# USING PEROVSKITE TO DETERMINE THE PRE-SHALLOW LEVEL CONTAMINATION MAGMA CHARACTERISTICS OF KIMBERLITE

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**ABSTRACT** (265 words)

It remains difficult to obtain reliable geochemical signatures of kimberlite magma from bulk rock studies due to the combined effects of crustal assimilation and element mobility during post-emplacement alteration processes. Groundmass perovskite ($CaTiO_3$), a typical accessory phase, from Orapa (Botswana) and Wesselton (South Africa) kimberlites have been used to evaluate the isotope and trace element composition of the pre-contamination magmas and the effects of shallow level contamination. In-situ trace element signatures of Orapa and Wesselton perovskite grains are broadly similar and unaffected by crustal contamination. Single grain $^{87}Sr/^{86}Sr$ isotope ratios of perovskites from Orapa (0.7030-0.7036) are significantly less scattered than bulk rock analyses (0.7063-0.7156), which are variably affected by contamination and late stage alteration. Initial $^{87}Sr/^{86}Sr$ isotope ratios of perovskites (0.7044-0.7049) from Wesselton overlap with the published whole rock studies on fresh hypabyssal kimberlites (0.7042-0.7047). The limited intra-kimberlite variation in Sr isotope ratios recorded by the perovskites are unlikely to be due to crustal contamination as the calculated liquid compositions in equilibrium with the perovskites analysed typically have >1500 ppm Sr, and most common crustal lithologies underlying these kimberlites have relatively low Sr contents and are not highly radiogenic. Calculated pre-shallow level contamination magma compositions of Orapa and Wesselton have significantly fractionated LREE and highly variable non-smooth trace element patterns. Initial Sr and Nd isotope ratios of both kimberlites fall on the mantle Nd-Sr array with enriched Sr and slightly depleted Nd signatures, similar to Group I kimberlites. Overall the trace elements and isotopic compositions of Orapa and Wesselton kimberlites are similar to the reported Group I kimberlites from Southern Africa, which are derived by very low degrees of partial melting from a LREE depleted metasomatised sub-continental lithospheric mantle (SCLM) source.

**Keywords:** Kimberlite, perovskite, magma composition, sub-continental lithospheric mantle

## 1. Introduction

Kimberlites are one of the more important rocks through which to study the geochemistry of the mantle. However, it can be difficult to establish the primary geochemical signatures of kimberlites as they typically contain considerable amounts of entrained material, and their bulk compositions may be strongly affected by secondary alteration after emplacement (Mitchell, 1986; Mitchell, 2008). Trace element characteristics, together with radiogenic ($^{87}Sr/^{86}Sr$ (Taylor Jr, 1980; McCulloch et al., 1983) and stable ($^{18}O/^{16}O$) (Eiler, 2001; Hoefs, 2009) isotope ratios are important tracers of crustal interaction with magmas of mantle origin (Smith, 1983; Fraser et al., 1985; Griffin et al., 2003). Variations in bulk rock $^{87}Sr/^{86}Sr$ ratios from kimberlites have been interpreted in terms of heterogeneous source characteristics and/or their interaction with the upper crust (Taylor Jr, 1980; McCulloch et al., 1983; Rollinson and Rollinson, 1993; Bachmann et al., 2007).

Careful sample preparation avoiding any visible contamination and cautious data interpretation has been used to minimise the effects of contamination and secondary alteration in kimberlitic bulk rocks (Le Roex et al., 2003; Becker and Le Roex, 2006; Tappe et al., 2013). However, it remains difficult to obtain reliable geochemical signatures from whole rock studies due to the combined effects of crustal assimilation and element mobility during post-emplacement alteration processes (Mitchell, 1986; Heaman, 1989). Recent developments in analytical technology have enabled analyses of either individual phases or mineral separates, which can circumvent these effects to a certain degree. Early-crystallising phases offer insights to the uncontaminated magma signature, and Malarkey et al. (2010) have suggested that phenocrystic olivine records the most representative Sr isotope signature of uncontaminated kimberlite magma. However, it remains difficult to find well-preserved olivine phenocrysts in kimberlites, as they are susceptible to serpentinisation during or after emplacement. Perovskite

($CaTiO_3$), a common groundmass mineral in kimberlites, is another phase that has been used to determine more robust Sr, Nd and Hf isotope signatures of the kimberlite magma (Heaman, 1989; Yang et al., 2008; Paton et al., 2009; Woodhead et al., 2009; Wu et al., 2010). Being a major repository of trace elements and REE, and with a very low Rb/Sr (<0.005) ratio, perovskite has great potential to record the Nd and Sr isotope ratios of uncontaminated kimberlite magma. It is also less susceptible to post-emplacement weathering compared to olivine. Moreover, the pre-degassing perovskites with mantle-like $\delta^{18}O$ values and the absence of perovskites with elevated $\delta^{18}O$ further suggest that they can be considered as a reliable archive of pre-contamination magma compositions (Sarkar et al., 2011). Recent LA-MC-ICP-MS studies have shown that $^{87}Sr/^{86}Sr$ ratios of perovskite from Indian, Chinese and Canadian kimberlites yield relatively uniform Sr isotope ratios compared to their corresponding bulk rock compositions (Paton et al., 2007b; Yang et al., 2009; Wu et al., 2010).

In this study, we report detailed geochemical analyses (trace element and Sr, Nd isotope ratios) of perovskites from Orapa (Botswana) and Wesselton (South Africa) kimberlites, so as to compare hypabyssal (Wesselton) and crater-facies (Orapa) kimberlites, and to determine the effects of shallow level contamination in kimberlitic magma. The geochemical characteristics of the magma, in equilibrium with perovskite, is estimated using the partition coefficients between kimberlite and perovskite, determined experimentally by Beyer et al. (2013).

