

Petrologic and crystal-chemical significance of some deep-seated phlogopites¹

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Abstract

Phlogopites with reverse pleochroism ($\alpha > \gamma \approx \beta$), but with rims of phlogopite with normal pleochroism ($\alpha < \gamma \approx \beta$), from South African kimberlites and associated ultramafic xenoliths were studied to assess their geochemical and petrologic significance. Reverse-phlogopite megacrysts and reverse phlogopites in peridotites are poorer in TiO_2 , Al_2O_3 , and Cr_2O_3 and richer in SiO_2 , MgO , and FeO^* than their rims of normal phlogopite, a difference we ascribe to as metasomatism and/or mantling of the reverse phlogopite by kimberlite. All reverse-core phlogopites have similar compositions and represent grains that crystallized *in situ* in mantle peridotite, the megacrysts being derived from disaggregated reverse-phlogopite-bearing peridotite. These reverse micas are higher in FeO^* and lower in Al_2O_3 and Cr_2O_3 than any previously described "primary" mantle phlogopites.

Optical-absorption spectra suggest that tetrahedrally coordinated Fe^{3+} , $\text{IV}(\text{Fe}^{3+})$, controls the phlogopite pleochroism, with reverse cores containing $\text{IV}(\text{Fe}^{3+})$, whereas the normal rims do not. If a preference of $\text{Si} > \text{Al} > \text{Fe}^{3+}$ is assumed for tetrahedral sites, then the type of pleochroism is best correlated with overall differences in the availability of $\text{Si} + \text{Al}$ in kimberlite and peridotite, rather than to differences in $\mu_{\text{Fe}^{3+}}$ between the two environments. However, some normal rims have tetrahedral-site deficiencies similar to those of the reverse cores, $8 - \text{Si} + \text{Al} = 0.1$ to 0.5 , but on the basis of their pleochroism do not contain $\text{IV}(\text{Fe}^{3+})$. All known reverse phlogopites contain $\text{Si} + \text{Al} + \text{Ti} < 8$, whereas normal phlogopites have $\text{Si} + \text{Al} + \text{Ti} > 8$. This correlation suggests that the sequence of tetrahedral site preference in phlogopites is $\text{Si} > \text{Al} > \text{Ti} > \text{Fe}^{3+}$. That is, normal phlogopites with $\text{Si} + \text{Al} < 8$ have normal pleochroism because Ti (as Ti^{4+} ?) substitutes preferentially to Fe^{3+} in tetrahedral sites. Therefore, an additional requirement for the incorporation of $\text{IV}(\text{Fe}^{3+})$ in phlogopite and the development of reverse pleochroism may be that $\text{Si} + \text{Al} + \text{Ti}$ be insufficient to fill the phlogopite tetrahedra.

Introduction

Phlogopite is a common constituent of many kimberlites and associated ultramafic xenoliths, and it is of considerable petrologic and geochemical interest. For example, the suggestion that some phlogopites in peridotite xenoliths represent primary phases that formed *in situ* in the upper mantle (Carswell, 1975; Dawson and Smith, 1975; Delaney

et al., 1980) not only has implications regarding the abundance and distribution of the volatile elements in the mantle (K, H_2O , F, Cl, etc.), but it has also led to speculation regarding the role phlogopite might play in the generation of primary alkalic magmas (Boettcher and O'Neil, 1980; Bravo and O'Hara, 1975; Modreski and Boettcher, 1972; 1973). Studies of the compositions of a wide variety of phlogopites interpreted to have formed directly from kimberlite magma have provided information regarding the physicochemical conditions of the

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crystallization of kimberlite (Smith *et al.*, 1978; Gittins *et al.* 1975).

One relatively overlooked property of the phlogopites in these rocks is the range of pleochroism that they display. In general, the phlogopites show either normal pleochroism ($\alpha < \gamma \approx \beta$) or reverse pleochroism ($\alpha > \gamma \approx \beta$), as recognized nearly 70 years ago by Wagner (1914). Grains with reverse pleochroism are characterized, in plane-polarized light vibrating parallel to α (*i.e.*, $\vec{E} \parallel \alpha$), by a red-brown color that has been attributed to optical absorption by tetrahedrally coordinated Fe^{3+} (Faye and Hogarth, 1968). Grains with normal pleochroism lack this red-brown color, and presumably also lack tetrahedral Fe^{3+} (hereafter denoted as $\text{IV}(\text{Fe}^{3+})$). In kimberlites and associated ultramafic xenoliths, the occurrence of phlogopites with different pleochroic schemes may reflect differences in the chemical potential (μ) of Fe^{3+} between individual grains, which, in turn, may reflect differences in the conditions under which the various phlogopites formed. For example, phlogopites may have formed in environments with different $\mu_{\text{Fe}^{3+}}$, resulting either from variations in f_{O_2} or variations in $\mu_{\text{Fe}^{3+}}$ with pressure (as suggested by Mysen and Virgo, 1978). Variations in the physical conditions of crystallization of the phlogopites could also influence the partitioning of Fe^{3+} between tetrahedral and octahedral sites and thereby influence the phlogopite pleochroism, independent of differences in the $\mu_{\text{Fe}^{3+}}$ of the surroundings. Other possibilities are imaginable, but it is clear that an understanding of the cause(s) of pleochroic shifts in phlogopite could yield important information regarding physico-chemical conditions in the mantle and in kimberlite magma.

The overall purpose of this study was to explore the possible geochemical and petrologic significance of pleochroism and phlogopite in a suite of South African kimberlites and associated ultramafic xenoliths. However, recent studies have revealed a wide variety of phlogopite types in kimberlites and xenoliths from South African localities, not all of whose origins are completely clear (see Delaney *et al.*, 1980, for review). In the samples studied here, however, many of the phlogopites are megacrysts in kimberlite and grains in peridotite xenoliths that consist of cores with reverse pleochroism and rims with normal pleochroism (*cf.* Boettcher and O'Neil, 1980). In these grains, the sequence in which phlogopite appeared during the formation of the kimberlites (reverse followed by normal phlogopite) seems

clear. For this reason, reverse core-normal rim phlogopites were chosen to study in detail. The purpose was to characterize the compositions and petrologic relationship between these two phlogopite types, and to use this information, along with optical absorption data regarding the nature of the light-absorbing constituents and the phlogopites, to assess the significance of the core of rim change in the phlogopite pleochroism.

