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Lithos



journal homepage: www.elsevier.com/locate/lithos

Ultrafresh salty kimberlite of the Udachnaya–East pipe (Yakutia, Russia): A petrological oddity or fortuitous discovery?

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ARTICLE INFO

Article history: Received 14 October 2011 Accepted 29 April 2012 Available online 8 May 2012

Keywords: Kimberlite Olivine Primary melt Carbonate Geochemistry Stable isotopes

ABSTRACT

An ultrabasic/ultramafic composition of kimberlite magmas is difficult to reconcile with existing models of the kimberlite mantle source and melting conditions, inferred magma temperatures and rheological properties, and the style of magma ascent and emplacement. The inconsistencies in current thinking indicate serious flaws in understanding kimberlite magma compositions. Much of the uncertainty over true kimberlite compositions may stem from almost ubiquitous hydration and leaching of kimberlite rocks. This study presents petrographic and geochemical data for kimberlite samples largely unaffected by postmagmatic modification, from the Devonian Udachnaya-East pipe in Siberia. These samples are unusually enriched in chlorine and sodium, yet they are essentially anhydrous. These features are consistent with the phase composition of the groundmass which is dominated by minerals such as Na-Ca carbonates, Na-K chlorides and sulphates which appear to be - in our samples – co-magmatic with common silicates and oxides, but are unknown in other kimberlites, or rarely found within magmatic assemblages. We suggest that a kimberlite parent melt of essentially non-silicate composition, with high concentrations of alkalis, CO₂ and Cl may be a viable alternative to the currently favoured water-rich, high-Mg model primary melt. Entrainment of mantle silicates into such a melt en route to the surface, followed by gravitational accumulation of mantle olivine and liquidus oxides (perovskite, Cr-spinel) at the bottom of vertically extensive magma bodies after emplacement, would explain the observed properties of kimberlite magma/rock, notably enrichment in olivine and trace elements in the hypabyssal kimberlite facies. A carbonate melt composition would retain attributes of the standard model such as trace element enrichment via low degrees of partial melting, it would explain low temperatures of crystallisation and the exceptional rheological properties that enable kimberlite primary melts to segregate from the lithospheric source and buoyantly ascend at high speed, while mixing and reacting with country rocks.

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1. Introduction

Despite their rarity, kimberlites have received a disproportionate amount of attention from the geoscience community, largely because they are the primary source of diamonds. Over more than fifty years, a large volume of information has been compiled about the tectonic setting, age distribution, emplacement styles, mineralogy and chemical composition of kimberlites. However, the processes responsible for the formation of kimberlite diatremes (pipes) and relationships between petrological, textural, geochemical and mineralogical properties of kimberlites and their diamond potential are still poorly understood.

The issue of kimberlite primary melt/magma compositions has been examined in many studies but still relies heavily on models based on contaminated and altered kimberlites (e.g., Kjarsgaard et al., 2009; Kopylova et al., 2007, and references therein). In what we call herein the 'current standard model', kimberlites are seen as carbonated, water-bearing ultramafic silicate melts (e.g., Kjarsgaard et al., 2009; Kopylova et al., 2007; le Roex et al., 2003; Price et al., 2000) which ascend rapidly, carrying a cargo of diamonds and various xenoliths/ xenocrysts from both mantle and crustal sources to form subsurface cylindric bodies (pipes) within continental crust. Kimberlite eruptions are thought to be explosive, and their constituents are subjected to intrusive-volcanic stratification on a vertical scale. Syn-magmatic chemical modification is ubiquitous. Processes including pre-emplacement alteration all leave their mark on the mineralogical and chemical composition of kimberlites, making identification of primary kimberlitic components and their parental melt composition very challenging.

The existing dogma about correspondence between compositions of whole rock kimberlites and their parental melt has been recently challenged by newcomers to the kimberlite scientific community (e.g., Brett et al., 2009; Kamenetsky et al., 2004, 2007a; Patterson et al., 2009), and even members of the classic school, such as R.H. Mitchell (2008), who concluded that "...there are no hypabyssal kimberlites which are



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^{0024-4937/\$ –} see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.lithos.2012.04.032

representatives of the initial primary magma; all kimberlites are hybrid and contaminated magmas which have undergone crystallization in the mantle prior to crystallization of the groundmass-mesostasis assemblages.". This definition of kimberlites is consistent with an earlier account of this major magmatic source of diamonds "...the kimberlitic rock is both a contaminated and altered sample of its parent melt" (Pasteris, 1984).

In our view, an ultramafic model kimberlite melt compositions encounters numerous problems, including:

- 1. The ultramafic composition (MgO>20 wt.%; Mg#>86; e.g., Kjarsgaard et al., 2009; Kopylova et al., 2007; le Roex et al., 2003; Price et al., 2000) of the kimberlite parental melt in the standard model is controlled by highly magnesian olivine (up to Fo₉₃₋₉₄). We contend that much of the olivine in the hypabyssal kimberlite facies is in fact of cumulate origin, as indicated by disequilibrium Mg/Fe²⁺ or Mg# relationships between inferred melt composition and olivine (e.g., Kopylova et al., 2007).
- 2. In addition to high olivine contents, whole rock-based kimberlite parental magmas also contain a significant Ca–Mg carbonate component; an aluminosilicate ("basaltic") component is conspicuously absent, implying inferred melt compositions characterised by a depletion in Al₂O₃ and Na₂O (<3 and <0.4 wt.%, respectively) that is unique among terrestrial silicate liquids.</p>
- 3. An ultramafic composition of the kimberlite parental melt requires either very high pressure (>70–80 kbar) or high degrees of melting (>30–40%), or both, of a mantle peridotite source, whereas trace element geochemical characteristics are consistent with low degrees of melting within garnet-bearing lithospheric mantle;
- 4. An ultramafic composition of the kimberlite parental melt requires high liquidus temperatures, even at inferred high H_2O contents (>1300 °C; e.g., Kamenetsky et al., 2010), which is not consistent with preservation of diamonds (e.g., Fedortchouk et al., 2005) and the absence of thermometamorphic effects on country rocks and surface-derived organic fragments (wood, leaves, animal and fish bones; e.g. Mitchell, 1986).
- An ultramafic composition of the kimberlite parental melt implies limited solubility of CO₂ and H₂O at crustal pressures, inconsistent with the high measured contents of these volatiles in kimberlites.
- 6. Kimberlite ascent is inferred to be driven by continuous volatile degassing (e.g., Russell et al., 2012; Wilson and Head, 2007) which appears inconsistent with non-vesicular textures in hypabyssal facies kimberlite.