# 2 Geology of the study area and samples

## 2.1 Orapa kimberlite

The Orapa A/K1 kimberlite is located in north-central Botswana, 240 km west of Francistown (Fig 1). It is the largest of a cluster of over sixty known kimberlite occurrences in this area. It is a

Group I kimberlite of Cretaceous age intruded into the Archean basement (granite-gneisses and tonalite) overlain by a sequence of Phaneorzoic Karoo sedimentary rocks and Jurassic basalt lavas of the Stormberg Formation (Carney et al., 1994; Field et al., 1997; Gernon et al., 2009). The kimberlite comprises two coalescing diatremes, which formed a single crater near the surface. Detailed mapping and borehole logging suggest the northern lobe intruded first and was then truncated by the southern lobe. The northern lobe is filled with layered pyroclastic kimberlite underlain by massive volcaniclastic kimberlite. The southern crater has more varied geology. The upper portion consists of epiclastic kimberlite mixed with shale, gritstone and sandstone. Below these epiclastics there are at least three phases of volcaniclastic kimberlites separated by basalt breccia (Field et al., 1997). Both pyroclastics and volcaniclastics of Orapa A/K1 kimberlite contain various fine-coarse lapilli and blocks of underlying basalt, sedimentary rocks and basement fragments (granite-gneiss). The matrix contains high proportions of eclogitic xenoliths and megacryst and macrocrysts of olivine (85%), garnet (7-10%), ilmenite (2%) and chrome spinel (1%)(Shee and Gurney, 1979). The apparent absence of peridotitic xenoliths might be due to the highly weathered nature of this kimberlite. The presence of diopside microlites and preliminary thermal remanent magnetism (TRM) studies indicate higher emplacement temperatures of the southern lobe (500-600$^{o}$C) than the northern lobe (<400$^{o}$C) (Field et al., 1997; Stripp et al., 2006; Gernon et al., 2009). The age of the Orapa kimberlite has been dated at 92±6 Ma using U-Pb TIMS zircon method (Davis, 1977; Allsopp, 1989). Fission track dating of zircons yielded ages of 92±6 Ma (Allsopp, 1989).

Several samples were collected from the different pyroclastic and volcaniclastic facies at the mine surfaces of the northern and southern lobes of the A/K1 pipe. Four drill cores were also chosen (three from the northern lobe: OREP 19, OREP 76 and OREP 97; one from the southern lobe: OREP 17) to collect samples from depths of up to 600 m from the floor of the mining level in July 2008. The least altered samples with minimum foreign materials were selected as hand specimens. Orapa kimberlite samples are heavily altered and dark green to black in colour, and most of the olivine phenocrysts are partially or completely serpentinised. In addition to olivine, phenocrysts of garnet, chrome diopside, and chrome spinel are set in a matrix of carbonate, serpentine, phlogopite, apatite, spinel, perovskite and ilmenite.

## 2.2 Wesselton kimberlite

The Wesselton kimberlite is situated 6.5 km southeast of Kimberley in the Northern Cape Province of South Africa and it is one of the five major diamondiferous kimberlite pipes found near Kimberley (Fig 1). The Wesselton kimberlite consists of a near surface kimberlite sill and dyke complex, which is cut by a kimberlite pipe made up of at least ten separate intrusions in its root zone (Shee et al., 1991). Although the Wesselton sill complex has not been dated isotopically, it predates the main pipe intrusion (Clement, 1982; Smith et al., 1989). Hawthorne (1968) suggests that there is no great time interval between the formation of the sills and the pipe, which is dated as Cretaceous in age (90±2 Ma) (Clement, 1982; Wu et al., 2010). The kimberlite sill complex is exposed in the 40 m level water tunnels at the Wesselton mine and it is directly related to and fed by precursor dykes in the immediate vicinity of the pipe. They make up part of the root zone kimberlite and are classified as hypabyssal-facies kimberlites. The sills intrude the contact zone between the upper Dwyka shales and the Karoo dolerite sill (Shee, 1985; Shee et al., 1991). The competent nature of dolerite is thought to have prevented breakthrough of the kimberlite magma to the surface and promoted the formation of kimberlite sills. The dolerite acted as a barrier to the upwelling kimberlitic magma, causing it to spread out laterally forming a stockwork of sills within the well-bedded Dwyka shales (Mitchell, 1986). Olivine macrocrysts, which are partially altered, are set in a fine-grained matrix containing fragments of shale and mantle xenoliths (White, 2005).

Samples for this study were selected from the pool of samples previously collected by Jenny White from the hypabyssal facies during her Masters project at the University of Bristol (White, 2005).

## 3 Analytical Procedures

After careful visual inspection, twenty-four samples were selected from Orapa; these included ten samples from three northern pipe cores (OREP NP), two samples from northern pyroclastics (NPK), six samples from southern pipe core (OREP SP), four samples from southern volcaniclastics (SVK) and two from southern pyroclastics (SPK). Eight samples from Wesselton were also selected for this study. A subset of eight samples thin sections from Orapa and five samples thin sections from Wesselton were prepared for petrographical and textural study of perovskite. Each sample was divided into two halves. One half was used for selective whole rock isotope studies and the other half was employed for perovskite grain separation. 0.5 to 1 kg of each sample was crushed to ca. 200µm, and perovskite grains were separated following standard heavy mineral separation techniques. Euhedral and relatively larger sized grains (50-70 µm) without any visible inclusions were handpicked and mounted in epoxy resin. The mounts were polished to expose a fresh surface of the perovskite grains. BSE images were taken from individually polished grain mounts using a Hitachi S-3500N SEM with a 15kV- 20kV accelerating voltage at the University of Bristol, UK. Major and minor element concentrations of perovskite were analysed in a Cameca SX100 electron microprobe with an accelerating voltage of 20 kV and beam current of 20 nA at Bristol. Analytical uncertainties (one sigma error) are 2-5% relative for major elements ($TiO_2$, CaO) but higher (10-15%) for the minor and trace elements.