Textural relationships of phlogopites

Megacryst phlogopites

Boettcher and O'Neil (1980) give localities and descriptions of all of the South African kimberlite and xenolith samples used in this study. In these samples, phlogopite occurs mainly as megacrysts in kimberlite matrix and as primary-looking euhedra in peridotite xenoliths. The megacrysts range from 0.1 mm to 1.0 mm in width; many are rounded and show evidence of partial resorption. None of the kimberlites contain fine-grained euhedral phlogopites that could be classed as matrix grains (Smith *et al.*, 1978), which, presumably, formed from the kimberlite at some late stage of crystallization. The rounding of megacrysts may result from reaction with the kimberlite magma or physical abrasion during emplacement of the kimberlite. Our studies suggest that these phlogopites are xenocrysts, being derived from disaggregated peridotite, as will be discussed later.

Parts of all the phlogopite megacrysts show reverse pleochroism, characterized by the following pleochroic formula: α = light to medium red-brown, $\gamma \approx \beta$ = light pink, light green, light brown. The red-brown color with $\vec{E} \parallel \alpha$ varies in intensity from grain to grain, but within any individual reverse grain there is little or no variation in hue or intensity. In contrast, the $\vec{E} \perp \alpha$ colors of the reverse grains are more varied, and often individual grains show alternating bands (parallel to cleavage) of light pink and light green. Curiously, microprobe line scans across the pink/green banding do not show any measurable change in composition. Either very small compositional changes lead to the $\vec{E} \perp \alpha$ color changes, or other factors, perhaps involving cation ordering, influence the observed colors of phlogopite. Although many of the phlogopite megacrysts show only reverse pleochroism, others are rimmed (or mantled) by phlogopite with normal pleochroism (α = colorless, $\gamma \approx \beta$ = yellow, pink, light green (Fig. 1)). The main difference between the pleochro-

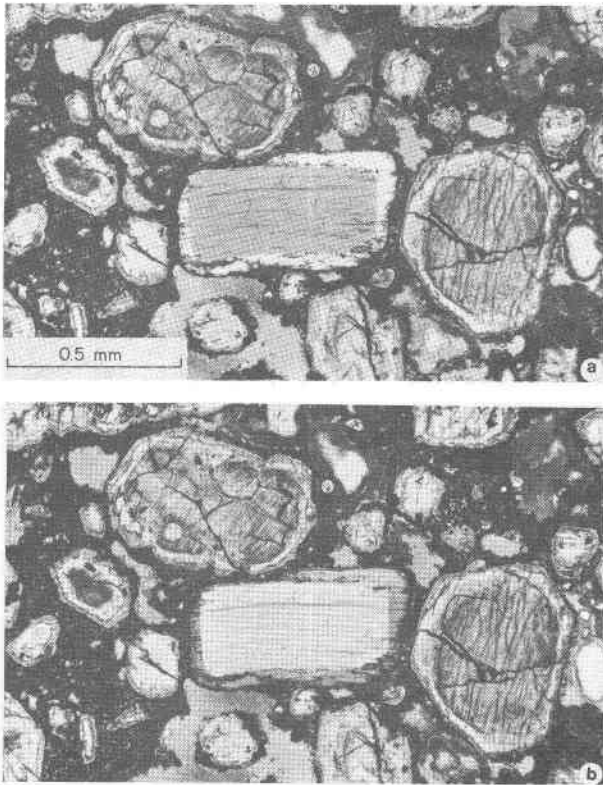


Fig. 1. Phlogopite megacryst (Kb 5-1a) with reverse core and normal rim in plane polarized light. (a) $\vec{E} \parallel \alpha$; (b) $\vec{E} \perp \alpha$, \vec{E} is polarization direction. Surrounding material consists mainly of kimberlite matrix and serpentinized olivines.

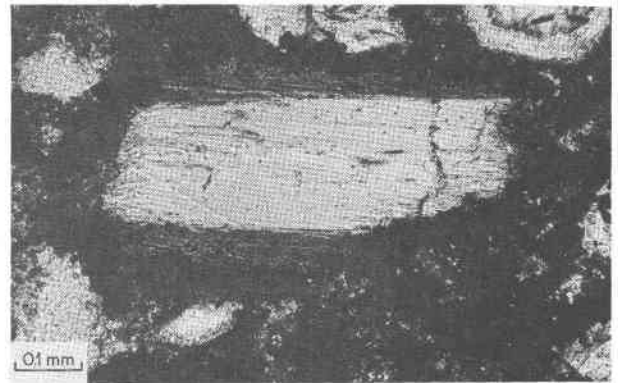


Fig. 2. Phlogopite megacryst (Kb 5-1a) showing partial resorption of reverse core and normal rim.

equilibrium with (but perhaps later than) the other peridotite mineral phases.

Phlogopite with normal pleochroism also rims the reverse phlogopite in the peridotite xenoliths. However, compared to the rims on the megacrysts, these rims are very irregular and form preferentially where a grain intersects one of the many veins that dissect all of the xenoliths (Fig. 4a). Normal phlogopite, with high relief and a blocky texture (Fig. 4b), also forms along cracks that cut the reverse grains. In addition, wisps of remnant phlogopite with reverse pleochroism occur within the normal areas of several of the peridotite phlogopites. All these features suggest that the rims of normal phlogopite on reverse phlogopite in peridotite xenoliths represent an alteration of the latter grains by the material passing through the veins. It is important to note that such obviously secondary features are not associated with the normal rims on the megacryst phlogopites.

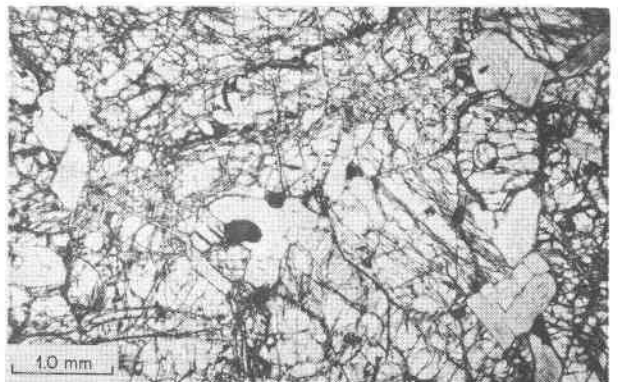


Fig. 3. Peridotite xenolith (Kb-1a) containing primary-textured phlogopite with reverse pleochroism.

ism of the cores and rims is that the latter do not, in general, absorb light in the $\vec{E} \parallel \alpha$ position. The rims themselves are not always continuous, commonly being more extensively developed parallel to cleavage planes. The boundary between core and rim is even, and the rims are fairly regular in thickness (0.05 to 0.1 mm), comprising up to one-third of the grain volume. The margins of the rims are commonly rounded, occasionally resorbed (Fig. 2), indicating that the rims formed before the emplacement of the kimberlites at crustal levels.

