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A Raman microprobe study of melt inclusions in kimberlites from Siberia, Canada, SW Greenland and South Africa

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ABSTRACT

Raman spectroscopy has been used for the identification of both common and uncommon minerals in melt inclusions in Group-I kimberlites from Siberia, Canada, SW Greenland and South Africa. The melt inclusions all contained high abundances of alkali-Ca carbonates, with varying proportions of cations, and Na–Ca–Ba sulphates. In accordance with its dry mineralogy, no hydrated carbonates or sulphates were detected in melt inclusions from the Udachnaya-East kimberlite. In contrast, the melt inclusions in kimberlites from Canada, South Africa and SW Greenland were found to contain bassanite, pirssonite, and hydromagnesite suggesting that greater amounts of water were present in their residual magmas. This suggests that enrichment in alkali carbonates and sulphates is widespread across a range of Group-I kimberlites and implies that they commonly have an alkali-, and sulphur-rich residual liquid.

1. Introduction

Kimberlites are economically important because they serve as carriers of diamonds and garnet peridotite mantle xenoliths to the Earth's surface. Their probable derivation from depths greater than any other igneous rock type, and the extreme magma compositions in terms of low silica content and high levels of incompatible trace element enrichment, make an understanding of kimberlite petrogenesis very important. In this regard, the study of kimberlites has the potential to provide information on the composition of the deep mantle, and melting processes occurring at or near the interface between the cratonic continental lithosphere and the underlying convecting asthenospheric mantle.

This study focuses on Group-I kimberlites, which are CO_2-rich ultramafic potassic igneous rocks dominated by a primary mineral assemblage of olivine, phlogopite, calcite, dolomite, perovskite, Ti-rich Cr-spinel, rutile, magnetite, monticellite and Fe–Ni–Cu sulphides. The xenocryst mineralogy, which more closely resembles a true composition of the igneous rock, consists of forsteritic olivine, pyrope garnet, Cr-diopside, magnesian ilmenite and spinel. Therefore, because of contamination and alteration, the true kimberlite melt composition is hard to recognise by traditional whole rock studies.

The study of melt inclusions trapped in magmatic phenocrysts during crystallisation reveals the composition of the kimberlite before it was affected by postmagmatic modifications. We have selected samples of kimberlites where the partial preservation of olivine phenocrysts has allowed the preservation of melt inclusions. Raman spectroscopy is one of the few methods available for the non-destructive analysis of the gases and solids trapped within these melt inclusions. The Raman technique can identify a wide range of covalently bonded molecules and crystals but some metals and ionic solids, such as simple chloride salts, are not readily identified by Raman spectroscopy. Preliminary Raman spectra for some melt inclusions have been previously reported [1–4] but this study presents a more detailed report including new minerals not reported earlier.

1.1. Sample description

All studied samples are characterised by the petrographic features, mineralogy, chemical and isotopic compositions of most common group-I or archetypal kimberlites [5] with the exception of the Siberian ~365 Ma Udachnaya-East kimberlite pipe. This pipe, located within the Daldyn field, is a part of the twin diatreme with complex structure, which reflects multiple events of magma injection [6]. The Udachnaya-East pipe contains unaltered olivine phenocrysts set in a dominantly carbonate matrix [2,4,7] and has a rich assemblage of chloride and sulphate minerals in its groundmass [4,8].

The Canadian kimberlites are represented by the ~45 Ma Aaron pipe [9] from the Lac de Gras kimberlite field in the east-central part of the Archaean Slave Province, the ~172 Ma Jericho pipe located ~150 km NNW from the Lac de Gras field [10], and the ~540 Ma

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Gahcho Kué cluster of kimberlite pipes in the southeast Slave Craton, ~150 km SSE from the Lac de Gras field [11]. The recently discovered diamondiferous kimberlites in southern Greenland are represented in this study by the ~564 Ma Majuagaa dyke (2.5 km long and up to 2 m wide) [12]. The kimberlites of South Africa are represented by the ~90 Ma samples from the Wesselton mine [13], near Kimberley in the Cape Province, R.S.A.