3.1 In-situ trace element and isotope analyses

Except in-situ Sr isotope analysis, which was conducted at University of Alberta, other in-situ studies were done at University of Bristol, UK. In-situ trace element (and REE) measurements were conducted using a Thermo Finnigan Element2 ICP-MS coupled with a New Wave UP 193HE ArF Excimer laser ablation system operated at 193 nm with a 4 hz pulse rate. Helium was used as a carrier gas and mixed with Ar into the plasma. Laser spot size was between 30-40 µm depending on the size of the grains. NIST 612 multi-element standard glass was used as a primary standard and to tune the instrument. NIST 610 glass and Ice River perovskite were used as secondary standards to monitor accuracy, instrumental drift and matrix effects. Due to the large variation of concentrations between different REE in perovskite, LREE were analysed in `analogue' mode while HREE and other low abundant elements were analysed in `counting mode'. Each spot analysis consisted of approximately 30 s background acquisition followed by 60 s sample data acquisition. The trace element abundances were calculated using GLITTER 4.0 software (GEMOC, Macquarie University; (Achterbergh et al., 2001) and calibrated using $^{40}$Ca as an internal standard and NIST 612 glass as an external reference material. The analytical uncertainties are within 5-10% (1$\sigma$) for all elements.

For in-situ isotope analyses (Sm-Nd) the laser was attached to a Thermo Finnigan Neptune MC-ICP-MS. Helium was used as carrier gas and mixed with Ar after the laser cell in a mixing bulb. $N_2$ was also introduced to keep the oxide generation minimal ($^{238}$U$^{16}$O/$^{238}$U <0.5%) following the procedures of Foster and Vance (2006). During laser ablation, Sm interference on $^{144}$Nd was corrected by measuring the $^{147}$Sm/$^{149}$Sm ratio directly on the sample, and by reverse mass bias correcting and peak stripping of $^{144}$Sm. The $^{143}$Nd/$^{144}$Nd ratio was then mass bias corrected using the conventional normalisation $^{146}$Nd/$^{144}$Nd ratio of 0.7219 and an exponential law, following the method of McFarlane and McCulloch (2007). Instead of using a standard Nd solution (e.g. La Jolla Nd standard solution) NIST 610 standard glass was used to calibrate the instrument. The average $^{143}$Nd/$^{144}$Nd ratio of NIST 610 (Sm/Nd ratio ~1) during a period of eight months was 0.511954 ± 0.000028 (2SD, n=47). In order to evaluate instrumental drift and matrix effects into the measured isotope ratio, Ice River perovskite and in-house titanite reference materials (SP-HUL, SP-REN) with variable Sm/Nd ratios (Sm/Nd ratio 0.2-0.3) were also analysed as secondary standards.

In-situ Sr isotope analyses were conducted using a UP213 nm laser system coupled to a Nu Plasma MC-ICP-MS at the Radiogenic Isotope Facility at the University of Alberta. At the beginning of each analytical session, parameters for the introduction system and the ion optics were optimized by aspirating a 100 ppb solution of the NIST SRM 987 Sr isotope standard. Strontium isotope data were acquired in static, multi-collection mode using five Faraday collectors and a 40-60 µm laser spot size, 100% laser power, and 10 Hz repetition rate, delivering ~15 J cm$^{-2}$ energy density to the sample. Isobaric interference of $^{87}$Rb on $^{87}$Sr was corrected using the natural abundance ratio of $^{85}$Rb/$^{87}$Rb of 0.3856 and an exponential law. It is possible to correct for the Rb interference quite accurately on perovskite due to their negligible Rb content (Rb/Sr =0.06) (Ramos et al., 2004; Paton et al., 2007b; Yang et al., 2009). Other interferences including Ca dimer and doubly charged rare earth elements were corrected offline following the method proposed by Ramos et al. (2004); Paton et al. (2007b). Laser data were partially monitored by repeated analyses of the in house Ice River perovskite standard with a reported value of 0.702838 ± 0.000051 by TIMS (Tappe and Simonetti, 2012). Following two laser ablation analytical sessions, an average value of 0.70298 ± 0.00021 (n=21) was measured for the Ice River standard.

## 3.2 Conventional solution isotope analyses

All solution analytical studies (Sr and Sm-Nd) were performed at the University of Bristol, UK. Individual perovskite grains with minimal visible surface alteration were handpicked under a binocular microscope. Perovskite solution works were done on single grains while approximately 50-100 μg of visibly unaltered samples were used for whole rock analyses. Because of their microscopic size, individual grains of perovskite were not weighed. During picking, the volume of each grain was calculated (assuming a cubic grain) and that yielded a total sample weight of around 3-5 μg per grain. The sample analysis technique is very similar to the method described by Foster and Vance (2006). Perovskite grains were first leached in 1N HCl for 15 min to remove surface contamination. Samples were further cleaned in an ultrasonic bath for 30 min in Milli-Q 18.2 MΩ water and acetone. The samples were then transferred into a PFA Teflon vial, spiked with a mixed $^{149}Sm$-$^{150}Nd$ tracer and digested in a mixed 15M $HNO_3$ and 24M HF solutions at 140°C-150°C for 48 hours. Nd and Sm were separated using standard cation exchange and Ln exchange columns. Rb and Sr fractions were collected during the cation exchange chemistry. They were converted into nitrates and Sr was separated from Rb by passing the sample through Sr-spec resin (Avanzinelli et al., 2005). A new Sr spec resin aliquot was used for each set of analyses.