Xenolith phlogopites

Phlogopites from the peridotite xenoliths also display reverse pleochroism and show the same range of pleochroism as the reverse megacrysts. The peridotite phlogopites are generally somewhat larger than the megacrysts, averaging about 1 mm in diameter (Fig. 3). The grains are subhedral to euhedral and display 120 degree grain boundary angles. These textural features suggest that the phlogopites grew *in situ* in the upper mantle, in

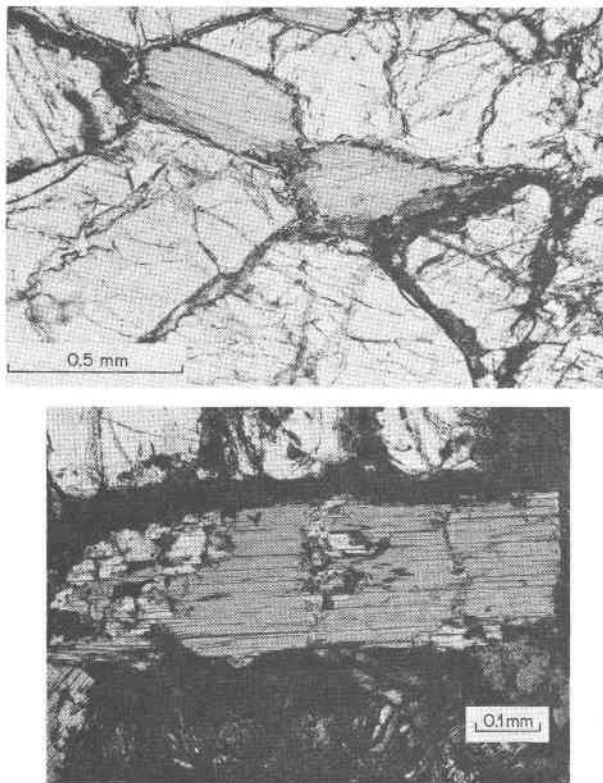


Fig. 4. Alteration of reverse phlogopites in peridotite xenoliths. (a) Irregular rims of normal phlogopite (darker areas on bottom margin of two reverse phlogopite grains) form at or near intersection of phlogopite with veins that pass between olivine grains (Kb 9-5). (b) Formation of normal phlogopite (light patches) along cracks within reverse phlogopite grains (Kb 9-16).

Composition of phlogopites

Microprobe determinations of the compositions of the two types of phlogopite shed additional light on the petrologic relationship between the phlogopite cores and rims. Analyses were made with the automated UCLA ARL-EMX electron microprobe with natural and synthetic mineral standards. Accuracy of the results (1–2% for major elements) was monitored via repeated analyses of a biotite control sample [sample RCsp-55 from Boettcher (1967)]. Instrument operating conditions were generally 15kV with an 18nA sample current. Analyses were corrected using methods of Bence and Albee (1968) and Albee and Ray (1970). Figure 5 shows that all the phlogopites with reverse pleochroism, whether in peridotite or kimberlite, plot together in a well-defined compositional range. Therefore, the chemical data suggest that at least the cores of the megacrysts were derived from disaggregated peridotite that originally contained phlogopite with re-

verse pleochroism. In addition, microprobe line scans (Fig. 6) reveal little or no compositional variation even within individual reverse phlogopite grains. Clearly the reverse phlogopites must have equilibrated under very uniform physical conditions, such as could be expected in the mantle. Therefore, both the textural and chemical evidence suggest that these reverse phlogopites are “primary” peridotite phases. The term “primary” is used to indicate that the reverse micas formed under mantle conditions before being brought to the surface by the kimberlite. All or most micas in the mantle may be manifestations of metasomatic events that introduced alkalis, volatiles, and other components (Boettcher and O’Neil, 1980). It should be noted that the reverse phlogopites are of a different composition than the reverse phlogopites that rim normal phlogopites in kimberlite matrixes (Fig. 5, Table 1). These reverse-rim phlogopites are much higher in FeO* and lower in Al₂O₃ than the reverse cores phlogopites, indicating that reverse pleochroism can occur in a variety of phlogopite compositions, and under a variety of conditions.

The reverse phlogopites in peridotites are also chemically different from other “primary” peridotite phlogopites, as defined by Carswell (1975) and Dawson and Smith (1975); the two types are compared in Table 1. Note that the peridotite phlogopites described here are much lower in Cr₂O₃ than the minimum value (0.5%) defined by Dawson and Smith (1975) for primary peridotite phlogopites, as shown in Figure 7. Such high Cr₂O₃ phlogopites (as in sample number 1141A, supplied courtesy of J. B. Dawson) display normal pleochroism characterized by α = colorless and $\gamma = \beta$ = light brown. Therefore, the two phlogopite types differ not only in composition but in pleochroism as well. We wish to emphasize that the *reverse* peridotite phlogopites represent mantle-derived micas discreetly different from the “primary” peridotite phlogopites described by others. The occurrence of reverse phlogopites in peridotite xenoliths in East Greenland kimberlites (Emeleus and Andrews, 1975) suggests that the formation of such phlogopites may be a wide-spread phenomenon in the upper mantle. Also note from Table 1 that the reverse phlogopites in peridotites are similar in composition to the MARID phlogopites described by Dawson and Smith (1977). The latter phlogopites may represent reverse megacrysts originally derived from peridotite.