We propose that the current standard model for kimberlite melt/ magma compositions needs to be revised substantially and that this is best done by focussing on kimberlites with low degrees of alteration. Where alteration is weak or absent, we can hope to find primary mineral grains and phenocryst-hosted melt inclusions suitable for careful microanalysis. In this paper we present a complete geochemical dataset for largely unaltered samples from the Udachnaya-East kimberlite in Siberia. Some samples from this pipe are completely free of serpentine and provide unique insights into the composition and temperature of possible primary melts; with this information, we can address issues such as the mantle source of kimberlite melts and the rheological properties of the kimberlitic magma. This study demonstrates an important role of accumulation of heavy minerals (olivine and oxides) in the kimberlite magma upon its emplacement and defines a truly melt component prior to its crystallisation and post-magmatic alteration of already solidified magmas.

2. Udachnaya-East kimberlite

2.1. General characteristics

Most of Russia's diamonds (~20% of global output) are mined in the Siberian (Yakutia) diamondiferous province. The Daldyn-Alakit field, the best studied part of this province, comprises > 50 pipes, ranging from 400–700 m in diameter. Most pipes are composed of tuff-breccias with altered olivine, but some contain blocks of massive, fresh kimberlite. The field contains more pipes with fresh, unaltered olivine than any other kimberlite region within the Siberian diamondiferous province. About 10% of the intrusions exhibit either two adjacent channel-ways or repeated intrusion of magma through the same pathway. The late-Devonian Udachnaya kimberlite pipe ($Y_{A}ay_{HA}\pi$ means *Fortuitous* discovery) was found in 1956, is the best-known example of these twin diatremes, and is located in the NW of the Daldyn field. It consists of two adjacent bodies (eastern and western) that become separated at 250–270 m depth. It is the largest diamond producer in Russia (>60% diamond quantity and value) and one of the largest in the world (~12%), supplying large gem-quality diamonds.

The rocks near the contact between the two kimberlite bodies progressively change from massive breccias with abundant fresh olivine phenocrysts in the eastern body, through intensely altered (serpentinised) and brecciated rocks, to altered kimberlite breccias of the western body. As a consequence, the two kimberlite bodies differ markedly in terms of mineralogy, petrography, composition, and degree of alteration. While alteration within the western body is similar to that in many other kimberlites, the eastern body is unique in its much lower degree of alteration; some sections are completely fresh and contain similarly fresh xenoliths of peridotite and eclogite, some of which are diamond-bearing (e.g., Spetsius and Taylor, 2008).

2.2. Previous studies of the Udachnaya-East kimberlite

Kimberlites from Udachnaya–East have provided detailed constraints on mineral assemblages and melt composition that are difficult (or impossible) to obtain in more altered kimberlite (Golovin et al., 2007; Kamenetsky et al., 2004, 2006, 2007a, 2007b, 2008, 2009a, 2009b, 2009c; Maas et al., 2005; Mernagh et al., 2011; Sharygin et al., 2007, 2008). These findings and constraints include:

- recognition of two populations of olivine, with distinct morphological and chemical features;
- 2) detailed characterisation of chemical, zoning and growth/resorption features in one of these (the euhedral) olivine population;
- 3) analysis of the mineral assemblage coexisting with liquidus (euhedral) olivine, based on crystal inclusions in olivine;
- characterisation of melt and fluid inclusions in olivine; thermometric experiments on these inclusions, directed at understanding temperature and pressure of crystallisation;
- 5) microanalytical analysis of melt and fluid inclusions (laser Raman spectroscopy, laser ablation ICPMS, proton-induced X-ray emission, electron microprobe, etc.) and identification of melt/fluid components at the time of olivine crystallisation;
- 6) characterisation of the composition and evolution (e.g., fractionation and degassing) of the primary kimberlitic melt from major and trace element compositions of olivine phenocrysts and olivine-hosted crystal, fluid and melt inclusions and groundmass minerals, including potassium- and chlorine-bearing sulphides;
- in situ radiogenic isotope (Sr–Nd) analysis in perovskite aimed at understanding the mantle source of kimberlites and effects of assimilation and alteration.

2.3. Petrography and mineralogy

The studied samples of the Udachnaya–East hypabyssal kimberlites come from a subvertical, cylindrical block located at ~400 m to 620 m depth within the central part of the pipe. The samples have much in common with other kimberlites in Siberia (including the twin Udachnaya–West pipe) and with kimberlites worldwide (Kamenetsky et al., 2009b): they show porphyroclastic textures, carry fragments of mantle- and crust-derived minerals and xenoliths, and the groundmass contains abundant olivine (euhedral) and carbonates (Fig. 1). On the other hand, our samples are unique in their lack of serpentine; it appears these rocks do not record the otherwise ubiquitous petrographic and chemical effects of the deuteric and postmagmatic alteration that is so common in kimberlites. Characteristically, these serpentine-free kimberlites have low contents of crustal fragments (<6%, c.f. > 15–30% in other kimberlite varieties from Udachnaya–East). Fractures filled with hydrothermal minerals (e.g., gypsum, calcite, halite) are rare or absent.

The samples contain abundant water-soluble minerals (>10 wt.%), among them halite, which imparts a strong salty (not bitter) taste. To protect these groundmass minerals, sample preparation (cutting, grinding and polishing to make thin sections) was carried out using oil or kerosene as a lubricant at all stages. Polishing was performed using oil-based 1 μ m diamond compounds on a silk-like surface.

Olivine is the most abundant mineral and represented by two morphologically distinct populations (Figs. 1 and 2; Kamenetsky et al., 2008). Large fragmental olivine grains are most likely derived from the lithospheric sources and/or by disintegration of peridotite xenoliths. The second olivine type forms small, perfectly euhedral grains in the groundmass and most likely represents olivine formed by crystallisation during magma ascent and emplacement. The euhedral olivine show complex major and trace element zonation patterns, with distinct cores and rims (Figs. 1 and 2), suggesting a complex history (Kamenetsky et al., 2008). Cores in different grains show much compositional variability while the rims are more homogeneous. This suggests at least two stages in the formation of groundmass olivine - intratelluric and syn-emplacement. The cores of groundmass olivine may be representative of deep crystallisation or/and disintegration of lithospheric peridotites and their entrapment in ascending kimberlite magma, followed by dissolution and replacement reactions en route to the surface. Only the rims of the groundmass olivine are considered to be unambiguously liquidus, i.e. formed in the presence of a melt by re-equilibration and crystallisation (Kamenetsky et al., 2008). The



Fig. 1. Optical (*a-e*) and back-scattered electron (*f*) images illustrating petrographic features of the Udachnaya–East kimberlites. Polished (*a*) and unpolished (*b*) blocks of kimberlite demonstrate abundance of olivine crystals and different colours of the groundmass. Thin sections (*c-e*) show clastic texture, abundance, sizes and shapes of olivine, presence of microxenoliths of country rocks, and heterogeneous groundmass, containing laths of phlogopite (brown crystals on Fig. 1d). Polished surface of kimberlite (*f*) is suitable for examination of zoning in olivine, and minerals composing the groundmass (alkali carbonate (dark grey), calcite (light grey), chlorides and oxides–perovskite, Cr–spinel, Ti–magnetite (white)).