Sm-Nd isotope ratios were measured in a Thermo Finnigan Neptune MC-ICP-MS. Mass fractionation of Nd isotopes was exponentially corrected by applying a $^{146}Nd/^{144}Nd$ ratio of 0.7219 outlined by Vance and Thirlwall (2002). 65 analyses of La Jolla Nd solution standard, during a period of 12 months, produced an average $^{143}Nd/^{144}Nd$ ratio of 0.511857 ± 0.000018 (2SD, n=65). Sr isotope ratios were measured in a Thermo Finnigan Triton thermal ionisation mass spectrometer (TIMS) using zone refined Re filaments. Isotope ratios were measured in dynamic mode, to nullify any drift of the detectors. Details of the instrumentation and procedure of sample loading on the Re filament are identical to that described in Avanzinelli et al. (2005). The average value of $^{87}Sr/^{86}Sr$ from NBS 987 was 0.710249 ± 0.000018 (2SD, n=40).

# 4 Results

## 4.1 Petrography

Perovskite is one of the minor groundmass phases (up to 10 volume %) in Orapa and Wesselton kimberlites. The grains are euhedral to subhedral in shape, and grain sizes range between 20-60 µm in diameter with some exceptional grains being > 100µm. Many grains are homogeneous although some show weak oscillatory zoning in BSE images. Most of the perovskite grains occur as discrete groundmass grains, but they also display complex intergrowths with spinel and form `garlands' around olivine phenocrysts (Sarkar et al., 2012). Serpentinised olivine and spinel inclusions within perovskite are common. Some perovskite grains appear fresh and unaltered while others are partially or completely altered. Altered grains are often fractured and replaced by calcite and rutile in the cracks. In some cases they have been completely replaced by rutile, although the original shapes are preserved as pseudomorphs.

Perovskite grains from Wesselton are larger (>50 µm) than those from Orapa. Apart from having similar textures to Orapa, perovskite also appears as a coexisting phase with earlier Ti bearing minerals, mostly groundmass ilmenite. In places, Wesselton perovskite occurs as inclusions within ilmenite or as remnants of early-formed grains, which currently exist as pseudomorphs. In general, perovskites from Wesselton look fresher and less altered than those from Orapa.

4.2 Major and trace element composition

Major and trace element analyses of perovskite from Orapa and Wesselton are listed in Tables 1-3. Major element compositions of Orapa perovskites remain close to ideal $CaTiO_3$ with CaO (36% to 37.2%), $TiO_2$ (52% to 54%) with minor amounts of FeO (0.9%-1.5%), $Nb_2O_5$ (0.9%-1.5%), $Na_2O$ (0.5%-0.9%) and REE Oxide (6%-9%), similar to the compositions of perovskites reported from kimberlites worldwide (Chakhmouradian and Mitchell, 2000; Chakhmouradian and Mitchell, 2001). Nb and REE are the principal substitutes for Ti while Na replaces Ca for charge balance (Boctor and Boyd, 1980; Boctor and Boyd, 1981). These perovskite grains also have high concentrations of Sr (2000-2300 ppm), Nb (5300-18600 ppm), Ta (660-1940 ppm), Zr (470-5300 ppm), Nd (5700-14000 ppm) and Sm (720-1400 ppm). There are no apparent compositional differences between perovskites from different parageneses or from different lithofacies of the Orapa kimberlite, and the average perovskite compositions of the North and South pipe are similar.

The Wesselton perovskites also have similar compositions to those from Orapa containing 5-9 % of trace elements and REE along with high CaO and $TiO_2$ contents (Table 1). The trace element contents of perovskite tend to be higher in Orapa than for those in Wesselton (e.g. La=~7000-13600 and ~4000-7000 times primitive mantle respectively). The primitive mantle-normalised REE patterns of the perovskites from all lithofacies from Orapa and Wesselton have smooth, highly fractionated trends with extreme LREE enrichment and no Eu anomalies (average $(La/Lu)_N$ from Orapa and Wesselton are ~2010 and ~1648 respectively) (Fig 2). In a primitive mantle-normalised multi element plot (spidergram), perovskite from both kimberlites exhibit extreme fractionation in LREE, U, Th, Nb and Ta and relative depletions in Pb, Sr and HFSE (Zr, Hf) (Fig 3).

4.3 Nd and Sr isotope ratios

The $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios of perovskite from both kimberlites, measured by in-situ and conventional isotope dilution methods, are listed in Table 2. The Nd isotope ratios, obtained by both processes on the same sample are identical within analytical uncertainties. The $^{143}Nd/^{144}Nd$ (measured by both methods) of perovskite from Orapa and Wesselton kimberlites vary between 0.512708-0.512771 (with an average 2 s.e. from individual analyses of ± 0.000035) and 0.512700-0.512708 (with an average 2 s.e. from individual analyses of ± 0.000008) respectively. The $^{147}Sm/^{144}Nd$ ratios of Wesselton perovskites (0.0809- 0.0826) are slightly higher than those of Orapa perovskites (0.0689-0774). However, the initial εNd of 161 analyses of perovskite by laser and solution methods from 24 samples from Orapa and Wesselton are tightly clustered between +1.19 to +2.94. Thirteen whole rock analyses from Orapa yielded lower and more scattered $^{143}Nd/^{144}Nd$ between 0.512420-0.512641 (with an average 2 s.e. from individual analyses of ± 0.000016) (εNd = -2.03 to +2.28)(Table 2).

