# Parental carbonatitic melt of the Koala kimberlite (Canada): Constraints from melt inclusions in olivine and Cr-spinel, and groundmass carbonate

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ABSTRACT

This study of the hypabyssal kimberlite with particularly fresh olivine from the Palaeogene Koala pipe (Ekati cluster, Slave craton, Canada) is focused on reconstruction of the kimberlite parental melt. The Koala kimberlite sample is a typical ultramafic rock (archetypal or Group-I kimberlite) containing large abundance of forsteritic olivine set in a carbonate-rich matrix. The euhedral olivine-II shows significant zoning in terms of forsterite content and trace elements. Only the rims of olivine-II are considered to be magmatic — they are uniform in terms of Fo ($91.5 \pm 0.2$ mol%) and host primary crystal (apatite, Cr-spinel) and melt inclusions. The magmatic spinel phenocrysts are strongly zoned from titanian magnesian chromite to pleonaste, with the cores having the same composition as spinel inclusions in olivine. The primary and pseudo-secondary melt inclusions in both magmatic Cr-spinel and olivine comprise a complex assemblage of daughter phases, dominated by carbonate minerals (dolomite, eitelite ($Na_2Mg(CO_3)_2$), shortite $Na_2Ca_2(CO_3)_3$, nyerereite $Na_2Ca(CO_3)_2$, zemkorite $(Na,K)_2Ca(CO_3)_2$, and fairchildite ($K_2Ca(CO_3)_2$)). In addition to the dominant carbonates, the melt inclusions contain phosphates, chlorides and sulphates (bradleyite ($Na_3Mg(PO_4)(CO_3)$, halite, sylvite, aphthitalite ($Na_{0.25} K_{0.75})_2SO_4$)), but the silicate component is represented by tetraferriphlogopite only. The melt inclusions in olivine studied in heating experiments show immiscibility of two carbonate liquids on heating and cooling, and homogenise at low temperature $< 700$ °C. The liquid immiscibility texture is also characteristic of the calcitic groundmass, and represented by irregularly shaped calcite segregations and near-spherical globules. The calcite in the globules is unusually enriched in $Na_2O$, SrO and BaO (in wt.%, 0.37–0.65, 1.17–2.40, 2.37–4.18, respectively). Such compositions are compared to secondary calcite replacing nyerereite and shortite in the natrocarbonatite lavas of the modern Oldoinyo Lengai volcano. The results on mineralogy, composition and homogenisation temperature of melt inclusions and the groundmass of the Koala kimberlite imply that the parental kimberlite liquid was a Si-poor Ca–Mg carbonate, enriched in alkali elements, lithophile trace elements, phosphorus, chlorine and sulphur.

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## 1. Introduction

Archetypal or Group-I hypabyssal kimberlites are composed of two principal components — olivine crystals and carbonate- and serpentine-rich groundmass; the proportion of olivine and carbonate in rocks from a given locality is highly variable, and olivine abundance may be enhanced by accumulation of olivine crystals of different provenance and non-cognate origin (e.g., Kamenetsky et al., 2008; Brett et al., 2009; Arndt et al., 2010). Besides olivine and diamond, other minerals derived from mantle peridotite, pyroxenite and eclogite and crustal lithologies are typically also encountered in kimberlites. Alkali basalts are also known to transport significant loads of mantle and crustal debris, but kimberlite is apparently the deepest derived and fastest ascending terrestrial melt.

Mitchell (2008) concluded "that there are no hypabyssal kimberlites which are representatives of the initial primary magma; all

kimberlites are hybrid and contaminated magmas which have undergone crystallisation in the mantle prior to crystallisation of the groundmass-mesostasis assemblages." In addition to contamination, crystallisation and degassing en route to surface, and olivine accumulation after emplacement, the original composition of kimberlite melts is further obscured by pervasive alteration by deuteric and meteoric fluids. This effectively prohibits reconstruction of parental melt compositions from bulk rock analyses, even for so-called aphanitic kimberlites (e.g., Price et al., 2000; le Roex et al., 2003; Harris et al., 2004; Kopylova and Hayman, 2008).