Fig. 2. Backscattered electron image and X-ray element maps showing euhedral zoned crystals of olivine (Si, Fe, Mg maps) set in the groundmass composed of S-bearing Na–K–Ca carbonates, calcite (highest intensity on Ca-map), halite, phlogopite (Al, Mg and K maps), sodalite (Al and Cl maps), apatite (P map), Fe-oxides and Cr–spinel (highest intensity on Fe-map). The maps are recorded on the electron microprobe JEOL JXA-8200 (Max Planck Institut für Chemie, Mainz).

occurrence of phlogopite, rutile, Cr-spinel and perovskite (Fig. 3) in both the kimberlite groundmass and as euhedral inclusions in the rims of groundmass olivine indicates co-crystallisation of these mineral with each other and with the olivine of specific composition ($89.0 \pm 0.2 \text{ mol}\%$ Fo; Kamenetsky et al., 2008).

A previously unknown chloride component, present throughout the kimberlite groundmass, occurs in the form of widespread halite and sylvite that are responsible for the salty taste of freshly exposed surfaces mentioned earlier (Kamenetsky et al., 2007a, 2007b). Other minerals host additional chlorine, notably sodalite and djerfisherite which appear in the groundmass and in reaction rims around and within mantle and crustal xenocrysts. Another unusual component - alkali carbonate - is pervasive in the studied samples and represented by Na- and K-bearing minerals (nyerereite, shortite, zemkorite; Egorov et al., 1988; Kamenetsky et al., 2007a, 2007b). The unusual alkali carbonate minerals are closely associated with chlorides, sodalite, K-bearing sulphides and common calcite, olivine, phlogopite, monticellite, perovskite, Cr-spinel and Ti-magnetite (Kamenetsky et al., 2009c; Fig. 3). The groundmass of the studied samples easily degrades by reaction with atmospheric moisture and recrystallises with formation of H₂O-bearing



Fig. 3. Crystal inclusions in euhedral olivine: (a) BSE images showing phlogopite inclusions at the core–rim interface of zoned olivine, note Fe-oxide and Cr-spinel (bright) in the outer rims; (b–e) – transmitted light images showing phlogopite (b), rutile (c), perovskite and Cr-spinel (d) and perovskite overgrown by Ti-magnetite (e) inclusions in the olivine rims.

carbonates (pirssonite, trona, hydrocalcite) and perfectly shaped crystals of halite and sylvite (Fig. 4).

2.4. Geochemistry

2.4.1. Major elements

The concentrations of most major elements in the studied kimberlites (Table 1; see Supplementary Table for a complete data set) are in a good agreement with previously published analyses from Udachnaya (e.g., llupin et al., 1974; Vasilenko et al., 2002) and typical group-I kimberlites (e.g., Kjarsgaard et al., 2009; Price et al., 2000). All samples are highly magnesian (27.8–35.9 wt.% MgO) and lie along the olivinecontrol line (Fig. 5), reflecting the high proportion of olivine fragments and euhedral crystals (46–67 wt.%), relative to other components of the kimberlite magma (Supplementary Table).

The samples are characterised by silica undersaturation $(23.9-33.7 \text{ wt.\% SiO}_2)$, relatively low FeO_t (6.9–9.5 wt.%), exceptionally low Al₂O₃ (1.1–2.3 wt.%), high CaO (8.1–18.2 wt.%), TiO₂ (0.9–1.9 wt.%) and P₂O₅ (0.3–0.8 wt.%), and very high CO₂ (4.1–14.1 wt.%) contents (Table 1). All these compositional parameters are virtually indistinguishable from the compositions of the so-called "fresh" kimberlites (Fedortchouk and Canil, 2004; Kjarsgaard et al., 2009; Kopylova et al., 2007; Price et al., 2000). However, the enrichment in alkali elements (up to 6.2 wt.% Na₂O and 2.2 wt.% K₂O), chlorine (up to 6.1 wt.%) and sulphur (up to 0.33 wt.%) and depletion in H₂O (0.2–4.5 wt.%) observed in our Udachnaya–East samples is unique (c.f. data in Kjarsgaard et al., 2009). High "loss on ignition" values (LOI = 6.7–14.7 wt.%) are largely due to volatilisation of abundant carbonates, chlorides and sulphates, whereas the contribution from H₂O-bearing minerals to LOI is minimal.

The elements (Na, Cl, K, and S) present in water-soluble minerals (chlorides, carbonates and sulphates) in the groundmass show correlations with each other and with H_2O . For example, the alkali elements correlate positively with both Cl and S (Figs. 6 and 7) reflecting the association of Na- and K-bearing chlorides (halite and sylvite) and sulphates (aphtitalite). Sodium and Cl contents are highest and most variable when H_2O is low (<0.5 wt%), but remain consistently low

(< 0.7 wt.%) in samples with higher H₂O (Fig. 6). This is clearly a result of meteoric water ingress, progressive dissolution of chlorides, and partial alteration of olivine to serpentine.

2.4.2. Trace elements

Primitive-mantle normalised trace element diagrams show strong enrichment in the most incompatible elements and depletion in heavy rare-earth elements (REE) and Y, resulting in very steep slopes (Fig. 8a and Table 1). All samples have broadly parallel trace element patterns and are characterised by negative anomalies in large-ion lithophile elements (LILE, e.g. K, Sr, Ba, Pb), some high-field strength elements (HFSE, e.g., Zr, Hf, Ti, P) and yttrium. The depletion in Ti relative to elements of similar incompatibility (e.g., $(Ti/Gd)_n = 0.88 \pm 0.19)$ is difficult to reconcile with a proposed affinity of kimberlites to high-Ti magmas (Mitchell, 2008). Primitive mantle-normalised REE patterns are almost linear, with strong enrichment in LREE (Fig. 8b); the $(La/Yb)_n$ ratio (138 ± 19) is within the typical range for kimberlites world-wide (80-200). The overall variations in the immobile trace elements increase from HREE to LREE from a factor of 2 to a factor of 2.8. LREE fractionation is high and near-constant in all studied samples ((La/Sm)_n = 7.5 ± 0.4), which reflects extremely low degrees of partial melting. Similarly, the heavy REE are strongly fractionated (e.g., $(Gd/Yb)_n = 7.5 \pm 1.0$), reflecting the presence of residual garnet in the mantle source.