Forty-seven TIMS analyses of individual perovskite grains from Orapa kimberlite range in $^{87}Sr/^{86}Sr$ between 0.703402-0.705407 (average 2 s.e. from individual analyses = ± 0.000010), and sixteen $^{87}Sr/^{86}Sr$ analyses from Wesselton perovskite vary from 0.704408 to 0.705580 (average 2 s.e. from individual analyses = ± 0.000019) (Table 3). Excluding a few outliers with relatively radiogenic Sr isotope ratios, which are interpreted as crustally contaminated, the $^{87}Sr/^{86}Sr$ ratios from Orapa perovskites are between 0.703402-0.704697 (4 excluded) and those from Wesselton vary between 0.704408-0.704898 (1 excluded). Twenty-nine in-situ Sr isotope ratios from Orapa perovskites have larger uncertainties but they tend to be lower and significantly less scattered between 0.70298-0.70363 ± 0.00037 (average 2 s.e. from individual analysis) (Table 3). Although very low quantities of analytes (total Sr ion signal between 0.2-0.5 V) produce relatively large analytical uncertainties during laser ablation Sr isotope analysis, there is less scatter in the $^{87}Sr/^{86}Sr$ ratios of perovskite. Perovskite grains from Orapa kimberlite are often quite fractured and filled with secondary minerals such as calcite. These fractures were avoided during in-situ laser ablation analysis. However, it is possible that some of these secondary contaminants were not completely leached from the cracks during whole grain dissolution and may have been responsible for the slightly higher and more scattered TIMS Sr isotope ratios in Orapa (Fig 4). We thus have used the $^{87}Sr/^{86}Sr$ ratios measured by the in-situ method to represent the isotopic composition of Orapa. No in-situ Sr analyses were undertaken on Wesselton perovskites during this study. Perovskites from Wesselton are relatively larger and less fractured with no calcite filled cracks. Moreover, the TIMS $^{87}Sr/^{86}Sr$ (0.704408-0.704898 ± 0.000019) values measured in this study agree well with the published in-situ data from perovskites from Wesselton (0.70448-0.70467 ± 0.00015) (Woodhead et al., 2009). Thus, the TIMS $^{87}Sr/^{86}Sr$ ratios have been used for the Wesselton perovskites. Due to their very low Rb/Sr ratios (<0.005) and the relatively young age of the kimberlites, no age correction was applied on the measured Sr isotope ratios to calculate the initial Sr isotope ratios. Thirteen whole rock analyses from Orapa yielded $^{87}Sr/^{86}Sr$ ratios ranging between 0.706378-0.715587 (average 2 s.e. from individual analyses = ± 0.000008) (Table 3).

# 5 Discussion

This study is concerned with the isotope and trace element compositions of kimberlite magma before it was modified by crustal contamination and/or post emplacement alteration.

## 5.1 Effects of contamination, and water-rock interaction

The bulk rock compositions of kimberlites are sensitive to the effects of contamination and post-emplacement alteration. Although kimberlites contain xenoliths from lithospheric mantle and the lower crust, a more evolved and isotopically enriched upper crust would modify the magma to a greater degree (Reiners et al., 1995). Near-surface liquid and meteoric water can also account for the secondary alteration of most of the minerals in many kimberlites (Stripp et al., 2006; Buse et al., 2010). Trace element characteristics, including mobile elements and $^{87}Sr/^{86}Sr$ ratios are typically used to explore crustal contamination in kimberlite magma.

In our dataset, there is relatively little difference between the trace element signatures of perovskites from Orapa and Wesselton kimberlites (Fig 3), and the primitive mantle-normalised REE patterns, measured by in-situ analyses, from the Orapa and Wesselton perovskites are very similar (Fig 2). Most of the mobile elements (Rb, Ba, K) are not compatible in the perovskite structure, except for Sr and its concentration is uniform (between 1900-2000 ppm) among all the perovskite grains analysed (Fig 5). Partition coefficient (D) of Sr between kimberlite magma and perovskite is close to unity (Beyer et al., 2013), thus the magma in equilibrium with perovskites also have homogeneous Sr content. This invariable Sr content of the magma can be used to argue against any considerable water-rock interaction. Both Orapa and Wesselton perovskites have very low Pb contents (<30 ppm) indicating minimal crustal interaction into the magma. The Orapa perovskites, and the kimberlite magma calculated to be in equilibrium with the perovskites, are well correlated in a La/Yb vs Sr/Yb diagram. They plot on a linear trend and do not scatter around the lower values where the possible contaminants plot (e.g. Archean crust, Granites, average continental crust) (see Fig 6) (Sarkar et al., 2011). Perhaps the strongest argument against considerable crustal contamination of the kimberlite magma from which the perovskite crystallised comes from the oxygen isotope signature of perovskites. $\delta^{18}O$ values of most of the perovskites from Orapa and Wesselton are around the mantle value of 4.2‰ while another group has negative $\delta^{18}O$ value, which has been attributed to fractionation during degassing (Sarkar et al., 2011). However, none of the perovskites have high $\delta^{18}O$, as expected if there was significant upper crustal contamination into the magma at this stage in its evolution.

