pipe (Boettcher et al., 1979, Table 1, anal. Kb-5-1-C) also plot within the minette field. It would appear that the micas being sought by Smith et al., (1978, p. 970) and Mitchell (1979, p. 165) that are chemically comparable to their kimberlite micas are to be found in minettes.

** Xenoliths in alkaline rocks (Fig. 6) **

Most of the 51 micas in this category have mg values lower than or in the same range as minette micas (five have higher); all the other oxides of importance are within the minette range with the exception of TiO₂ in six megacrysts from Mongolian alkaline basalts (Ryabchikov et al., 1982): these micas have 9.0-12.2 wt.% TiO₂ and are the most Ti-rich micas known to us from any rock type anywhere. Micas matching those in minettes are found in peridotite and pyroxenite xenoliths in alkaline lavas or pyroclastic rocks from southwest Uganda (Lloyd and Bailey, 1975, Table 2, anal. S23-214, S23-209), Victoria, Australia (Ellis, 1976, Table 3, anal. 7), the West Eifel area of West Germany (Aoki and Kushiro, 1968, Table 4, anal. 2; Becker, 1977, Table 3, anal. GM29, GM17, ME11), Paramore Crater, Arizona, U.S.A. (Evans and Nash, 1979, Table 4, anal. PC76-2), and the Lashaine Volcano, Tanzania (Dawson et al., 1970, Table 7, anal. 2).

Twelve of 19 analyses of phlogopites from garnet lherzolite and megacrystalline nodules in minette plugs or diatremes in the Navajo field of northwestern Arizona and contiguous parts of New Mexico, U.S.A. (Ehrenberg, 1979, Table 3, anal. 144TH, 175TH; Ehrenberg, 1982, Table 8, anal. YAT8, 710, 171, 174, X078-1, X078-2, B712, F077, 249, R078) are wholly minette-like. The other seven phlogopites narrowly miss being minette-like by having mg values marginally higher than those of minette micas of equivalent TiO₂ and Al₂O₃ contents (two have less titania than any minette mica).
Of all the micas in xenoliths in alkaline rocks, the phlogopites in the xenoliths in minettes, on average, have simultaneously the lowest TiO$_2$ and Al$_2$O$_3$ contents and highest mg values (in this latter respect they are virtually the “least evolved” micas in this group). When compared to the micas in kimberlites (previous section) the micas in xenoliths in minettes are seen to be identical to many Type II-groundmass micas (Smith et al., 1978, Table 4) and secondary rims on phenocrysts or megacrysts (e.g., Boettcher et al., 1979, Table 1, anal. Kb-5-1-rim and Kb-5-13-rim). They also are comparable to many of the phlogopites occurring in peridotite xenoliths in kimberlites (next section).

Xenoliths in kimberlites (Fig. 7)

Three of these analyses are of micas included in diamonds (Giardini et al., 1974; Prinz et al., 1975; Gurney et al., 1979) and are dissimilar to analyses of minette micas.

Most of the micas in high-pressure xenoliths in kimberlites are wholly distinct from minette micas: they have lower TiO$_2$ and Al$_2$O$_3$, higher SiO$_2$, and higher mg values. These chemical characteristics are typical of “primary” phlogopites (e.g., Carswell, 1975, Table 1) and phlogopites in the MARID suite (Aoki, 1974, Table 1; Dawson and Smith, 1977, Table 2). Some micas in xenoliths in kimberlites, however, are identical to minette micas in all respects. These minette-like phlogopites are predominately described as being of “secondary” mantle origin (“secondary-textured”) and commonly occur as rims on earlier phlogopites or other minerals in eclogites or deformed (sheared) garnet peridotites. One of these micas occurs in a xenolith included in the Peuyuk kimberlite of Somerset Island, Canada (Clarke and Mitchell, 1975, Table 1, anal. 6), the others are in xenoliths in South African kimberlites (Boettcher et al., 1979, Table 1, anal. Kb-8-8-rim, Kb-9-9-A-rim, Kb-9-9-B-rim, B-16-7; Danchin, 1979, Table 2, anal. RVD-152, RVD-501; Rawlinson and Dawson, 1979, Table 6, anal. BD2027-core; Jones et al., 1982, Table 5, anal. 10c, 11a, 12a, 12b).