The high contents of strongly compatible elements (Co, Ni) in the studied kimberlites reflect accumulation of olivine (SiO₂ and MgO) (Fig. 5 and Table 1), however, MgO does not correlate with Cr, an even more compatible element. Other compatible elements (Sc, Mn, Cu, Zn, Ga) correlate positively with each other and the REE, possibly representing variations in the non-olivine components in this suite of rocks. An interesting geochemical feature, never recorded in kimberlites or other ultramafic rocks (e.g. picrites, komatiites), is a correlation between most compatible Cr (mostly hosted by Cr-spinel) and the lithophile trace elements, including the most incompatible ones (e.g., Nb; Fig. 9).



Fig. 4. Backscattered electron images showing crystallisation of salt and hydrocarbonate minerals on polished surfaces of most "salty" kimberlite samples. This interpreted to be an interaction with moisture in the air.

2.4.3. Stable isotope composition (O, C) of carbonate fraction

Stable isotope compositions were analysed in the Central Science Laboratory, University of Tasmania carbonate isotope data using a modified method of McCrea (1950). Samples were reacted in sealed, evacuated Pyrex glass tubes with 93% H_3PO_4 at 50 °C in a water bath for 24 h. The generated CO₂ was separated from any traces of water vapour by passing it through a trap at the freezing point of acetone (-95 °C), before collection under liquid nitrogen. The CO₂ was analysed on a Micromass Optima Stable Isotope mass spectrometer using a reference gas calibrated against NBS-19. Results are expressed relative to V-SMOW (for oxygen) and PDB (for carbon). Reproducibility

is \pm 0.06‰ for δ^{13} C and \pm 0.1‰ for δ^{18} O based on numerous analyses of the ANU-M1 standard calcite.

The C budget in the studied Udachnaya–East kimberlite samples is controlled by various carbonates, notably calcite, Na–Ca–carbonate, and alkali–Ca–carbonate. "Bulk" $\delta^{13}C_{PDB}$ values vary from -1.6% to -5.3%. (Fig. 10 and Table 1; average $-3.4 \pm 0.8\%$) and are within the range of compositions observed in other Siberian kimberlites ($\delta^{13} C = -1.3$ to - 9.9%; Galimov and Ukhanov, 1989), carbonates from other kimberlite rocks ($\delta^{13} C = -1.2$ to -8.9%; e.g., Deines and Gold, 1973; Kirkley et al., 1989; Kobelski et al., 1979; Sheppard and Dawson, 1975; Wilson et al., 2007), magmatic carbonatites ($\delta^{13} C = -2$ to -7%; e.g., Deines, 1989; Deines and Gold, 1973; Keller and Hoefs, 1995; Keller and Zaitsev, 2006; Taylor et al., 1967; Zaitsev and Chakhmouradian, 2002) and diamonds belonging to the peridotite paragenesis ($\delta^{13} C = -2$ to -9%; e.g., Cartigny, 2005). δ^{13} C in our samples increases with increasing CaO and CO₂ contents (Fig. 11).

 $\delta^{18}\text{O}$ values are in the range of + 12 to + 18‰, except for two samples (>20‰, Fig. 10); these samples also have the lowest δ^{13} C. The oxygen isotope ratios in the Udachnaya–East carbonates are in the middle of the range reported for magmatic carbonates in carbonatites ($\delta^{18}\text{O}=4$ to 28‰; Deines and Gold, 1973) and at the high end of the compositional field for carbonates in kimberlites from Siberia, South Africa and Canada ($\delta^{18}\text{O}=2$ to 23‰; Fig. 10). A positive correlation between $\delta^{18}\text{O}$ in the carbonate fraction and H₂O in the bulk Udachnaya–East samples is noted (Fig. 11), but no other significant correlations with measured petro- and geochemical parameters (Supplementary Table) have been found.

3. Discussion

3.1. How fresh are the Udachnaya-East kimberlites?

The kimberlite samples studied here, from a block of kimberlite located at the 400-600 m mine level within the Udachnaya-East pipe, are distinct from the kimberlite found higher up in the same pipe, from those in the twin Udachnaya-West pipe, and from kimberlites elsewhere, in containing no serpentine after olivine. Serpentinisation of olivine requires water, which is sourced either from the magma (deuteric) or from the crustal host rocks. The absence of serpentine is consistent with bulk rock water contents in many of our samples that are unusually low for kimberlites (<1 wt.% in 14 out of 28 samples). The low H₂O contents in our samples are coupled with extraordinary enrichment in Na₂O (up to 6 wt.%), hosted in water-soluble alkali carbonates; where H₂O contents are higher (>1 wt.%), Na₂O decreases below 0.5 wt.% (Fig. 6). Both components are negatively correlated on the log-log plot (Fig. 6). In contrast, H₂O contents in all other hypabyssal kimberlite compositions reported to date, including the "archetypal" kimberlites from South Africa and Lac de Gras, Canada (see review in Kjarsgaard et al. (2009), are>3 wt.% while Na₂O contents are low (<0.4 wt.%, Fig. 6). High H₂O in ultrabasic melts (c.f. standard model) is inconsistent with the strongly reduced H₂O solubility in such melts at crustal pressures (e.g., Newman and Lowenstern, 2002), while low Na₂O is atypical of terrestrial magmas. The Na₂O contents in altered whole rocks are significantly lower (by a factor of 3-30) than in melt inclusions in primitive olivine and Cr-spinel phenocrysts from the same samples (e.g., Kamenetsky et al., 2010). This implies that Na is removed from the groundmass where water is abundant, and suggests that H₂Orich and Na₂O-poor compositions in "archetypal" kimberlites result from post-emplacement modifications caused by common alteration of what may have been water-poor and sodium-rich rocks similar to those at Udachnava-East.

In addition to alkali carbonates, the anhydrous groundmass of our Udachnaya–East kimberlites contains another set of water-soluble minerals, represented by Na-K chlorides and sulphates. Collectively, this mineralogy confirms the remarkably good preservation of many of our samples. The "dryness" of the Udachnaya–East samples coupled

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Selected analyses of Udachnaya-East kimberlites, representing ranges in major, trace and volatile element compositions.