The research on melt inclusions aids in constraining parental melts in terms of their liquidus assemblage, chemistry, volatile content, temperature, and evolutionary paths (Sobolev, 1996; Danyushevsky et al., 2002; Kamenetsky and Kamenetsky, 2010). The studies of melt inclusions hosted in early crystallising olivine and Cr-spinel have been instrumental in understanding primitive or parental melts for the principal mafic or ultramafic terrestrial rock types like mid-ocean ridge basalts, oceanic island basalts, flood basalts, komatiites, supra-subduction zone

picrites and basalts. Since studies of melt inclusions trapped in magmatic phenocrysts permit isolation of magmatic attributes prior to postmagmatic modification, the method has great potential for application in kimberlites (e.g., Kamenetsky et al., 2004; Golovin et al., 2007; Kamenetsky et al., 2009b), in which olivine and Cr-spinel are recognised as early liquidus phases (Mitchell, 2008; Roeder and Schulze, 2008). Here we present the results of a melt-inclusion study completed on olivine and Cr-spinel phenocrysts in archetypal Koala kimberlite from the Slave craton, Canada.

## 2. Koala kimberlite pipe: geology and sample description

The Koala kimberlite belongs to the Ekati cluster of kimberlite pipes located in the Lac de Gras Kimberlite Field of the Central Slave Province, Canada. Detailed description of local geology and pipe structure can be found in several papers (Nowicki et al., 2004; Porritt and Cas, 2011; Porritt et al., 2011). The ~53 Ma (Creaser et al., 2004) kimberlite intruded the Archaean granodioritic Koala batholith and Cretaceous marine and Palaeocene lacustrine sediments (siltstones, sandstones and muds). The latter occur only as xenolithic fragments in the kimberlite, having been completely eroded from the central Slave craton, together with a few hundred metres of upper parts of the pipe (Nowicki et al., 2004). The Koala pipe has a nearly round outline ~4.5 ha at the surface and a steep-sided inverted cone-like shape. The pipe is described as unusual among kimberlites from the Ekati property (Nowicki et al., 2004) owing to its stratigraphy, represented by sub-horizontal, variably bedded and often well-sorted volcaniclastic rock types, each distinctly different from each other (Porritt and Cas, 2011).

The sample in this study was supplied from a small volume of coherent kimberlite that occurs underlying dominant fragmental deposits, within the massive poorly sorted, olivine-rich lapilli tuff, at the bottom of the pipe (Porritt and Cas, 2011). The rock is classified as fresh hypabyssal archetypal olivine-rich kimberlite, based on a massive texture and phlogopite-poor matrix. Olivine occurs as largely fresh crystals varying in size (<0.1 to 10 mm) and shape (anhedral, round, ovoid, subhedral, euhedral). Euhedral olivine grains tend to have smaller size (<0.7 mm) and well developed zoning (Fig. 1). Most olivine grains have minor serpentine alteration on the margins and along fractures, especially where melt inclusions are present. Based on morphology, size, zoning and types of inclusions, the olivine belongs to two main populations, similar to those described in other kimberlites (e.g., Kamenetsky et al., 2008; Brett et al., 2009; Kamenetsky et al., 2009b; Arndt et al., 2010). Olivine-I (macrocrysts), large round and anhedral, uniform in composition, with inclusions of Cr-diopside, orthopyroxene and garnet, is most likely derived from disaggregated peridotite xenoliths entrained by the kimberlite magma. Another mineral of undoubtedly mantle origin was found as a solitary orthopyroxene grain, strongly resorbed at the contact with the groundmass and surrounded by reaction products (olivine and monticellite, Fig. 2). Olivine-II ("groundmass") is finer grained, has subhedral to euhedral shapes, with often well-developed zoning and inclusions of Cr-spinel, phlogopite, apatite and melt in their rims (Fig. 1). It is recognised as related in part to crystallisation of the kimberlite melt (Kamenetsky et al., 2008). Zoned phlogopite crystals with Ba-rich (kinoshitalite) rims are subordinate to olivine, grade in size significantly (0.05–0.5 mm) and contain euhedral inclusions of apatite and Cr-spinel and sulphide blebs. The phenocryst assemblage also contains zoned spinel (Ti-rich chromite to pleonaste) with typically euhedral habit, variable size (up to 0.5 mm), and melt inclusions trapped in their cores (Fig. 3).