As is apparent in Figure 6, the areas of normal pleochroism in any grain, including megacrysts, are

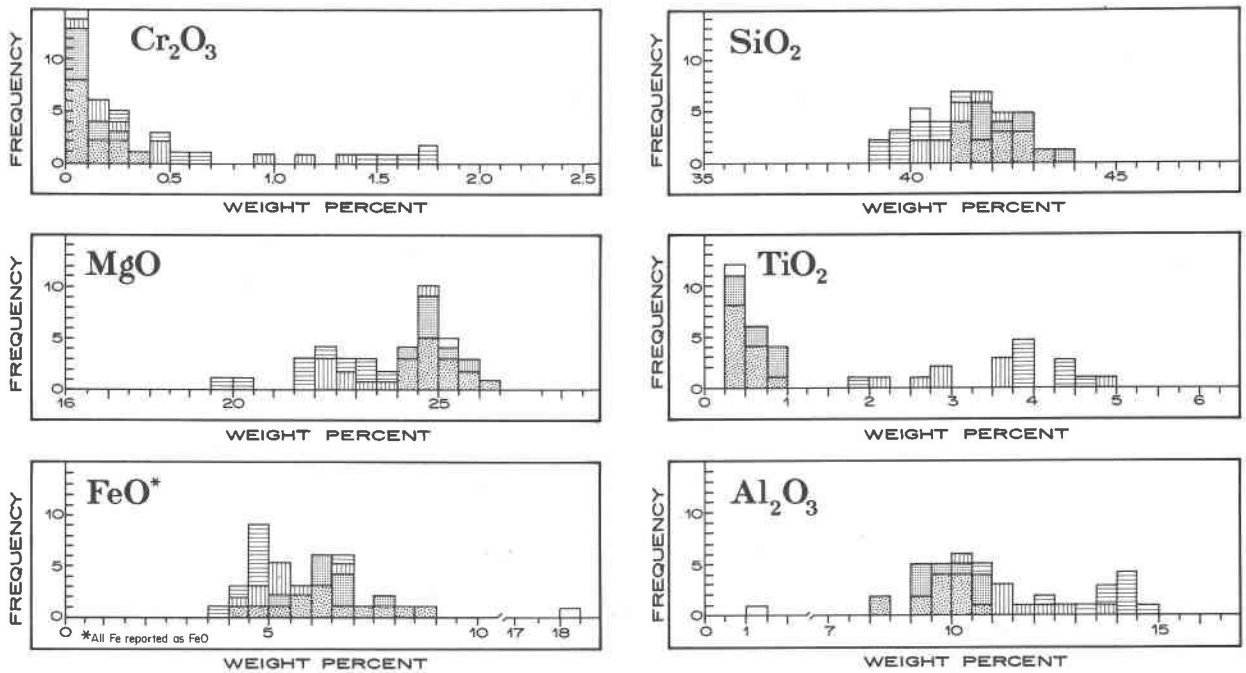


Fig. 5. Histograms of phlogopite compositions. Fine stipple indicates reverse-core megacrysts in kimberlite; course stipple indicates reverse-core grains in peridotite; horizontal lines indicate normal rims on reverse mica megacrysts; vertical lines indicate normal rims on reverse micas in peridotite; blank indicates rim on normal mica matrix grain in kimberlite. Data from this study and Boettcher and O'Neil (1980).

demarcated by sharp chemical as well as optical boundaries. Therefore, all normal-rim phlogopites are considered to be secondary with respect to the reverse cores. Every normal rim is richer in TiO_2 , Cr_2O_3 , and Al_2O_3 and poorer in MgO and SiO_2 than the host reverse core (Boettcher and O'Neil, 1980), although as a group, the normal rims range widely in composition (Fig. 5). However, the range of compositions of the rims is approximately the same in kimberlite and peridotite grains, possibly indicating a similar secondary origin for all the rims. One

obvious source of the secondary material is the kimberlite, in which the xenoliths and megacrysts were immersed. The compositional difference between cores and rims is similar to that between average garnet lherzolite and kimberlite matrix (Dawson, 1967, *i.e.*, higher TiO_2 , Cr_2O_3 , Al_2O_3 and lower MgO and SiO_2 in the latter). This observation may indicate that 1) the main factor controlling the composition of phlogopites is the overall chemical composition of the crystallizing environment, and 2) that the reverse phlogopites did form in peridotite, whereas the normal rims formed as a result of interaction between pre-existing mantle phlogopite and kimberlite magma.

Table 1. Mean compositions of reverse and normal phlogopites and of selected other phlogopite types

	1a	1b	2a	2b	3	4	5
SiO_2	42.1±0.7	42.4±0.7	41.1±0.7	40.2±0.6	42.2	42.2±0.6	41.3
Al_2O_3	9.7±0.8	10.1±0.7	11.8±1.1	13.6±1.3	1.4	10.2±0.8	12.6
TiO_2	0.5±0.2	0.6±0.2	3.3±0.8	3.9±0.8	0.4	1.3±0.5	0.32
Cr_2O_3	0.2±0.2	0.2±0.1	0.3±0.4	1.2±0.6	0.1	0.2±0.1	0.70
FeO^*	6.5±1.4	6.5±0.8	5.4±0.9	4.8±0.7	18.3	6.4±1.1	2.77
MgO	25.0±0.5	25.1±0.6	23.1±0.9	22.1±1.3	25.0	24.0±1.2	26.8
NiO	n.d.	n.d.	n.d.	n.d.	n.d.	0.14±0.05	n.d.
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	0.03±0.02	0.02
CaO	0.1±0.2	0.1±0.1	0.1±0.1	0.1±0.1	0.2	0.02±0.02	0.02
Na_2O	0.2±0.2	0.2±0.2	0.3±0.1	0.2±0.1	0.1	0.12±0.07	0.74
K_2O	10.2±0.5	10.6±0.5	10.0±0.5	10.3±0.6	9.3	10.4±0.3	9.35
TOTAL	94.5	95.8	95.6	96.4	95.1	95.0	94.4

1a - mean ± 1σ of 13 reverse phlogopites in peridotite; 1b - mean ± 1σ of 8 reverse phlogopite megacrysts; 2a - mean ± 1σ of 9 normal rim phlogopites in peridotite; 2b - mean ± 1σ of 10 normal rim phlogopites or megacrysts; 3 - mean of 2 reverse rim phlogopites, Bachelor Lake kimberlite, Quebec (sample courtesy K. D. Watson; see also Watson 1967, 1978); 4 - mean ± 1σ of MARID phlogopites, Dawson and Smith (1977); 5 - mean of high Cr_2O_3 primary peridotite phlogopite, Carswell (1975).