An additional two micas, one in an eclogite nodule (Aoki and Kushiro, 1968, Table 4, anal. 4) and one forming a secondary rim on an earlier phlogopite in a peridotite xenolith (Boettcher et al., 1979, Table 1, anal. Kb-5-10-rim), qualify as minette-like on Figure 7 and the mg vs. wt.% Al$_2$O$_3$ diagram but fall just outside the lower-left boundary of the minette field of the atomic (Mg+Fe$^{2+}$)-Ti-Al triangular diagram.

Three minette-like micas are found not in clearly mantle-derived xenoliths but in two lower-crustal garnet granulites and a garnet websterite in kimberlites in northeastern Lesotho where they appear to be in equilibrium with the anhydrous phases in the xenoliths (Griffin et al., 1979, Table 4, anal. K3, LQ1, L2T). A mica from a garnet websterite xenolith from the Monastery Mine, South Africa (loc. cit., anal. PHN2630/1) plots in the field of the anomalous micas of the Pendennis minette and matches these micas in all respects save that it has an elevated Al$_2$O$_3$ content.

Discussion

As micas whose compositions are essentially identical may have formed under similar physical and/or chemical conditions, it is of petrogenetic significance that minette micas match many micas in the diverse groups of mantle-derived rocks discussed above; the chemical identity is yet another piece of evidence that the liquids from which minettes crystallize are themselves mantle-derived. Those minette mica analyses that are clearly identifiable as representing the cores of phenocrysts have TiO$_2$ concentrations of 2.0–11.3 wt.% and mg values of 0.74 to 0.90. We assume that these cores crystallized at elevated subcrustal pressures.

High-pressure experiments of, e.g., Edgar et al., (1976, 1980), Ruddock and Hamilton (1978, and pers. comm., 1978) Ryabchikov and Green (1978), and Barton and Hamilton (1982) have demonstrated that phlogopites are liquidus or early-crystallizing phases in a variety of potassic hydrous ± carbonate-bearing systems (including a model minette) at pressures of 10–35 kbar, temperatures of 1150–1300°C, $f_0_2$ between the NNO and HM buffers, and molar CO$_2/$(CO$_2$+H$_2$O) ratios of 0.00 to 0.50. Phlogopites produced in these studies have mg values of 0.82–0.90 and TiO$_2$ contents of 1.8 to 8.1 wt.% (the phlogopite with the highest titania content was produced under conditions of T = 1300°C, P = 30 kbar, 2.4 wt.% H$_2$O and 5.9 wt.% CO$_2$, CO$_2/$(CO$_2$+H$_2$O) = 0.50). Some of the primary (as opposed to quench) phlogopites crystallized by Edgar et al., (1976, Tables 3 & 5; 1980, Table 8) and Ryabchikov and Green (1978, Table 3) are chemically

---

3 It should be noted, however, that MARID micas cannot be separated from minette micas on the NiO vs. mg or Cr$_2$O$_3$ vs. FeO$_7$ diagrams used by Dawson and Smith (1977, Fig. 6).
identical to cores of minette-mica phenocrysts (as well as other minette micas). In attempting to ascertain the conditions under which minette micas may have crystallized in the light of these experimental studies, the main difficulty lies in separating the effects of temperature, pressure, \( f_{O_2} \), and fluid and liquid compositions. These studies demonstrate that, under mantle conditions, phlogopite crystallizes early only from \( H_2O \)-rich, \( CO_2 \)-poor systems and the \( TiO_2 \) content of the phlogopite increases with increasing \( f_{O_2} \) (Fe\(^{+3} \) content of melt), decreasing pressure, \(^4\) decreasing water content of the system, and decreasing mg value of the crystals and liquid; increasing \( CO_2 \) content of the system lowers the temperature at which phlogopites crystallize. The consensus is that temperature and, perhaps more importantly, \( f_{O_2} \) are the major controls on \( TiO_2 \) content (see also Arima and Edgar, 1981). It therefore would appear that minette micas, which are notably rich in \( TiO_2 \) as well as some of the micas in certain other lamprophyres, potassic rocks, kimberlites (phenocryst rims and groundmass, largely), and high-pressure xenoliths in alkaline volcanic rocks, and “secondary metasomatic” micas—crystallized under higher \( f_{O_2} \) conditions and/or higher temperatures than most “primary,” “primary metasomatic,” and “mari-
suite micas in kimberlites and xenoliths in kimberlites.