The groundmass of the Koala hypabyssal kimberlite is dominated by coarse-grained calcitic carbonate and fine-grained serpentine, often showing euhedral shapes of very small (<0.07 mm) pseudomorphed olivine. Other fine-grained (<0.1 mm) minerals uniformly distributed through the groundmass are Ba-rich phlogopite, apatite, pyrochlore $(Na,Ca)_2Nb_2O_6(OH,F)$, monticellite, Fe-, Fe–Ni, Fe–Cu and Fe–Ni–K

sulphides, djerfisherite $K_6Na(Fe,Cu,Ni)_{25}S_{26}Cl$, Fe–Ti oxides and barite. The prevailing groundmass carbonate, apart from interspersing with other minerals, is also present in large amoeboid segregations (up to 2 mm), surrounded by olivine grains (Fig. 4A–C) and sub-spherical and round formations (nodules or globules up to 0.3 mm). The irregular-shaped carbonate segregations have sharp contacts with olivine, but usually gradational with the respect to the kimberlite matrix (Fig. 4A–C; see also Armstrong et al., 2004 and Wilson et al., 2007 for descriptions of the groundmass carbonates in the Ekati kimberlites). The contacts between round nodules and the groundmass are often sharp and accentuated by serpentine and porous carbonate (Fig. 4E, F, although not always a case — see Fig. 4D). Both irregular segregations and near-spherical nodules contain zoned rhombic calcite crystals (0.05–0.15 mm across) that project inward from a boundary with the groundmass into "matrix" calcite. The crystals are usually rimmed by serpentine, and Mg-rich calcite (darker in back-scattered electrons (BSE), Fig. 4D–F). In general, rhythmic colloform banding, botryoidal texture and sharp contacts between serpentine-bearing microcrystalline and porous "fringing" carbonate material and "smooth" calcite are more typical of round formations (Fig. 4D–F).

## 3. Analytical techniques

Melt inclusions in olivine and spinel were studied on polished surfaces. Mineral grains were hand-picked from the kimberlite specimen, mounted in epoxy resin, and exposed by hand polishing in a water-free environment, to prevent damage to soluble daughter minerals. The grinding was carried out using kerosene as a lubricant, and final polishing was done on a silk-covered surface using an oil-based, water-free 1 μm diamond compound. After exposure the samples were platinum-coated and stored in a desiccator to avoid interaction with atmospheric moisture.

Backscattered electron (BSE) imaging and energy dispersive X-ray spectrometry (EDS) were performed on (1) a FEI Quanta 600 scanning electron microscope (SEM) equipped with a tungsten filament and an EDAX Genesis Sapphire SUTW Si(Li) EDS system using an accelerating voltage of 25 kV (Figs. 1, 2, 4), and (2) a Hitachi SU-70 Schottky field emission SEM fitted with Oxford INCA Energy XMax 80 silicon drift detector EDS system at 7 kV (Figs. 3, 8–10). The element maps in Fig. 2 are region of interest maps and not background corrected. In the maps shown in Figs. 9 and 10 full X-ray series peak deconvolution and background subtraction have been performed. Although quantification of the SEM–EDS data would be possible in general, quantitative analysis of the melt inclusion phases is compromised by several limiting factors: the rough and porous surface of the inclusions leads to anisotropic X-ray emission. The soft melt inclusion phases are susceptible to electron beam damage, causing selective mobilisation of elements. Furthermore, many grains are smaller in size than the X-ray generation volume, resulting in mixed phase analyses and potential issues with the matrix correction. The extent of secondary fluorescence in neighbouring phases is also not known. Because of these uncertainties we consider quantitative data not reliable and will only use ED spectra and distribution maps in this publication (Supplementary Figures).

Spinel and olivine analyses (Tables 1 and 2, also see Supplementary Table 1) were acquired on a Cameca SX100 electron microprobe equipped with a tungsten filament and 5 wavelength dispersive spectrometers (WDS) using a focussed beam with 15 kV accelerating voltage and 30 nA beam current. Elements were acquired using Kα lines and analysing crystal LLiF for Mn, Fe, Ni, V, Cr, Zn, LPET for Ca, Ti, and TAP for Si, Al, Mg. Calibration standards were bustamite for Mn, hematite for Fe, rutile for Ti, nickel silicide for Ni (all Astimex Scientific Ltd), V metal for V, and clinopyroxene (Delegate, Australia) for Ca and Si. Peak (background) counting times were 20 (6) s for Fe, 30 (20) s for Ca, Mn, Si, Al, Mg, Ti, V, Cr, Zn, and 40 (30) s for Ni. A linear background correction was performed for all elements except Mn and V, where only one background on the high side was used with a slope factor. Corrections