Strontium isotope compositions can also be used as supporting evidence against significant crustal contamination of the magma from which the perovskite crystallised. $^{87}Sr/^{86}Sr$ ratios from bulk rock analyses from Orapa and Wesselton scatter between 0.7063-0.7156 (this study) and 0.7042-0.7047 respectively (Nowell et al., 2004; Becker and Le Roex, 2006) , while those of individual perovskites range between 0.7030-0.7036 in Orapa and 0.7044-0.7049 in Wesselton (Table 3). It has been suggested that the Sr isotope compositions from groundmass perovskite are more representative of the uncontaminated kimberlite magma than those from bulk rock studies, which are often contaminated (Paton et al., 2007a; Yang et al., 2009). Our data from Orapa and Wesselton perovskites are also in accord with this hypothesis. While whole rock studies on carefully chosen unaltered hypabyssal kimberlites from Wesselton have similar range in $^{87}Sr/^{86}Sr$ ratios (0.7042-0.7047), to what we found in perovskites (0.7044-0.7049), this hypothesis is more valid for fragmental, massive volcaliclastic or pyroclastic kimberlites as found in Orapa. However, perovskites from most of the South African kimberlites do not have uniform Sr isotopic compositions, as is seen in some of the Indian and Chinese kimberlites (Woodhead et al., 2009). The values and range in $^{87}Sr/^{86}Sr$ shown by both Orapa and Wesselton perovskites are typical of other kimberlites reported from South Africa (Nowell et al., 2004; Becker and Le Roex, 2006; Woodhead et al., 2009). Although it could be argued that this range in $^{87}Sr/^{86}Sr$ in perovskites from Southern African kimberlites might be due to upper crustal contamination, it is difficult to alter the Sr isotope ratios of the magma through interaction with most common crustal lithologies, because the calculated liquid compositions in equilibrium with the perovskite analysed typically have >1500 ppm Sr. Average Sr contents of the South African Group I kimberlites are also between 1100 – 1700 ppm (Le Roex et al., 2003). Sr isotope ratios are also in general insensitive to the timing of perovskite crystallisation due to the very small P-T window in which perovskite crystallises from kimberlite magma. Perovskites crystallising very late, e.g. after near surface degassing, also crystallised from uncontaminated magmas as there is no systematic correlation between $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ measured on same grains (Fig 7) (Sarkar et al., 2011). Thus, we can conclude from the trace element data, oxygen isotope and $^{87}Sr/^{86}Sr$ ratios that there was no significant contamination into the kimberlite magma from which the perovskite crystallised. This also suggests that the isotope and trace element compositions of perovskites from both kimberlites are more likely to represent pre-shallow level contamination magma characteristics.

## 5.2 Pre-shallow level contamination magma characteristics

Different approaches have been taken to determine the composition of pre-shallow level contamination kimberlite magma. Apart from careful sample preparation, different geochemical criteria, for example the contamination index (C.I.) of Clement (1982), increase in HREE and Pb have been used to remove the effects of crustal contamination and post emplacement alteration on the bulk rock geochemistry. However, it is not possible to completely eradicate the effects of contamination and alteration in bulk rock studies from volcaniclastic or pyroclastic kimberlites (Paton et al., 2007a; Yang et al., 2009; Wu et al., 2010). Mineral separates offer an alternative approach with which the primary uncontaminated kimberlite magma characteristics can, in principle, be unraveled.

Our data shows that the geochemical characteristics of the magmas inferred from the compositions of perovskite are little affected by shallow level contamination and thus, by using the partition coefficients (D) of different trace elements between perovskite and melt it is possible to characterise the pre-shallow level contamination magma composition of kimberlite in equilibrium with perovskites. However, the magma characteristics calculated from perovskite is unlikely to be its primary composition, as various phenocrysts are likely to have crystallised from the magma before groundmass perovskite. Although there have been a few previous experimental studies (Corgne and Wood, 2002; Corgne et al., 2005), recently Beyer et al. (2013) reported a relatively larger set of D values of incompatible elements (15 elements) between perovskite, kimberlite and carbonatite melt. Melluso et al. (2008) took a different approach and calculated the crystal/whole rock partition coefficients in natural kamafugites and kimberlites. In spite of the different approaches taken by the two studies, most of the reported D values agree well within their uncertainties (Table 4). We therefore used the D values listed in Beyer et al. (2013) and calculated the average pre-shallow level contamination trace element composition of the Orapa and Wesselton kimberlite magma in equilibrium with perovskite (Table 4). D values from Melluso et al. (2008) have been used for a few elements that are not available in Beyer et al. (2013).

The calculated Orapa and Wesselton kimberlites have highly variable trace element compositions. HFSE and LREE abundances are high (Zr=400-11000 ppm; Nb=320-500 ppm; Th=32-88 ppm; La=380-540 ppm; Ta=17-41 ppm) and exhibit well-defined correlations. For a given La content Orapa has slightly higher Nb (350 -500 ppm) ppm and Th (70-88 ppm) than Wesselton (Nb = 300-360 ppm and Th= 32- 45 ppm) (Fig 8a, b). In contrast large ion lithophile elements (LILE) (Sr = 970-1200 ppm; Pb = 2.4-24 ppm) behave less coherently and they do not have strong correlations with the HFSE. Generally both kimberlites have similar trace element contents compared to other Group I kimberlites from Southern Africa (Fig 8a-c) (Le Roex et al., 2003; Harris et al., 2004; Becker and Le Roex, 2006). Certain diagnostic trace element ratios of Orapa and Wesselton (La/Nb<1.12, Th/Nb <0.135, Ce/Pb<22) are also similar to South African Group I kimberlites (Fig 8c, d, e, f) (Le Roex et al., 2003; Harris et al., 2004; Becker and Le Roex, 2006). Primitive mantle-normalised REE patterns from both kimberlites are highly fractionated and also match well with the published average trace element characteristics of Group I kimberlites from