Sample	K25/05	Uv-k1-05	Uv-k1-10	K2-03	YBK-3	YBK-1	K4/05	YBK-0	K24/04
Depth of sampling	500-520	440-480	440-480	440-480	<450	<450	440-480	<450	480-500
SiO ₂	29.72	27.26	24.82	29.95	25.24	26.08	26.48	27.06	25.88
TiO ₂	0.85	1.03	1.22	1.33	1.40	1.12	1.21	1.23	1.75
Al ₂ O ₃	1.87	1.8	1.6	2.03	2.11	1.74	1.66	2.13	2.27
FeO	7.53	7.07	6.86	8.53	6.92	7.16	7.57	7.63	9.86
MnO	0.13	0.12	0.12	0.15	0.13	0.13	0.14	0.15	0.2
MgO	32.61	29.92	28.64	32.66	27.79	29.59	30.18	29.41	31.54
CaO	13.25	9.44	11.47	9.54	12.41	12.04	12.62	12.70	13.96
Na ₂ O	0.43	6.23	6.16	3.94	5.06	4.33	3.49	3.47	1.08
K ₂ O	1.14	1.88	1.82	1.61	2.23	2.17	1.86	1.85	0.86
P ₂ O ₅	0.34	0.34	0.36	0.45	0.41	0.42	0.46	0.49	0.82
Cl	0.21	5.68	6.11	1.34	3.11	2.97	2.35	2.24	0.08
LOI	10.68	7.84	9.55	6.74	11.34	10.72	10.3	10.28	10.41
Total	98.76	98.60	98.72	98.27	98.64	98.90	98.32	99.08	98.70
S	0.05	0.31	0.27	0.28	0.33	0.27	0.24	0.22	0.06
	9.6	/./	9.4	6.3	10.71	10.27	10.1	9.83	9.9
H ₂ O	1.04	0.17	0.16	0.42	0.63	0.45	0.23	0.45	0.56
	0.77	0.75	0.81	0.83	1.13	0.99	0.85	0.90	0.50
II Ph	0.07	0.07	0.08	0.07	0.10	0.06	0.09	0.08	0.12
RD	451	462	199	472	00.J 1211	04.9 1172	502	1120	507
Da W	204	402	400	4/2	1/1	102	2 71	0.07	257
Th	7.16	7.48	8.49	9.43	9.14	10.71	11 73	11 69	18.63
II	1.10	1.86	2.05	2 15	2.14	4 19	2.52	2.80	2.87
Nh	100	105	12.05	141	139	131	152	153	205
Та	4 95	5 30	676	633	823	7 14	6.88	8 17	11 37
La	54.3	62.1	68.4	73.0	74.9	81.3	87.4	97.4	133
Ce	98	106	119	135	129	140	159	167	247
Pb	5.08	3.99	5.19	4.20	6.98	5.35	3.94	3.53	3.87
Pr	10.1	11.0	12.4	13.9	13.47	14.71	16.2	17.51	26.1
Мо	1.82	2.09	1.94	3.98	1.61	1.14	2.28	1.21	1.36
Sr	1018	689	780	881	897	838	937	892	1070
Nd	35.0	37.7	42.8	48.4	44.8	48.9	55.8	58.2	90.7
Sm	4.96	5.16	5.75	6.59	6.03	6.53	7.46	7.80	12.28
Zr	77	77	90	104	101	98	111	115	181
Hf	1.75	1.86	2.12	2.33	2.25	2.18	2.56	2.49	4.25
Eu	1.31	1.31	1.45	1.71	1.58	1.73	1.92	2.03	3.08
Sn	1.04	1.13	1.10	1.31	2.69	4.52	1.07	1.52	3.13
Sb	0.21	0.14	0.15	0.20	0.18	0.14	0.13	0.13	0.14
Ti	5197	6689	7966	8991	8379	6741	8380	7371	10460
Gd	3.11	3.22	3.53	4.10	3.78	4.04	4.55	4.90	7.30
ID	0.36	0.39	0.40	0.47	0.43	0.46	0.51	0.56	0.82
Dy	1.66	1.03	1.76	1.99	1.94	2.02	2.26	2.51	3.44
LI	21.3 7.17	13.7	15.0	12.0	13.3	12.2	13.0	13.9	20.0
Y Uo	/.1/	0.82	7.40	8.13	7.75	/./3	8.92	10.25	12.57
ПU Fr	0.27	0.27	0.28	0.50	0.30	0.52	0.54	0.39	1.04
Tm	0.01	0.08	0.00	0.05	0.02	0.75	0.75	0.55	0.12
Vh	0.07	0.08	0.42	0.03	0.08	0.03	0.03	0.10	0.12
Iu	0.05	0.06	0.06	0.45	0.40	0.06	0.06	0.08	0.09
Be	1 1 2	1 33	1.04	0.00	1 41	0.00	0.72	1 33	1.05
Sc	8.40	8.16	8.93	11 13	13.1	11.4	10.94	12.85	17.04
V	68	88	94	107	114	93	104	102	119
Cr	807	869	822	1227	1755	1002	1223	1167	1601
Mn	974	970	936	1232			1202		1478
Со	79	79	71	90	72	77	81	79	79
Ni	1288	1204	1002	1332	995	1102	1146	1053	958
Cu	45	49	49	58	55	55	58	64	83
Zn	53	52	51	66	58	59	59	61	72
Ga	3.61	3.48	3.39	4.22	5.25	4.68	3.49	6	6.28
δ ¹³ C _{PDB}	- 1.6	-3.8	-4.1	-4.8	- 3.1	-3.4	- 3.2	- 3.3	-3.4
$\delta^{18}O_{SMOW}$	17.6	14.5	15.6	12.3	14.4	13.8	12.6	13.0	13.0

Major elements, Cl, S, LOI (loss on ignition), CO₂ and H₂O are in wt.%, trace elements are in ppm, stable isotope values are in ‰.

Depth of sampling (in meters) reflect most possible position in the mining pit for most samples taken from stockpiles.

Complete data set can be found in Supplementary Table.Complete data set can be found in Supplementary Table.

with enrichment in alkalis, chlorine and sulphur (Figs. 6 and 7) suggests these compositional features are inherently related and of primary origin. The trend from high Na and low H₂O towards low Na and higher H₂O in altered Udachnaya samples is interpreted to reflect degradation of the samples and removal of primary magmatic Na-H₂O signatures. This is supported by comparison with observations made at the active Oldoinyo Lengai volcano in Tanzania. Alkali carbonatites at Oldoinyo Lengai are H_2O -poor and Cl-rich when erupted, but gain H_2O and lose Na rapidly (hours to days) thereafter (e.g., Zaitsev and Keller, 2006; Zaitsev et al., 2008). This degradation is due to secondary alteration as the carbonatite melts themselves are unlikely to develop an aqueous fluid capable of removing hydrophile elements (Gittins, 1989).

