



Major- and trace-element compositional variation of phlogopite from kimberlites and carbonatites as a petrogenetic indicator

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ABSTRACT

Ferromagnesian trioctahedral micas are a common macrocryst/phenocryst phase in kimberlites and carbonatites. We explored the possibility of using the chemistry of ferromagnesian micas to discriminate between these rocks in order to assess their economic potential. We determined the extent of major- and trace-element variations of micas from 14 selected kimberlite and carbonatite localities worldwide representing several different kimberlite fields and alkaline-carbonatite provinces. Phlogopite macrocrysts from kimberlites follow two principal evolutionary trends: primary macrocrystic (involving an increase in Ba, Al, Ti, Cr, Zr, Nb and Sr contents at decreasing Mg towards the rim) and transitional macrocryst-groundmass trend (involving an increase in kinoshitalite component at decreasing Fe, Ti and Cr contents). Micas from (dolomite-)calcite carbonatites cover a much greater compositional range than those from kimberlites, defining evolutionary trends towards annite, tetra-ferriphlogopite and kinoshitalite. Our data confirm that macrocrystic micas from kimberlites cannot be reliably distinguished from carbonatitic phlogopite on the basis of their major-element compositions. Exceptions are Fe–Al-rich [$\text{Fe}/(\text{Fe} + \text{Mg}) \geq 0.2$] and Na-rich (>0.3 wt.% Na_2O) micas that seem to be virtually restricted to carbonatites. The generally higher levels of Na in carbonatitic micas relative to those from kimberlites can be explained by the lower Na abundances in the latter relative to carbonatites. Our data indicate that the trace-element composition of mica determined by LA-ICP-MS can be used as a reliable petrogenetic indicator. Kimberlitic phlogopite is characteristically enriched in Cr (up to 12030 ppm), Ni (up to 1600 ppm) and Co (40–70 ppm), and depleted in Mn (≤ 280 ppm), Nb (≤ 28 ppm), Sr (≤ 55 ppm), Sc (≤ 8 ppm), Zr (≤ 12 ppm) and, to some extent, Cs (≤ 7 ppm) and Ta (≤ 3 ppm) with respect to carbonatitic micas (≤ 315 ppm Cr, ≤ 470 ppm Ni, ≤ 34 ppm Co, up to 17200 ppm Mn, 1080 ppm Nb, 830 ppm Sr, 80 ppm Sc, 105 ppm Zr, 27 ppm Cs and 19 ppm Ta). With the exception of Zr, the observed differences in trace-element composition of mica probably reflect the contrasting trace-element geochemistry of kimberlitic and carbonatitic magmas. The depletion of kimberlitic phlogopite in Zr (and possibly, Nb + Ta) can be explained by sequestration of these elements in the earlier-crystallized ilmenite. Variations in Ba, Rb and V contents are similar in mica from both rock types and cannot be used as a petrogenetic indicator.

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1. Background information and objectives

There is a number of volatile-rich mantle-derived rocks, including carbonatites, olivine melilitites and ultramafic lamprophyres, that may resemble kimberlites in terms of their textural, chemical and mineralogical characteristics (e.g., Mitchell, 1986, 1995; Chakhmouradian et al., this issue; Srivastava et al., this issue). Although some of these rocks have been reported to contain diamonds (e.g., Tappe et al., 2004; De Stefano et al., 2006), the bulk of diamond production by value comes from kimberlites or their associated secondary deposits. Hence, correct petrographic identification of silica-undersaturated mantle-derived rocks is crucially important for the assessment of their economic potential.