Studied hypabyssal facies kimberlites are texturally similar to each other and composed of euhedral and fragmented olivine grains (up to 40–50 vol.%) in the serpentine-free (Udachnaya-East) and serpentine-bearing (other samples) calcite ± dolomite–phlogopite–(Fe–Ti–Cr)-oxides–perovskite ± monticellite groundmass [4,7,14]. In a given sample olivine grains hosting secondary and pseudo-secondary melt inclusions are compositionally variable (85–93 mol% Fo), and heterogeneity can be present within individual crystals [7].

2. Experimental

Raman spectra of crystals in the melt inclusions were recorded on a Dilor® SuperLabram spectrometer equipped with a holographic notch filter, 600 and 1800 g/mm gratings, and a liquid N_2 cooled, 2000 × 450 pixel CCD detector. The inclusions were illuminated with 514.5 nm laser excitation from a Melles Griot 543 Series argon ion laser, using 5 mW power at the samples, and a single 30 s accumulation. A 50× ULWD Olympus microscope objective was used to focus the laser beam and collect the scattered light. The focused laser spot on the samples was approximately 2 μm in diameter. Due to the small size of the crystals (typically <10 μm), often more than one crystal was illuminated by the laser during the analysis. Wavenumbers are accurate to ±1 cm^{-1} as determined by plasma and neon emission lines.

3. Results and discussion

3.1. Udachnaya-East kimberlite

The melt inclusions in olivine crystals from the Udachnaya-East kimberlite occur in clusters along healed cracks and growth planes and are likely to be pseudo-secondary.

They consist of multiple (up to 10) translucent and opaque daughter phases and a deformed vapour bubble. No gases were detected in the vapour bubble by Raman spectroscopy which could be due to the relatively small size of the vapour bubble or the fact that the bubble was often hidden or overlain by other solid phases. Colourless material is present as microcrystalline aggregates and well-shaped isotropic and birefringent crystals, many of which are cubic or rhombohedral in shape (Fig. 1). Typical Raman spectra obtained from these crystal aggregates are shown in Fig. 2 which also includes a small contribution from the host olivine crystal as well. Fig. 2(a) is dominated by a sharp, intense band at 1115 cm^{-1} and several moderately intense, sharp bands at 119, 178, 218, and 246 cm^{-1} which correlate with the spectrum of northupite [$Na_5Mg(CO_3)Cl$] (see Table 1). This spectrum is in good agreement with the spectra of northupite reported by [2] and in the RRUFF database [15]. Moderately intense bands are also observed at 994 and 1066 cm^{-1} which correspond with the spectrum of burkeite [$Na_6CO_3(SO_4)_2$] (see Table 1). Korsakov et al. [16] have previously reported the Raman identification of burkeite in melt inclusions in olivine from sheared lherzolite xenoliths from the Udachnaya-East kimberlite. The common occurrence of this mineral in melt inclusions in this kimberlite is confirmed in our studies.

Fig. 2(b) was obtained from a different melt inclusion and shows the Raman spectrum of the host olivine and three relatively intense, sharp bands in the region typical of the $CO_3{}^{2-}$ symmetric stretch (1050–1150 cm^{-1}). The band at 1100 cm^{-1} correlates with dolomite [$CaMg(CO_3)_2$] (see Table 1) although no other bands of dolomite are observed in the spectrum. The presence of dolomite in melt inclusions in the Udachnaya-East Kimberlite was also previously reported by Korsakov et al. [16]. The intense band at 1089 cm^{-1} has been assigned to holdawayite [$Mn_6(CO_3)_2(OH)_7$(Cl, OH)] which also has bands at 151, 164, 222 and 701 cm^{-1} (see Table 1) but the spectrum is also similar to shortite [$Na_2Ca_2(CO_3)_3$] (see Table 1). The third sharp band at 1074 cm^{-1} is slightly lower than that of gregoryite [(Na_2,K_2,Ca)CO_3] (see Table 1) and may represent a slightly impure form of that mineral. The spectrum of gregoryite recorded with 514.5 nm laser excitation has a rising background below 350 cm^{-1} which corresponds to the higher background in this region in Fig. 2(b). However, the weak band at 1006 cm^{-1} is not observed but this may be due to the orientation of the crystal relative to the laser beam. Other Raman spectra (not shown here) indicate the presence of calcite [$CaCO_3$] and possibly nyerereite [$Na_2Ca(CO_3)_2$] (see Table 1) in some inclusions.