We consider the Udachnaya–East samples with lowest H_2O and highest Na_2O , Cl and S (Fig. 6 and Table 1) to be "least altered", in



Fig. 5. Compositional parameters of the Udachnaya-East kimberlite representing olivine (Mg, Si, Ni, Co) and carbonate (CO₂) components.



Fig. 6. Relationships between contents of alkali elements, chlorine, water and sulphur. Two trends are identified and represent the processes of leaching chloride out (*solid line*) and pervasive hydration causing alteration of carbonates and sulphates (*dashed line*). Compositional covariations of Na₂O and H₂O in the Udachnaya–East kimberlites are compared with those in"archetypal" kimberlites from South Africa, Siberia, W. Greenland, India and Canada (*crosses*, numerous literature sources).



Fig. 7. Covariation of sulphur with alkali elements, reflecting presence and abundance of aphtitalite $(Na_{0.25}\,K_{0.75})_2SO_4\!.$

the sense that very small degrees of post-magmatic change may be difficult to detect; alteration of essentially non-silicate groundmass of kimberlites is not a linear process. Unlike silicate minerals and glass, chlorides are ductile and can act to 'seal' the rock by preventing water ingress via fractures (the Russian navy used sugar to achieve a similar effect to protect naval mines, see http://ru.wikipedia.org/? oldid=37317903). However, once the chloride "seal" is leached and removed by groundwaters, the rest of the groundmass assemblage and Na-Ca carbonate are prone to alteration. This process is well illustrated by the rapid degradation (dissolution and re-deposition) of water-



Fig. 8. Primitive mantle – normalised (after Sun and McDonough, 1989) lithophile trace element composition of the Udachnaya–East kimberlites.



Fig. 9. Covariation of Nb (incompatible lithophile) and Cr (compatible metal) in the Udachnaya–East kimberlites and other carbonate-rich kimberlites (*crosses*), such as Wesselton, South Africa (Shee, 1985), Jericho pipe, Canada (Kopylova and Hayman, 2008; Price et al., 2000) and Ekati property, Canada (Nowicki et al., 2008).

soluble components on polished surfaces of our kimberlite samples (Fig. 4) when left in air, and by two contrasting trends (leaching of chloride and alteration of carbonates/ sulphates) on the diagrams showing relationships between Cl and H₂O, K₂O and S (Fig. 6). Additionally, the



Fig. 10. Stable isotope (O and C) compositions of the Udachnaya–East kimberlites compared to other rocks, shown by fields: 1 – carbonates of the Siberian craton (Brasier and Sukhov, 1998); 2 – Siberian kimberlites (Galimov and Ukhanov, 1989); 3 – South African and Canadian kimberlites (Deines and Gold, 1973; Fedortchouk and Canil, 2004; Kirkley et al., 1989; Price et al., 2000); 4 – kimberlites from Lac De Gras, Canada (Wilson et al., 2007). The kimberlite data for the δ^{18} O histogram is from (Deines, 1989).



V.S. Kamenetsky et al. / Lithos 152 (2012) 173-186

Recognition of mantle stable isotope compositions is complicated by isotopic variations between different phases within a single rock sample (Deines, 1989; Kobelski et al., 1979; Maruoka et al., 2004), and even within a single crystal (Boyd et al., 1987; Gurenko and Chaussidon, 2002). Stable isotope ratios in mantle-derived melts are controlled by the composition of the source, isotopic fractionation during melting (probably very small), possible exchange with country rocks during ascent to the surface, and especially by melt crystallisation and degassing during cooling. The factors influencing stable isotope fractionation are numerous and include, for example, composition of coexisting phases, pressure and temperature (e.g., Deines, 1989); however, our understanding of their cumulative impact on the whole system and individual phases is limited. Stable isotope work in kimberlites has its own problems because they are very heterogeneous and because they are so prone to post-emplacement change.

Measured δ^{18} O values for the Udachnava–East carbonate fraction are within the range defined by other kimberlites (Fig. 10), but outside the "mantle carbonate box" ($\delta^{18}O = 6-9\%$; see "CBT" field in Wilson et al., 2007). Differences in carbonate- δ^{18} O from carbonatites and kimberlites have been noted many times. For example, Deines (1989) states that "only 7% of the kimberlite analyses fall in range from 6 to 9‰, and there is a strong maximum at about 12%; similar to the values shown by many extrusive carbonatites". δ^{18} O in carbonates from the Wesselton kimberlite averages 11.7% (Kirkley et al., 1989) and a number of Canadian kimberlites, such as Leslie and Aaron (8.4–17.4‰; Fedortchouk and Canil, 2004) and Jericho (16.3-16.6%; Price et al., 2000) are characterised by carbonate oxygen isotope compositions heavier than those in carbonatites and kimberlites studied by Wilson et al. (2007). Clearly, the Canadian kimberlites, and by inference kimberlites from other provinces, are characterised by variable and often high carbonate– δ^{18} O values, even though these carbonates are considered to be truly magmatic (e.g., Fedortchouk and Canil, 2004; Price et al., 2000).

In our view, the divergence between δ^{18} O in Udachnaya–East olivine $(5.6 \pm 0.1\%;$ Kamenetsky et al., 2008) and the associated bulk carbonate component implies low equilibration temperatures (< 600 °C) rather than contributions from a crustal oxygen source. Such low temperatures are confirmed by our micro-thermometry results for olivine- and phlogopite-hosted melt inclusions (Golovin et al., 2007; Kamenetsky et al., 2004, 2007a, 2009c). Calculation of expected oxygen isotope fractionations in such a complex low-temperature magmatic system (e.g., sulphate, silicate, oxide and inferred fluid) requires knowledge of temperature, proportion and exact composition of components involved, and experimental data on the oxygen isotope partitioning, all difficult to constrain with confidence. We therefore contend that elevated δ^{18} O in Udachnaya–East carbonate minerals is not necessarily a sign of crustal contamination as implied by Kjarsgaard et al. (2009).