South Africa (Le Roex et al., 2003; Harris et al., 2004; Becker and Le Roex, 2006) (Fig 9). They both have very high LREE contents ($La/Sm_N$=6±1.25, $La/Yb_N$=167±38) with La abundances in the range of 1000-1400 times primitive mantle and Lu at ~4-12 times primitive mantle. Wesselton has slightly depleted MREE patterns compared to Orapa. In a primitive mantle-normalised multi element plot, both kimberlites have strongly fractionated non-smooth patterns and broadly similar trace element abundances; however, Zr and Hf have different concentrations. Orapa kimberlite has strong positive Zr and negative Hf anomalies whereas Wesselton kimberlite has Zr and Hf abundances similar to typical Group I kimberlites (Fig 10). The causes of the variations in Zr and Hf content between the two kimberlites are unknown. The primitive mantle-normalized patterns for both Orapa and Wesselton kimberlites are characterized by negative Pb anomalies (Fig. 10), with that for the latter being more pronounced. This negative Pb anomaly is a diagnostic characteristic of Group I kimberlites (Le Roex et al., 2003; Harris et al., 2004; Becker and Le Roex, 2006).

The initial Sr and Nd isotopic compositions of Orapa ($^{87}Sr/^{86}Sr$ = 0.7030-0.7036, εNd = +1.19 to +2.94) and Wesselton ($^{87}Sr/^{86}Sr$ = 0.7044-0.7049, εNd = +0.98 to +1.59) kimberlites define a narrow range, which falls on the mantle Nd-Sr array and overlaps the field defined by bulk rocks from Group I kimberlites from South Africa (Le Roex et al., 2003; Harris et al., 2004; Nowell et al., 2004; Becker and Le Roex, 2006) (Fig 11). The Sr isotopic compositions of perovskites from Orapa and Wesselton are also indistinguishable from reported values for perovskites from other southern African kimberlites ($^{87}Sr/^{86}Sr$ = 0.7026-0.7046) (Woodhead et al., 2009). Data from this study and Woodhead et al. (2009) support the fact that initial Sr isotope ratios from perovskite are slightly offset towards lower ratios compared with the bulk-rock data from most of the South African kimberlites and also have a more restricted spread. This is attributed to the robust nature of the former during crustal assimilation and post-emplacement alteration (Paton et al., 2009; Woodhead et al., 2009; Yang et al., 2009). Moreover, the initial isotopic composition of Group I kimberlites display a larger spread in $^{87}Sr/^{86}Sr$ with almost constant $\varepsilon Nd$ (Nowell et al., 2004; Becker and Le Roex, 2006). As Nd isotope ratios are not sensitive to small degrees of crustal contamination or alteration, most of the variation in $^{87}Sr/^{86}Sr$ ratios towards more radiogenic values might therefore be due to variable degrees of crustal contamination in whole rock analyses. However, it is worth noting that the contrast between $^{87}Sr/^{86}Sr$ isotope ratios of perovskite and whole rocks are not as dramatic as reported by (Paton et al., 2007a) for Indian kimberlites. In fact, bulk rock studies from very fresh hypabyssal samples from Wesselton have indistinguishable $^{87}Sr/^{86}Sr$ isotope ratios from those of perovskites (Nowell et al., 2004; Becker and Le Roex, 2006). Extreme homogeneity of initial $^{87}Sr/^{86}Sr$ of perovskites from the Wajrakarur and Narayanpet kimberlite fields has been argued to be related to their derivation from a homogeneous source, probably asthenosphere (Paton et al., 2007a; Paton et al., 2009). However, most South African kimberlites do show some variation in their initial Sr isotope ratios as observed in Orapa and Wesselton perovskites in this study and by Woodhead et al. (2009).

Highly fractionated non-smooth primitive mantle normalised trace element patterns from Orapa and Wesselton with certain diagnostic ratios ($La/Nb<1.12$, $Th/Nb<0.135$, $Ce/Pb<22$) and Sr-Nd isotopic compositions (Orapa $^{87}Sr/^{86}Sr$ = 0.7030-0.7036, $\varepsilon Nd$ = +1.19 to +2.94 and Wesselton $^{87}Sr/^{86}Sr$ = 0.7044-0.7049, $\varepsilon Nd$ = +0.98 to +1.59) support their derivation from a time-integrated LREE depleted metasomatised SCLM source, suggested for most of the South African Group I kimberlites (Le Roex et al., 2003; Becker and Le Roex, 2006; Wu et al., 2010; Donnelly et al., 2011). EM I-like Sr and Nd isotope ratios are perhaps indicative of a relatively short time gap between mantle metasomatism and kimberlite genesis as sustained interaction between metasomatised melt and depleted SCLM would result in significant isotope evolution (higher Sr, lower Nd isotope ratios). It might even be a continuous process of mantle metasomatism and kimberlite generation from the metasomatised sub-continental lithospheric mantle. The presence of metasomatised garnet lherzolite xenoliths in South African Group I kimberlites are also in accord with this model (Hawkesworth et al., 1990; Gregoire et al., 2002; Gregoire et al., 2003).

# 6 Conclusion

This study emphasises the fact that perovskite may better estimate the geochemical signature of uncontaminated kimberlite magma than whole rock, which is almost always contaminated to some degree; in particular when early crystallising phases such as olivine are not suitable for analysis. Both trace elements and Sr isotope signatures of perovskites from Orapa and Wesselton kimberlites do not show any effects of crustal contamination. Calculated uncontaminated magma compositions, using the experimental D values between perovskite and melt, are broadly similar to the reported Group I kimberlites from Southern Africa; they display highly variable trace element compositions with extreme fractionation in LREE and other incompatible elements. Initial Sr and Nd isotope ratios of both kimberlites fall within a narrow zone of the Group I kimberlite field, which is similar to the Bulk Silicate Earth composition. The measured $^{87}Sr/^{86}Sr$ bulk rock ratios from Orapa (0.7063-0.7156) are more variable than those measured from perovskites, while published bulk rock Sr isotope ratios from fresh hypabyssal kimberlites from Wesselton (0.7042-0.7047) have similar range as found in perovskites. Thus the Sr isotope ratios measured from Orapa (0.7030-0.7036) and Wesselton perovskites (0.7044-0.7049) are a better approximation of the uncontaminated primary kimberlite magma than those from bulk rocks, especially for the fragmented volcaniclastic and pyroclastic kimberlites, as in case of Orapa.