The timing of any such interaction between kimberlite and peridotite material remains unclear. The rounding and resorption of the normal rims on the megacrysts indicate that the rims existed before the kimberlite reached crustal levels, but the regularity in size and shape of the rims of the xenocrysts, compared to their counterparts in the peridotite grains, suggests that the rims formed by interaction with kimberlite after incorporation into the melt, rather than in the constrained space of the peridotite. Rather than being alteration zones, as in the peridotite phlogopites, these normal rims may

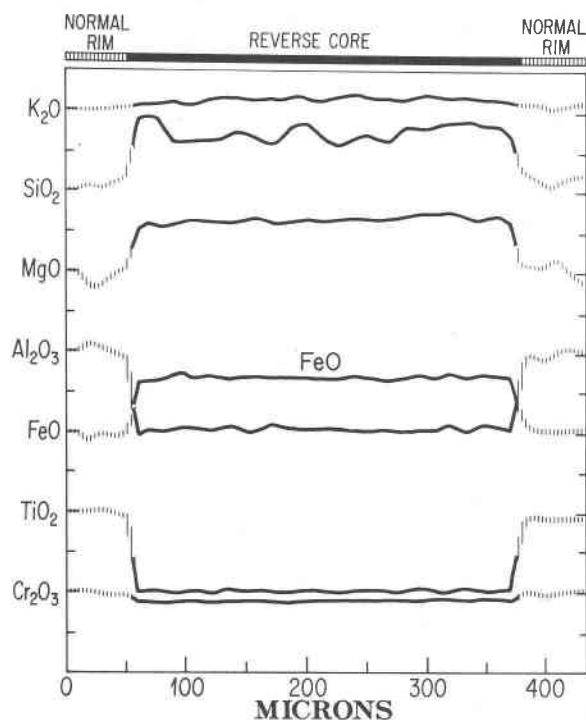


Fig. 6. Line scans across rimmed phlogopite Kb-1a. Changes in the absolute wt.% of each oxide are represented by the tick marks on the ordinate, each of which represents 2 wt.% for any oxide. For example, TiO_2 ranges from 4.4 wt.% at the left grain margin to about 0.3% in the reverse core, a decrease of about 4% TiO_2 from rim to core. The order of oxides on the ordinate is arbitrary. Data are from microprobe determinations at 10- μm intervals across the grain. Compositional changes across the boundary between core and rim occur over an interval of < 10 μm .

actually be overgrowths that grew directly from the kimberlite melt. This could account for the lack of remnant reverse phlogopite wisps in the xenocryst rims. The significant compositional variation in the rims, particularly evident in Figure 7, may reflect changes in the composition of the kimberlite during crystallization, with rim formation occurring over a relatively long time. Similar variations in the compositions of kimberlite phenocryst and matrix phlogopites have been reported by Gittens *et al.* (1975) and Elthon and Ridley (1979).

Origin of pleochroic variations

Polarized absorption spectra were obtained to assess the change in pleochroism from core to rim in terms of specific light absorbing species. Analyses were run at the Caltech facilities (courtesy G. R. Rossman) on Cary 17-1 Spectrometer using a KLC polarizer. Representative spectra for a reverse core

and a normal rim phlogopite are shown in Figure 8, along with microprobe analyses of these grains. The grains were mounted on standard polished microprobe thin-sections, but the resulting spectra suffered from 1) the small size of the normal rims, leading to a high noise-to-signal ratio, particularly at longer wavelengths (the spectra presented here have been hand-smoothed) and 2) imperfect optical orientation of the grains. In addition, the thickness of individual grains could not be measured accurately, making it impossible to assess possible intrinsic changes in the intensity of particular absorption features between individual grains. Therefore, the spectra provide only qualitative information regarding the absorbing species in the phlogopites. Nevertheless, the $\vec{E} \parallel \alpha$ spectrum obtained for the reverse core grain (Kb5-14) is essentially identical to that of a reverse "carbonatitic" phlogopite (Faye and Hogarth, 1968). The main absorption features are several sharp bands centered at 19,000, 20,300 and 22,700 cm^{-1} , superimposed on the low energy wing of an intense absorption band centered in the ultra-violet (u.v.) range. These absorption features result in the red-brown color of the reverse phlogopites. Faye and Hogarth (1968) interpreted the sharp peaks as spin-forbidden d-d transitions of tetrahedrally coordinated Fe^{3+} , with the broad background absorption resulting from a $\text{Fe}^{3+} - \text{O}^{2-}$ charge transfer. Regardless of the exact absorption involved, there seems little doubt that the red-brown color, and therefore the $\vec{E} \parallel \alpha$ visible absorption features, result from tetrahedral Fe^{3+} . Synthetic tetraferriphlogopites produced in our laboratory (Robert Luth, personal communication, 1980) have

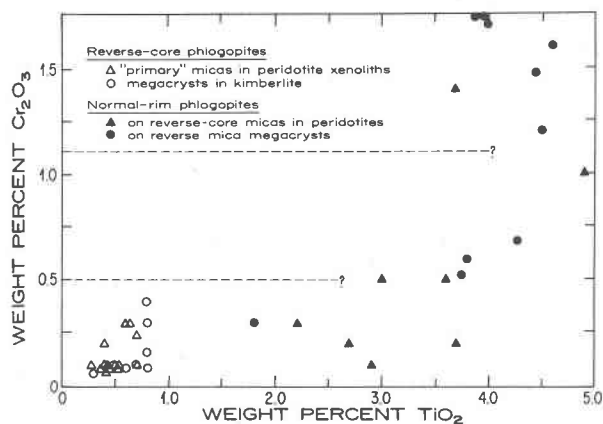


Fig. 7. Cr_2O_3 vs. TiO_2 for phlogopites. Dashed lines bound region defined by Carswell (1975) and Dawson and Smith (1975) for "primary" peridotite phlogopites.