Further insights are once again provided by observations at Oldoinyo Lengai. Within days of eruption, δ^{18} O values in natrocarbonatite lavas increase from +6.5% in the gregoryite–nyererite rocks to +11.8-+12.4% in the nyerereite carbonatite with hydrous Na–Ca carbonate, gaylussite Na₂Ca(CO₃)₂•5H₂O. (Keller and Hoefs, 1995; Keller and Zaitsev, 2006). As equilibration with atmospheric moisture progresses, δ^{18} O rises ever more, reaching +15.5-+18% in the pirssonite Na₂Ca(CO₃)₂•2H₂O carbonatites and +23-+27% in the calcite carbonatites. The studied Udachnaya–East samples, collected from the stockpiles, have been exposed to the air for several (not known exactly) years. Thus, if analogy with Oldoinyo Lengai is valid, carbonate δ^{18} O would be expected to have risen relative primary values over the time of stockpiling.

The results for Udachnaya–East show a positive correlation between carbonate $\delta^{18}O$ and bulk rock H₂O contents (Fig. 11). Carbonates in severely altered Udachnaya samples show extreme $\delta^{18}O$ (28.3 \pm 4.4‰; Bratus' et al., 1998), suggesting low-temperature isotope exchange with surface waters. The lowest $\delta^{18}O$ values, recorded in kimberlite groundmass carbonate (~12‰) and chloride-carbonate nodules in the

Fig. 11. Covariation between carbon isotope compositions and a carbonate component (Ca, CO₂), reflecting fractionation of carbonate minerals, and between oxygen isotope compositions and H₂O, reflecting hydration of samples.

lack of correlations between fluid-mobile (e.g., Na, K, Cl, S, Cs, Rb, Ba, U, Pb, Mo, and Sr) and immobile (e.g., REE, HFSE) lithophile elements suggests that post-magmatic redistribution of certain elements still occurred.

3.2. Do Udachnaya-East kimberlites fit into "mantle oxygen isotope box"?

The unusual compositions we have reported for kimberlites from Udachnaya-East have been highly controversial. Two areas appear particularly contentious: our interpretation of these compositions as "fresh" or "least altered" (Kjarsgaard et al., 2009) and our assertion that they represent mantle-derived melt (Kostrovitsky et al., 2012). Critics cite the C-O stable isotope compositions of our rocks (Table 1 and Fig. 10) to support their arguments. For example, Kjarsgaard et al. (2009) observed that our carbonate δ^{18} O values "fall outside the primary carbonatite carbonate box", towards isotopically heavier carbonate oxygen. Moreover, our $\delta^{13}\,\text{C-}\delta^{18}\text{O}$ data appear to trend towards those reported for Cambrian sedimentary carbonates of the Siberian craton (Fig. 10), encouraging suspicion that high chloride and sulphate levels may originate through contamination of the kimberlite melt by sedimentary evaporites. Although we have shown that radiogenic isotope (Sr, Nd, Pb) compositions of the water-soluble, labile minerals in the groundmass of least altered Udachnaya-East kimberlites are consistent with a mantle origin and free of obvious sedimentary contributions (Kamenetsky et al., 2009c; Maas et al., 2005), the high δ^{18} O values of the carbonate fraction require additional comment.



Fig. 12. Correlation between FeO in the kimberlite groundmass (after substraction of the olivine component, see text for details) and lithophile and metallic trace elements of different incompatibility and affinity.

same samples (12.3–13.9%; Kamenetsky et al., 2007a), are considered here as the best approximation of "primary magmatic" compositions at the temperature of solidification. However, we cannot exclude that some carbonates may have had even lower δ^{18} O prior to exposure to the air.

3.3. Two mantle components in kimberlites

Petrographic features (Figs. 1–4) and geochemical trends (Figs. 5, 8 and 9) of the Udachnaya–East kimberlites allow reconstruction of their parental magmatic liquids. The ultramafic composition of the whole rocks, expressed in high MgO contents (Fig. 5 and Table 1), is controlled by a large proportion of magnesian olivine $(55 \pm 6\%)$, whereas low SiO₂ and Al₂O₃ and high CaO contents reflect significant quantitites of the aluminosilicate-free components (carbonates, chlorides, sulphates and oxides), as well as the Si-undersaturated composition of the main kimberlite silicates–olivine, phlogopite, as well as serpentine and monticellite, if present. Anticorrelations between olivine-hosted (Mg, Si, Ni, Co) and carbonate-hosted (Ca, CO₂) components (Fig. 5, Supplementary Table) suggest that their host mineral phases are mutually "exclusive".

An estimate of the aluminosilicate and carbonate-chloride-sulphate components can be made by mathematically removing the olivine content. For this calculation, we assume that the carbonate component lacks Ni, which is mostly hosted in olivine (Fig. 5). The amount of olivine in a given Udachnaya–East kimberlite is calculated using an average olivine composition with 89.5 mol.% Fo and 2180 ppm Ni (Kamenetsky et al., 2008; see also Supplementary Table). These estimates of olivine contents are probably somewhat low because the model Ni concentration of 2180 ppm is based on surface measurements and fails to take

into account that the interior of euhedral olivine grains tends to have lower Ni contents than the grain surfaces. Nevertheless, the calculated olivine component (46-67 wt.%, Supplementary Table) is consistent with estimates for other hypabyssal kimberlites (e.g., prior to nearsurface emplacement the "magmas' which form these rocks consist on average of multiple generations of macrocrysts (c. 25 vol.%) and microphenocrystal olivine (c. 25 vol.%) incorporated within a Ti-rich, H₂O-bearing carbonate-silicate liquid (c. 50 vol.%)) (Mitchell, 2008). Subtraction of the olivine component from the whole rock compositions shows that apart from the dominant carbonate-chloride component the kimberlite groundmass contain an aluminosilicate component (e.g. phlogopite), and Fe-Ti-bearing oxide component (e.g., Ti-magnetite, Ti-rich chromian spinel, rutile and perovskite). The carbonate component of the groundmass is devoid of significant quantities of MgO and SiO₂ (at most 10 wt.% each, as it follows from the intersection of the "olivine control" line at 0 ppm Ni).

The amount of "residual" FeO in the rocks after subtraction of the olivine component varies and correlates well with the trace elements (Fig. 13), suggesting coupled enrichment of the groundmass (i.e., melt component) in Fe-bearing and trace element bearing minerals. Moreover, gravitational settling and accumulation of heavy minerals in the hypabyssal kimberlites is independently supported by a positive correlation between highly incompatible Nb and other trace elements hosted by perovskite (Kamenetsky et al., 2009c) and highly compatible Cr hosted by Cr-spinel; correlations of this type are also observed in some other carbonate-rich kimberlites (Fig. 9). On the other hand, the "excess" of SiO₂ after subtraction of olivine correlates well with Al₂O₃ and HREE (Fig. 12), thus defining the amount of lithospheric garnet and orthopyroxene, dissolved in the carbonate-chloride melt during its formation and ascent to the surface (e.g., Kamenetsky et al., 2009a).