The minerals identified by Raman spectroscopy in the melt inclusions in the Udachnaya-East kimberlite are in accord with previous studies of the kimberlite and its melt inclusions [2–4,7,8]. Kamenetsky et al. [8] reported that the chloride–carbonate nodules from this kimberlite contained anhydrous and hydrated Na–Ca carbonates with variable Ca/Na ratios and that shortite was found in close association with northupite and calcite. In some places pirssonite [$Na_2Ca(CO_3)_2{\cdot}2H_2O$] was found to replace the original Na–Ca carbonate and an alkali sulphate, aphthitalite [$(K,Na)_3Na(SO_4)_2$], is reported to be a minor but widespread component of the nodules. Melt inclusions in shortite are reported [8] to contain zoned apatite and northupite associated with crystals of phlogopite, tetraferriphlogophite, halite, aphthitalite, alkali-Ca-carbonates, sulphate and chloride minerals. The presence of these minerals reflects the unusual enrichment of the Udachnaya-East kimberlite in Na_2O and Cl (up to 6 wt.% each) [8,14].

3.2. Kimberlites from the Slave Craton (Canada)

The melt inclusions in kimberlites from the Slave Craton have been previously described [4] and, as above, they contain multiple translucent and opaque daughter phases and a vapour bubble. Typical Raman spectra obtained from melt inclusions from the Aaron kimberlite are shown in Fig. 3. Fig. 3(a) shows an olivine spectrum and a number of other relatively intense bands at 143, 1048, 1073 and 1090 cm^{-1} respectively. The intense bands at 143 and 1048 correlate well with the spectrum of nahcolite [$NaHCO_3$] (see Table 1). Bands at 1073 and 1089 cm^{-1} are assigned to shortite [$Na_2Ca_2(CO_3)_3$].

The Raman spectrum obtained from another melt inclusion in apatite from the Aaron kimberlite is shown in Fig. 3(b). Four moderate to intense Raman bands are observed at 426, 670, 987 and 1145 cm^{-1} which correlate well with the spectrum of bassanite [$CaSO_4{\cdot}5H_2O$] (Table 1). Raman spectroscopy also indicated the presence of aragonite, celestite [$SrSO_4$] and aphthitalite [$(K,Na)_3Na(SO_4)_2$] in other melt inclusions in the Aaron kimberlite. SEM-EDS studies and element mapping of melt inclusions from the Aaron kimberlite have reported the presence of phases rich in Ca, Na, K, Ba, Cl, S, and P that are inferred to be carbonates, chlorides, sulphates and phosphates [4]. The application of Raman spectroscopy has now enabled the identification of some of these phases.

The Raman spectrum obtained from a selected melt inclusion in olivine from the Jericho kimberlite pipe is shown in Fig. 4(a). The intense Raman band at 1085 cm^{-1} could be assigned to calcite [$CaCO_3$] but we prefer to assign it to nyerereite [$Na_2Ca(CO_3)_2$] (Table 1) due to the higher background below 500 cm^{-1} in Fig. 4(a) which is similar to that observed in the Raman spectrum of nyerereite [17]. Fig. 4(b) shows the Raman spectrum of a melt inclusion