Both kimberlites and carbonatites are commonly characterized by an inequigranular texture arising from the presence of macrocrysts set in a finer-grained carbonate-rich mesostasis. Some of the macrocrysts are believed to represent relatively high-pressure phenocrysts precipitated from the parental magma, whereas others are clearly xenocrysts formed by fragmentation of mantle rocks (Mitchell, 1995). Distinction between cognate and exotic macrocrysts is difficult and often based on equivocal textural criteria. Ferromagnesian trioctahedral micas are a common macrocryst/phenocryst phase in both kimberlites and carbonatites. The most common of these minerals is phlogopite [$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH},\text{F})_2$], which forms extensive solid solutions with Fe-rich members of the group, including annite [$\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$], tetra-ferriphlogopite [$\text{KMg}_3\text{FeSi}_3\text{O}_{10}(\text{OH})_2$] and siderophyllite [$\text{KFe}_2\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$]. Intermediate members of this complex solid solution are normally referred to as biotite. The composition of these minerals is

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sensitive to changes in temperature, pressure and chemistry of their crystallization environment, which, in addition to their long crystallization span in many rock types (including kimberlites and carbonatites), makes them an important petrogenetic indicator (e.g., Bagdasarov et al., 1985; Tischendorf et al., 2001). Mica compositions have been used to discriminate between kimberlites and some texturally similar rocks (e.g., Mitchell and Bergman, 1991) and constrain the conditions of magma emplacement and evolution (e.g., Brod et al., 2001). The major-element chemistry of ferromagnesian micas from kimberlites and carbonatites has been addressed in many studies (e.g., Farmer and Boettcher, 1981; Gaspar and Wyllie, 1987; Mitchell, 1986, 1995; Chakhmouradian and Zaitsev, 2002; Brod et al., 2001; Lee et al., 2003; Zurevinski et al., 2008). In addition, there is a voluminous literature on the trace-element composition of phlogopite from metasomatized mantle xenoliths found in kimberlites and alkaline basaltic rocks (see Appendix A and references therein). By contrast, there are very little published data on the trace-element composition of phlogopite from kimberlites and carbonatites (e.g., Melluso et al., 2008).

In this work, we explored the possibility of using the chemistry of ferromagnesian micas from Group-1 (i.e. archetypal) kimberlites and calcite carbonatites (with an emphasis on trace elements) to discriminate between these rocks. We determined the extent of compositional variation of micas from 14 selected kimberlite and carbonatite localities worldwide representing several different kimberlite fields and alkaline-carbonatite provinces (Appendix A). Only large crystals (macrocrysts and phenocrysts larger than 250 μm) were selected for this purpose because groundmass micas are normally too small or too heavily included for accurate trace-element analysis. Particular care was taken to avoid xenocrystic material, i.e. phlogopite fragments from disaggregated mantle xenoliths. Any grains deviating in their optical properties or chemical composition from the main group (identified individually for each sample) were excluded from consideration. All examined kimberlites are from intracratonic settings; some were emplaced into crystalline basement rocks (e.g., Lac de Gras and Lake Timiskaming fields in Canada), others formed in a platform environment, where the basement is not exposed (e.g., Kuoika and Markha fields in Yakutia). The examined carbonatites are mostly from extensional intracratonic environments (e.g., Ottawa graben and Kola Alkaline Province), with a few representing other tectonic settings (Appendix A).

2. Analytical techniques and procedures

Energy-dispersive spectrometry in combination with back-scattered electron (BSE) imaging was used for mineral identification in polished thin sections and selection of areas for elemental analysis. The major-element composition of micas (444 analyses) was determined by wavelength-dispersive spectrometry (WDS) using a Cameca SX-100 automated electron microprobe operated at 15 kV and 20 nA with a defocused beam (10 μm across) to avoid beam-induced sample damage. Depending on the grain size and modal abundance of phlogopite, at least three (and as many as 11) crystals were analyzed per sample; multiple analyses were performed on each of the crystals (Appendix A). Peaks and backgrounds were measured with a counting time of 20 s for all elements, and the data were reduced using the ZAF correction procedure. The following natural and synthetic standards were employed in the analysis: diopside (Si, Ca), albite (Na), andalusite (Al), olivine (Mg, Fe), orthoclase (K), barite (Ba), titanite (Ti), chromite (Cr), spessartine (Mn), tugtupite (Cl), riebeckite (F). The $K\alpha$ lines were used for all of the elements listed except Ba, for which the $L\alpha$ line was used. The independent Ba and Ti standards and an LiF spectrometer were employed to eliminate analytical artifacts due to Ba–Ti line overlap. A strong negative correlation between the Ba and Ti contents in most Ba-rich samples (PED-2 and AR-31/40) clearly indicates that Ba–Ti line overlap was not an issue. The calculated lower limits of detection for both Ba and Ti are in the 400–500 ppm range.