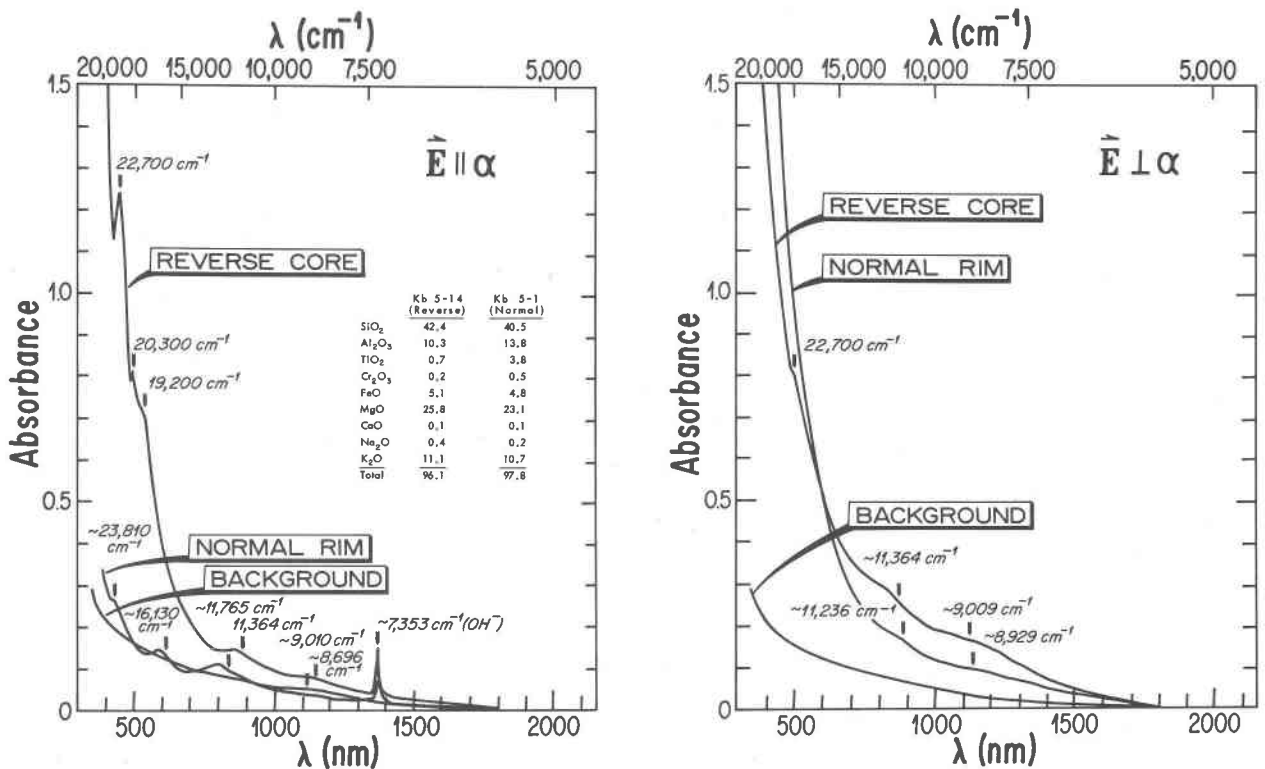


Fig. 8. Polarized optical-absorption spectra for reverse-core (Kb 5-14) and normal-rim (Kb 5-1) phlogopites. (a) shows $\vec{E} \parallel \alpha$; (b) $\vec{E} \perp \alpha$ spectra. Compositional data given in Fig. a.

reverse pleochroism, and only those synthetic micas reported by Hazen and Wones (1972, Table 5) that contain tetrahedral Fe^{3+} are characterized by $\alpha = \text{red-brown}$.

The $\vec{E} \parallel \alpha$ spectrum of the normal-rim phlogopite (Fig. 8a, Kb5-1) clearly lacks those peaks attributed to tetrahedral Fe^{3+} . In particular, there is no intense charge-transfer absorption in the visible (accounting for the $\alpha = \text{colorless}$ in rims). The peaks at wavelengths $>14,300 \text{ cm}^{-1}$ could result from octahedrally coordinated Fe^{3+} or Ti^{3+} , whereas the peaks at wavelengths $<14,300 \text{ cm}^{-1}$ may involve octahedral Fe^{2+} (Robbins and Strens (1972); Kliem and Lehmann 1979; Burns, 1970). Note that the $\vec{E} \perp \alpha$ spectra (Fig. 8b) for reverse and normal grains are similar and are characterized by another broad background absorption centered in the u.v. ($\text{Fe}_{\text{oct}}^{2+} \text{O}^{2-}$ or $\text{Fe}_{\text{oct}}^{3+} \text{O}^{2-}$ charge transfers) with low-energy bands similar to the $\vec{E} \parallel \alpha$ spectra.

The variations in the Fe^{3+} content of the tetrahedral sites that appear to control the phlogopite pleochroism seem to be most easily correlated with the Si + Al content of the micas. As shown in Figure 9, all the reverse phlogopites have Si + Al

less than the ideal value of 8 (Deer *et al.*, 1965), calculated on the basis of 22 oxygens, leading to apparent tetrahedral site deficiencies ($\Delta T = 8 - \text{Si} + \text{Al}$) of 0.05 to 0.45. Assuming a site preference in the phlogopite tetrahedral of $\text{Si} > \text{Al} > \text{Fe}^{3+}$, a deficiency in Si + Al could have allowed the incorporation of $\text{IV}(\text{Fe}^{3+})$. Most normal rims have Si + Al of about 8, or greater, suggesting that the kimberlite contained sufficient Si and Al to fill the tetrahedral sites and to exclude $\text{IV}(\text{Fe}^{3+})$.

Wet-chemical analyses (Table 2) further suggests that the Fe^{3+} content of the reverse phlogopites may approximate, on an atomic basis, the ΔT of the grains, and they reveal that even small proportions of $\text{IV}(\text{Fe}^{3+})$ can create reverse phlogopites (*e.g.*, Kb 9-1). Therefore, it seems possible to use the pleochroism of a phlogopite as a sensitive indicator of $\text{IV}(\text{Fe}^{3+})$. On this basis, we conclude that peridotite phlogopites with normal pleochroism ($\alpha = \text{colorless}$) do not contain $\text{IV}(\text{Fe}^{3+})$, a conclusion supported by a Si + Al of ~ 8 for these grains. Apparently the normal phlogopites crystallized in a mantle environment with sufficient Si + Al to fill tetrahedral sites, whereas the reverse peridotite

Table 2. Chemical analyses of individual reverse phlogopites*

	Kb 9-4	Kb 9-1
SiO ₂	41.7	42.3
Al ₂ O ₃	8.2	10.3
TiO ₂	0.4	0.8
Cr ₂ O ₃	0.2	0.6
Fe ₂ O ₃	4.71	0.66
FeO	4.68	2.85
MgO	24.5	25.0
CaO	0.2	0.1
Na ₂ O	0.2	0.1
K ₂ O	10.2	9.9
TOTAL	94.99	92.41
Atoms per 22 oxygens		
Si	6.06	6.15
Al	1.40	1.76
Fe ³⁺	0.52	0.07
Ti	0.04	0.09
Cr	0.02	0.05
Fe ²⁺	0.57	0.35
Mg	5.31	5.41
Ca	0.03	0.02
Na	0.06	0.03
K	1.89	1.83
TOTAL	15.90	15.76

*Fe²⁺ and Fe³⁺ analyzed via wet chemical methods by J. B. Bodkin; all other elements are microprobe analyses.

phlogopites did not. However, the reverse peridotite phlogopites have a much higher total Fe content than the normal grains, so that variations in the $\mu_{\text{Fe}^{3+}}$ may have existed between the crystallizing environments of these two phlogopite types and influenced the proportion of $\text{IV}(\text{Fe}^{3+})$, regardless of the availability of Si + Al.