Fig. 13. Correlation between SiO_2 in the kimberlite groundmass (after substraction of the olivine component, see text for details) and garnet- and orthopyroxene-hosted major (Al₂O₃) and trace (Yb) elements.

3.4. Contrasting views on kimberlite parental melt

The parental kimberlite melt compositions proposed here essentially carbonatite (+ chloride) rich in sodium and poor in H_2O differs markedly from the ultrabasic/ultramafic model parental melt compositions proposed by others (Becker and le Roex, 2006; Edgar and Charbonneau, 1993; Edgar et al., 1988; Harris et al., 2004; Kjarsgaard et al., 2009; Kopylova et al., 2007; le Roex et al., 2003; Nielsen and Sand, 2008; Price et al., 2000). Based on "aphanitic" kimberlites from South Africa, Canada and Greenland, these model melt compositions show wide ranges in SiO₂ (18–35 wt.%), MgO (20–34 wt.%) and H₂O (5-12 wt.%) which reflect the dominance of olivine and serpentine over the carbonate component. To our knowledge, an explanation for such high H₂O contents in ultramafic melts (at low pressures) has not yet been provided. Some authors consider even more magnesian precursor melts, even though the compositions of "aphanitic" kimberlites overlap with those of komatiites (Harris et al., 2004). Moreover, there is no consensus on how to define the term "aphanitic" (i.e. absence of olivine macrocrysts) as applied to kimberlites: the thresholds, used by different authors, for the size of olivine phenocrysts and amount of olivine macrocrysts vary by an order of magnitude. Surprisingly, there are no detailed mineralogical studies of "aphanitic fresh" kimberlites focused at recognising olivine zonation and compositions. The euhedral olivine (olivine-II; Kamenetsky et al., 2008) in the "aphanitic" kimberlite in this study (Fig. 1a) is characterised by high-Fo cores (Fig. 1f) which are thought to be derived from lithospheric mantle, leaving < 50% of this olivine to be formed from the kimberlite melt (25% according to Mitchell, 2008, and even<5% according to Brett et al., 2009). We conclude that aphanitic kimberlites contain very high proportions of inherited magnesian silicate (ultramafic) component even within their groundmass, and therefore are a poor proxy for the parental melt.

4. Concluding remarks

Unlike other kimberlites, the Udachnaya–East kimberlite contains no primary or secondary serpentine and very little water. It composed of magmatic alkali and alkali-earth carbonates, sulphates, and most importantly chloride-bearing minerals, which are not present in other kimberlites and terrestrial magmatic rocks, in general. We propose that the presence of such compositions at Udachnaya–East kimberlites reflects the lack of significant postmagmatic alteration in sections of this pipe. We also propose that similar minerals may have been present in other kimberlites but have been partially or completely lost due to more extensive alteration or sample preparation methods that involve water. A secondary origin of the chloride- and carbonate-bearing minerals within the pristine Udachnaya–East kimberlites from aqueous crustal fluids (e.g., Kjarsgaard et al., 2009) is highly unlikely based on petrographic and radiogenic isotope data (Kamenetsky et al., 2009c; Maas et al., 2005). Instead, we suggest that the key characteristics of kimberlitic magmas proposed by Kjarsgaard et al. (2009) – low sodium and high water contents – may relate to postmagmatic alteration that affected most kimberlites worldwide.

We propose that the Udachnaya–East kimberlite formed from carbonate magmas that were originally rich in Na, K and halogens, yet were essentially anhydrous and low in aluminosilicate components. Our melt inclusion data (Golovin et al., 2007; Kamenetsky et al., 2004, 2007a, 2009b, 2009c) indicate that crystallisation of this melt in the crust occurred at relatively low temperatures (<700 °C). Our work, published in a series of papers since 2004, further suggests that the initial kimberlite melt originated as a chloride-carbonate liquid in the mantle and evolved to become olivine-saturated through entrainment and partial resorption of mantle olivine and complete resorption of orthopyroxene crystals picked up from wall-rocks during ascent. This scenario forms the basis of a recent experimental model of kimberlite ascent by Russell et al. (2012); unfortunately, Russell et al. failed to properly acknowledge the ultimate origin of their ideas.

An important implication from the kimberlite melt composition proposed here is that it removes H₂O as a major control on the rheological properties of the Udachnaya-East kimberlite magma. The apparent similarity of the inferred Udachnaya-East kimberlite melt and natrocarbonatites from Oldoinyo Lengai suggests that kimberlite magmas were mobile not because of their high water content but because they were carbonatitic. If the Oldoinyo Lengai analogy holds, the kimberlite magma may have been characterised by exceptionally low density and viscosity (<2170 kg/m³ and 0.1–5 Pa s, respectively at Oldoinyo Lengai), ensuring rapid transport to the surface, even with entrained significant load of mantle xenocrysts and xenoliths. Radiogenic isotope (Sr, Nd, Hf, Pb) compositions for Udachnaya-East groundmass samples and individual minerals from both groundmass and mantle xenoliths (perovskite, halite, phlogopite, carbonates, clinopyroxene and garnet) confirm a mantle origin of the alkali-enriched carbonate-chloride melt component. The low concentrations and strong fractionation among HREE, as well as very low Al and Ga, point unequivocally to residual garnet in the source that resides in the lithospheric mantle. Enrichment in the incompatible elements is a result of either enrichment of the mantle source, or exceptionally low degrees of partial melting, or both.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.lithos.2012.04.032.

Acknowledgements

We thank P. Robinson, S. Gilbert, K. McGoldrick and C. Cook for analysing samples, and A. Sobolev, G. Yaxley, K. Faure, O. Navon, O. Safonov and G. Brey for fruitful discussions. The original manuscript was significantly changed to account for critical comments by M. Kopylova and anonymous reviewer. We appreciate editorial handling by G. Markl in the situation when the standpoints of the authors and reviewers were radically different. The work was supported by the Alexander von Humboldt Foundation (Germany) in the form of the Wolfgang Paul Award to A. Sobolev, the Friedrich Wilhelm Bessel Award to V. Kamenetsky and sponsoring the PERALK-CARB 2011 meeting in Tübingen, the Australian Research Council Research and University of Tasmania Professorial Fellowships and research funding to V. Kamenetsky and the Russian Foundation for Basic Research (project 10-05-00575) to A. Golovin.

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