The abundances of selected trace elements (310 analyses, see Appendix A for details) were measured by laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using a 213-nm Nd-YAG Merchantek laser connected to a Thermo Finnigan Element 2 sector-field mass-spectrometer. The trace-element compositions were obtained in polished thin sections (30 μm in thickness) using line profiles ranging from 140 to 150 μm in length. Matching BSE and reflected-light images of the areas analyzed by WDS were used to accurately position a laser beam on the sample. A beam size of 30 μm , laser-energy density of ca. 7.21 J/cm² and repetition rate of 10 Hz were used for all analyses. Ablation was done in Ar and He atmospheres. Oxide production rate was monitored during instrument tuning by measuring the ThO/Th ratio and kept below 0.2%. Synthetic glass standard NIST SRM 610 (Norman et al., 1996) was employed for calibration and quality control. Several test analyses of a reference phlogopite sample conducted at low (~300) and medium (~4000) resolution produced nearly identical results with the exception of ⁶⁹Ga and ⁴⁴Ca values, which were affected by spectral interferences. After taking into account potential spectral overlaps and molecular interferences, the following isotopes were chosen for analysis: ²⁹Si, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶⁵Ho, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta. All analyses were performed in a low-resolution mode (~300) using Pt skimmer and sample cones. Data reduction was carried out online using the GLITTER software (van Achterbergh et al., 2001). The Si concentrations determined by WDS were used as an internal standard for all analyses. The quality control was achieved by carefully selecting the portion of the laser signal that kept fractionation at less than 10% and fractionation/error ratio at less than three. The complete dataset combining recalculated WDS and LA-ICP-MS data is given in Appendix A.

3. Petrography

All carbonatites examined in the present work are intrusive and characterized by diversified mineralogy, highly variable proportions of major and minor phases, and an inequigranular texture. We restricted this review to calcite (\pm dolomite) carbonatites because calcite is the principal carbonate mineral in kimberlites, whereas dolomite is developed almost exclusively at the expense of calcite and other minerals in altered kimberlites (see Chakhmouradian et al., this issue for discussion and references). Hence, calcite carbonatites are the easiest to be potentially misidentified as kimberlites (and vice versa). The inequigranular texture of the examined carbonatites is due to large crystals of phlogopite and other ferromagnesian silicates, apatite and magnetite (Appendix A) set in a carbonate mesostasis. In the majority of samples, the latter is composed predominantly of calcite with minor dolomite, developed interstitially and along fractures in the earlier-formed phases. All carbonatite samples contain variable proportions of mica, ranging from 10 vol.% (AR-26/35) to 40 vol.% (PL-4). This mineral forms strongly pleochroic subhedral to euhedral grains ranging in size from less than 0.4 mm (AR-121/2) to several cm (AR-31/40). In the Fuerteventura carbonatite (AR-121/2), mica is altered along the margins and locally fully replaced by chlorite. Large phlogopite crystals frequently contain inclusions of earlier-crystallized phases, most commonly apatite and magnetite.

Several different textural types of carbonate-rich kimberlite were examined (Appendix A). In the majority of these samples, the macrocryst suite is represented by (serpentinized) olivine, phlogopite, spinel and ilmenite. The mode of occurrence and modal proportion of calcite vary greatly among the samples: from lath-shaped phenocrysts (PED-2) to rhombohedral phenocrysts (97-35-01, Ob-1) to minute euhedral crystals in calcite-serpentine segregations (Kom-35a) to mosaic-textured monomineralic segregations (Kom-35a, SYT-16, GP-29) to thin fibrous veinlets and pseudomorphs (GP-29) to scattered anhedral grains in the groundmass (AR-89). Fine-grained groundmass is composed predominantly of serpentine and calcite with subordinate

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