Although the normal phlogopite rims do cluster about the Si + Al = 8 line in Figure 9, several rims have Si + Al values significantly less than 8 (7.70–7.90). Either the apparent $\Delta T > 0$ in these rims is an artifact of the analyses or the calculation of the structural formulas, or cations other than Fe^{3+} are filling the tetrahedral sites. The latter case implies that these cations substituted in favor of Fe^{3+} in the tetrahedral sites (assuming there was sufficient Fe^{3+} in the kimberlite to at least partially fill any deficiencies developing in the rims). Ti^{4+} has been suggested as a possible tetrahedral-site cation in silicate minerals (Hartman, 1969), and there has been recent evidence for such a substitution in Ti-rich garnets (Huggins, 1977; Oba and Kawachi, 1981). Interestingly, all published analyses of reverse phlogopites have insufficient Ti to fill the tetrahedral site deficiencies ($\text{Ti} < \Delta T$), whereas all normal phlogopites have $\text{Ti} \geq \Delta T$ (Fig. 9). This relationship suggests that Ti influences phlogopite pleochroism, perhaps by substituting in favor of Fe^{3+} in tetrahedral sites. However, if $\text{IV}(\text{Ti}^{4+})$ does exist, it may be asked why a $\text{Ti}^{4+}\text{-O}^{2-}$ charge

transfer is not observed in normal rims with the tetrahedral-site deficiencies. But as Faye (1968b) points out, pure TiO_2 , is often white, suggesting that such a charge transfer may not always occur.

Phlogopites studied by Edgar (1979) from a Ugandan biotite mafurite also are in accord with our proposed relationship between Ti and pleochroism. The groundmass phlogopites in a sample provided by A. Edgar (Bm 1942) have a high atomic Ti (~ 0.4), but with $\text{Ti} < \Delta T$ ($\Delta T \approx 1.2$). These grains show reverse pleochroism. Phenocryst phlogopites in the same sample have $\Delta T = 0.3$, $\text{Ti} = 0.9$ ($\text{Ti} > \Delta T$), and normal pleochroism. Therefore, it is possible to predict the pleochroism of phlogopite on the basis of Si, Al, and Ti abundances alone. Additional data are needed, particularly to evaluate the effect of $\text{Ti}^{4+}/\text{Ti}^{3+}$ and $\mu_{\text{Fe}^{3+}}$ variations on the cation-site occupancy and resulting pleochroism of phlogopite.

Conclusions

We conclude that reverse core and normal rim phlogopites represent crystallization in two entirely different chemical environments, the former in peridotite and the latter in kimberlite. The phlogopite pleochroism is itself controlled by $\text{IV}(\text{Fe}^{3+})$. However, if the abundance of Si + Al controls the number of tetrahedral vacancies available for filling by Fe^{3+} , then the difference in pleochroism between phlogopite cores and rims is best correlated with differences in Si + Al in their respective crystallizing environments. Differences in the $\mu_{\text{Fe}^{3+}}$ between the peridotite and kimberlite could have

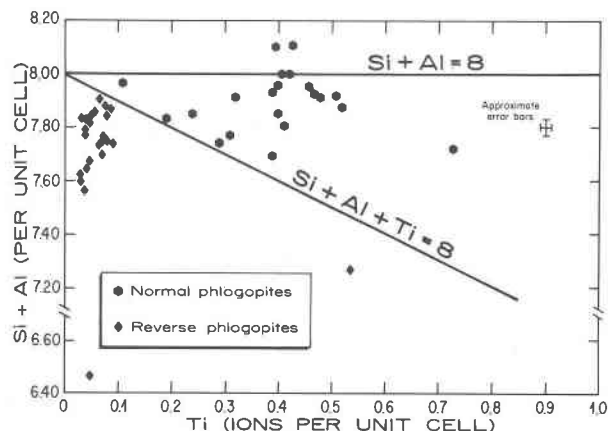


Fig. 9. Si + Al vs. Ti for normal and reverse phlogopites. Data from this study, Boettcher and O'Neil (1980), Dawson and Smith (1975), and Edgar (1979). Error bars (1σ) refer to analyses from this study only. Errors were from replicate analyses of same reverse phlogopite grain (Kb 5-1) at regular intervals during study period.

existed, but need not be invoked to explain the observed change in pleochroism. However, it appears that Ti (tetravalent?) may indirectly influence the pleochroism of phlogopite by substituting into tetrahedral sites in preference to Fe^{3+} . As a result, the pleochroism of the phlogopites may have been controlled by the available Si + Al + Ti, rather than by Si + Al alone.

Phlogopites with reverse pleochroism occur in rocks other than kimberlites and mantle xenoliths (Boettcher, 1967; Rims kaya-Korsakova and Sokolova, 1964). Continued research on these micas will provide useful petrogenetic information.