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## Figure Captions

**Fig 1:**

Map of South Africa showing the locations of Orapa and Wesselton kimberlite sampled during this study. Surface expression of Orapa and cross section of Wesselton kimberlite are shown in inset.

**Fig 2:**

Primitive mantle-normalised REE plot of perovskites from different lithological units from the Orapa and Wesselton kimberlites. Normalising values are from Sun and McDonough (1989). NPK=northern pyroclastic kimberlite, SPK=southern pyroclastic kimberlite, SVK=southern volcaniclastic kimberlite, NP=north pipe core, SP=south pipe core.

**Fig 3:**

Primitive mantle-normalised multi-element plot of perovskites from different lithological units from the Orapa and Wesselton kimberlites. Normalising values are from Sun and McDonough (1989). NPK=northern pyroclastic kimberlite, SPK=southern pyroclastic kimberlite, SVK=southern volcaniclastic kimberlite, NP=north pipe core, SP=south pipe core.

**Fig 4:**

a) Variation in $^{87}Sr/^{86}Sr$ ratios in perovskites from Orapa measured in-situ by laser ablation methods and by TIMS. The laser analyses are significantly less scattered, even with larger uncertainties. Most of the TIMS uncertainties are smaller than the symbols.
b) Probability density plot and histogram showing the distribution of $^{87}Sr/^{86}Sr$ ratios of perovskites from Orapa. The blue bars represent analyses done in-situ by laser ablation methods while red bars display results from single grain TIMS analyses.

**Fig 5:**

A plot showing Zr vs Sr contents of perovskites from Orapa and Wesselton kimberlites.

**Fig 6:**

La/Yb - Sr/Yb in perovskite from Orapa kimberlites (triangles), the calculated liquid compositions in equilibrium with the perovskite (squares), upper crust and typical granites (grey area) to represent crustal melt. Taken from Sarkar et al. (2011) using the coefficients from Beyer et al. (2013).

**Fig 7:**

Variation in $^{87}Sr/^{86}Sr$ ratios measured in-situ by laser ablation methods and $\delta^{18}O$ in perovskites from Orapa. $\delta^{18}O$ values are taken from Sarkar et al. (2011).

**Fig 8:**

Selected trace element and trace element ratio variations in Orapa and Wesselton kimberlite magmas calculated from their respective perovskite compositions. The shaded area represents fields of typical South African Group I and Group II kimberlites (Le Roex et al., 2003).

**Fig 9:**

Primitive mantle-normalised REE plot of the kimberlite magma, calculated from perovskites using the D values from Beyer et al. (2013) and Melluso et al., (2008). The shaded area represents the published average REE distribution in group I kimberlites, measured from bulk-rock analyses (Becker and Le Roex, 2006). Average REE pattern of the perovskite, used in this study, have also been plotted for comparison. Normalising values are from Sun and McDonough (1989).

**Fig 10:**

Primitive mantle-normalised spidergram plot of the kimberlite magma, calculated from perovskites using the D values from Beyer et al. (2013). The shaded area represents the published average multi element distribution in Group I kimberlites, measured from bulk-rock analyses (Becker and Le Roex, 2006). The trace element pattern of the source garnet lherzolite has also been plotted for comparison (Gregoire et al., 2003; Le Roex et al., 2003). Normalising values are from Sun and McDonough (1989).

**Fig 11:**

εNd vs $^{87}Sr/^{86}Sr$ of perovskites from Orapa (blue circles) and Wesselton (red circles) kimberlite. Group I, Group II and transitional kimberlite fields have been taken from Nowell et al. (2004) and Becker and Le Roex (2006). Different mantle reservoir fields including EMI, EMII, HIMU, OIB and MORB have been plotted for comparison (taken from Hofmann (1997)). Ranges of the initial $^{87}Sr/^{86}Sr$ ratios of perovskites from Indian and Chinese kimberlites are also shown to compare the Sr isotope data of Orapa and Wesselton with Wajrakharur and Mengyin kimberlites (Paton et al., 2007a; Yang et al., 2009).

**Table captions**

**Table 1**

Average major, minor and trace element concentrations of perovskite from twelve Orapa and one Wesselton kimberlite samples.

**Table 2:**

Nd isotope compositions of whole rocks and perovskites from the Orapa and Wesselton kimberlites. Both laser and solution MC-ICPMS analyses from same samples are in agreement within analytical uncertainties. Bulk rock analyses of the Orapa kimberlite were only performed by conventional solution methods.

**Table 3:**

Initial Sr isotope ratios (from both TIMS and in-situ methods) of perovskites from Orapa and Wesselton kimberlites, bulk Orapa kimberlites and leachates from Orapa perovskites. Due to very low Rb/Sr ratios <0.005, no age corrections were made on these perovskite analyses for in-situ decay of Rb over a period of 90 to 93 Ma. $\delta^{18}O$ values are from Sarkar et al. (2011)

**Table 4:**

Table 4: Average trace elements compositions of uncontaminated Orapa and Wesselton kimberlite melt in equilibrium with perovskite, calculated using the partition coefficients (D)

from Beyer et al., (2013) and Melluso et al., (2008) (for the elements with no D available in Beyer et al., (2013)).