Luhr and Carmichael (1981) report equilibration temperatures (based on the partitioning of oxygen isotopes between olivine, pyroxene, and magma) of 1070° to 1200°C and \( f_{O_2} \) values (calculated) between the NNO and HM oxygen buffers for petrographically pristine late-Quaternary minette lavas intimately associated spatially and (probably genetically) with leucite basanites in western Mexico. These values of temperature and \( f_{O_2} \), are in agreement with those under which phlogopite was crystallized in the high-pressure experiments.

Garnet peridotite xenoliths in the Navajo minettes called The Thumb and Ship Rock equilibrated at depths of ~110 km and at temperatures ranging from 950° to 1230°C (Ehrenberg, 1979, 1982), nearly the same conditions (\( T \approx 1150°C, P \approx 42 \) kbar) obtained by Mercier (1976) for a diopside xenocryst in the Ship Rock minette. It is improbable that the Navajo minette mafmas formed at shallower depths than the xenoliths they bear. As the xenoliths contain phlogopites that are chemically identical or very similar to minette micas, it is clear that, irrespective of whether there has been interaction between the xenoliths and minette magma, such micas can form in the upper mantle at temperatures as great as 1250°C and pressures of 40 kbar or more, conditions essentially equivalent to those under which ultrapotassic rocks and kimberlites originate.

The chemical identity of minette micas and many of the “secondary metasomatic” micas of kimberlites and mantle xenoliths indicates that metasomatism and consequent mantle heterogeneity are important factors in the origin of both minettes and kimberlites (but see Wyllie and Sekine, 1982, for an alternative explanation). On the basis of a large number of experimental and theoretical studies in recent years on peridotite–\( H_2O-\)CO\(_2 \) systems, it appears that source-rock composition—as influenced by metasomatism, partial melting, and reaction between liquids and solids—as well as the absolute and relative abundances of \( H_2O, CO_2 \), and halogens at the time of magma generation are decisive factors in determining whether the magma produced from a K-rich mantle source will be minette-like, kimberlitic, or ultrapotassic (see, e.g., Ryabchikov and Green, 1978; Baldridge et al., 1981; Luhr and Carmichael, 1981).

The inter- and intra-grain chemical variations seen in minette micas are probably due to small-scale magmatic heterogeneities produced by mixing of batches of magma of similar but differing composition, as suggested by Smith et al., (1978) and Mitchell and Meyer (1980), as well as high- and low-pressure evolution of minette magma.

**Acknowledgments**

We would like to thank D. B. Clarke and R. M. MacKay of Dalhousie University for assistance in the use of the electron microprobe facilities. J. W. Nicholls, University of Calgary, kindly sent us corrected versions of the tables from his Ph.D. dissertation for which we are grateful. A. D. Edgar, University of Western Ontario, is thanked for supplying us with an English translation of Ryabchikov and Green (1978). We are grateful for the helpful comments of R. H. Mitchell in his review of the manuscript. This work was supported in part by grants from the Natural Science and Engineering Research Council of Canada to S. W. B.

**References**


Barrière, M. and Cotten, J. (1979) Biotites and associated minerals as markers of magmatic fractionation and deuteric
equilibration in granites. Contributions to Mineralogy and Petrology, 70, 183–192.


American Geophysical Union, Washington, D.C.


Griffin, W. L. and Taylor, P. N. (1975) The Fln damkjernee: petrology of a “central complex kimberlitie”. Physics and...
BACHINSKI AND SIMPSON: Ti-PHLOGOPITES OF THE SHAW’S COVE MINETTE

Chemistry of the Earth, 9, 163–177.


mond: Their Geology, Petrology and Geochemistry, p. 161–171. American Geophysical Union, Washington, D.C.


Appendix—Source papers for mica analyses

(Full references are given only for those publications not cited in the list of references or earlier in this appendix. Sources are listed in alphabetical order within rock-type subdivisions).


Scott, 1979; Smith et al., 1978;