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References

- Albee, A. L. and Ray, L. (1970) Correction factors for electron probe microanalysis of silicates, carbonates, phosphates and sulfates. *Analytical Chemistry*, 42, 1408-1414.
- Bence, A. E. and Albee, A. L. (1968) Empirical correction factors for the electron microprobe analysis of silicates and oxides. *Journal of Geology*, 76, 382-403.
- Boettcher, A. L. (1967) The Rainy Creek alkaline-ultramafic igneous complex near Libby, Montana. I: Ultramafic rocks and fennites. *Journal of Geology*, 75, 526-553.
- Boettcher, A. L. and O'Neil, J. R. (1980) Stable isotope, chemical, and petrographic studies of high-pressure amphibole and micas: evidence for metasomatism in the mantle source regions of alkali basalts and kimberlites. *American Journal of Science*, 280-A, Part II, 594-621.
- Bravo, M. S. and O'Hara, M. J. (1975) Partial melting of phlogopite-bearing synthetic spinel- and garnet-lherzolites. In L. H. Aherns *et al.*, Eds., *Physics and Chemistry of the Earth*, Vol. 9, p. 910-944. Pergamon Press, New York.
- Burns, R. G. (1970) *Mineralogical Applications of Crystal Field Theory*. Cambridge Univ. Press, Cambridge.
- Carswell, D. A. (1975) Primary and secondary phlogopites and clinopyroxene in garnet lherzolite xenoliths. In L. H. Aherns *et al.*, Eds., *Physics and Chemistry of the Earth*, Vol. 9, p. 417-435. Pergamon Press, New York.
- Dawson, J. B. (1967) Geochemistry and origin of kimberlite. In P. J. Wyllie, Ed., *Ultramafic and Related Rocks*, p. 269-278. Wiley, New York.
- Dawson, J. B. and Smith, J. V. (1975) Chemistry and origin of phlogopite megacrysts in kimberlite. *Nature*, 253, 336-338.
- Dawson, J. B. and Smith, J. V. (1977) The MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths in kimberlite. *Geochimica Cosmochimica Acta*, 41, 309-323.
- Deer, W. A., Howie, R. A. and Zussman, J. (1966) *An Introduction to the Rock Forming Minerals*. Longman Group Limited, London.
- Delaney, J. S., Smith, J. V., Carswell, D. A. and Dawson, J. B. (1980) Chemistry of micas from kimberlites and xenoliths—II. Primary- and secondary-textured micas from peridotite xenoliths. *Geochimica Cosmochimica Acta*, 44, 857-872.
- Edgar, A. D. (1979) Mineral chemistry and petrogenesis of an ultrapotassic-ultramafic volcanic rock. *Contributions to Mineralogy and Petrology*, 71, 171-175.
- Elthon, D. and Ridley, W. I. (1979) The oxide and silicate mineral chemistry of a kimberlite from the Premier mine: Implications for the evolution of kimberlitic magmas. In F. R. Boyd and H. O. A. Meyer, Eds., *Kimberlites Diatremes and Diamonds: Their Geology, Petrology and Geochemistry*, p. 206-216. American Geophysical Union.
- Emeleus, C. H. and Andrews, J. R. (1975) Mineralogy and petrology of kimberlite dyke and sheet intrusions and included peridotite xenoliths from south-west Greenland. In L. H. Aherns *et al.*, Eds., *Physics and Chemistry of the Earth*, Vol. 9, p. 179-197. Pergamon Press, New York.
- Faye, G. M. (1967) The optical absorption spectra of certain transition metal ions in muscovite, lepidolite, and fuchite. *Canadian Journal of Earth Science*, 5, 31-38.
- Faye, G. M. and Hogarth, D. D. (1969) On the origin of "reverse" pleochroism of a phlogopite. *Canadian Mineralogist*, 10, 25-34.
- Gittens, J., Hewins, R. H. and Lavrin, A. F. (1975) Kimberlitic-carbonatitic dikes of the Saquenay River Valley, Quebec, Canada. In L. H. Aherns *et al.*, Eds., *Physics and Chemistry of the Earth*, Vol. 9, p. 137-148. Pergamon Press, New York.
- Hartman, P. (1969) Can Ti^{4+} replace Si^{4+} in silicates? *Mineralogical Magazine*, 37, 366-369.
- Hazen, R. M. and Wones, D. R. (1972) The effect of cation substitutions on the physical properties of trioctahedral micas. *American Mineralogist*, 57, 103-129.
- Huggins, F. E., Virgo, D. and Hucklewholzh, H. G. (1977) Titanium-containing silicate garnets. I. The distribution of Al, Fe^{3+} , and Ti^{4+} between octahedral and tetrahedral sites. *American Mineralogist*, 62, 475-490.
- Kliem, W. and Lehmann, G. (1979) A reassignment of the optical absorption bands in biotites. *Physics and Chemistry of Minerals*, 4, 65-75.
- Modreski, P. J. and Boettcher, A. L. (1972) The stability of phlogopite and enstatite at high pressures; a model for micas in the interior of the earth. *American Journal of Science*, 272, 852-869.
- Modreski, P. J. and Boettcher, A. L. (1973) Phase relationships in the system $\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ to 35 kilobars; a better model for micas in the interior of the earth. *American Journal of Science*, 273, 385-414.
- Mysen, B. O. and Virgo, D. (1978) Influence of pressure, temperature and bulk composition on melt structures in the system $\text{NaAlSi}_2\text{O}_6-\text{NaFe}^{3+}\text{Si}_2\text{O}_6$. *American Journal of Science*, 278, 1307-1322.
- Oba, T. and Kawachi, S. (1981) Petrography and mineralogy of

- xenoliths from the Yatsugatake volcanic chain, Central Japan. I. Ti-garnet. *Journal of the Faculty of Science, Hokkaido Univ. Series IV*, 19, 485-494.
- Rinskaya-Korsakova, O. M. and Sokolova, E. P. (1964) On ferromagnesian micas with a reverse absorption formula (in Russian). *All-Union Mineralogical Society Notes*, 93, 411-423.
- Robbins, D. W. and Strens, R. G. H. (1972) Charge-transfer in ferromagnesian silicates: The polarized electronic spectra of trioctahedral micas. *Mineralogical Magazine*, 38, 551-563.
- Smith, J. V., Brennesholtz, R. and Dawson, J. B. (1978) Chemistry of micas from kimberlites and xenoliths—I. Micaceous kimberlites. *Geochimica Cosmochimica Acta*, 42, 959-971.
- Wagner, P. A. (1914) *The Diamond Fields of Southern Africa. The Transvaal Leader, Johannesburg. Second Impression, 1971.* Cape Town, Struik (Pty) Ltd., 355 p.
- Watson, K. D. (1967) Kimberlites of Eastern North America. In P. J. Wyllie, Ed., *Ultramafic and Related Rocks*, p. 312-323. Wiley, New York.
- Watson, K. D., Bruce, G. S. W. and Halladay, L. B. (1978) Kimberlitic dyke in Keith Township, Ontario. *Canadian Mineralogist*, 16, 97-102.

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