D. Graham Pearson Herman S. Grütter Jeff W. Harris Bruce A. Kjarsgaard Hugh O'Brien N. V. Chalapathi Rao Steven Sparks *Editors* 

# Proceedings of 10th International Kimberlite Conference Volume 1

Dedicated to Roger H. Mitchell







Proceedings of 10th International Kimberlite Conference D. Graham Pearson Herman S. Grütter • Jeff W. Harris Bruce A. Kjarsgaard Hugh O'Brien • N. V. Chalapathi Rao Steven Sparks Editors

# Proceedings of 10th International Kimberlite Conference

Volume 1

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## The 10th International Kimberlite Conference

International Kimberlite Conferences (IKCs) are special events that are held across the world once in 4–5 years. IKC is the confluence platform for academicians, scientists and industrial personnel concerned with diamond exploration and exploitation, petrology, geochemistry, geochronology, geophysics and origin of the primary diamond host rocks and their entrained xenoliths and xenocrysts (including diamond) to get together and deliberate on new advances in research made in the intervening years. Ever since the organization of the first IKC in 1973 and its tremendous success, the entire geological world eagerly looks forward to subsequent such conferences with great enthusiasm and excitement. The scientific emanations from IKCs continue to make significant impact on our understanding of the composition, nature and evolution of the planet we live on. The previous conferences were held at Cape Town (1973), Santa Fe, New Mexico (1977), Clermont-Ferrand, France (1982), Perth, Western Australia (1987), Araxa, Brazil (1991), Novosibirsk, Russia (1995), Cape Town (1998), Victoria, Canada (2003) and Frankfurt, Germany (2008).

The 10th IKC was held at Bangalore, India between 6 and 11th February 2012. The conference was organized by the Geological Society of India in association with the government organizations, academic institutions and Indian diamond mining companies. About 300 delegates from 36 countries attended the conference and 224 papers were presented. The papers include 78 oral presentations and 146 poster presentations on following topics: Kimberlite geology, origin, evolution and emplacement of kimberlites and related rocks, petrology and geochemistry of metasomatised lithospheric mantle magmas, diamond exploration, cratonic roots, diamonds, diamond mining and sustainable developments and policies and governance of diamond exploration. Pre- and post-conference field trips were organized to (i) the diamond bearing kimberlites of Dharwar Craton in South India, (ii) lamproites of Bundelkhand Craton in Northern India and (iii) diamond cutting and polishing industry of Surat, Gujarat in Western India. A series of social and cultural programmes depicting cultural diversity of India were organized during the conference. The Kimberlite fraternity enjoyed yet another socially and scientifically successful conference.



Cultural programmes organized during the 10th IKC

### **About the Editors**

**Dr. D. Graham Pearson** is Canada Excellence Research Chair—Arctic Resources in the Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada. Dr. Pearson obtained his B.Sc. from the Royal School of Mines, Imperial College, London and his Ph.D. from Leeds University. He taught at Durham University for 15 years, becoming Professor of Geochemistry and now holds a CERC research chair in Arctic Resources specialising in diamonds, kimberlites and cratonic roots. Pearson has been a member of the International Kimberlite Conference Advisory Committee since 2007.

**Dr. Herman S. Grütter** is currently associated with the Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada. Dr. Grütter has over 20 years' senior-mining, junior-mining and consulting experience in kimberlite targeting, exploration and early stage resource definition on projects spanning the globe. He obtained a B.Sc. (Hons) from the University of Cape Town in 1986 and a Ph.D. in metamorphic petrology from the University of Cambridge in 1993. He maintains applied research interests in mantle mineralogy and petrology, and in craton evolution.

**Dr. Jeff W. Harris** retired in 2006 after a distinguished academic career at the University of Glasgow. Since retirement he has held an Honorary Research Fellowship at Glasgow. For over 30 years, he was a consultant to De Beers Consolidated Mines, managing their worldwide outside diamond research programmes conducted at Universities and equivalent institutions; a research endeavour which played a major part in furthering our understanding of geochemical processes operating in the mantle.

**Dr. Bruce A. Kjarsgaard** is a Senior Research Scientist in Geological Survey of Canada, Ottawa, Canada. Dr. Kjarsgaard received his Ph.D. in Geology (experimental petrology) from the University of Manchester, England in 1990. He has been with the Geological Survey of Canada (GSC) in Ottawa since 1990, working as an economic geologist. His research involves broad-based petrological studies (including mineralogy, geochemistry and volcanology) of mantle-derived volatile-rich ultramafic magmas (kimberlite, lamprophyre, nephelinite–carbonatite) and their attendant economic mineralization (diamonds, and niobium and REE, respectively).

**Dr. Hugh O'Brien** is a Senior Research Scientist in Finland Isotope Geosciences Laboratory (SIGL), Geological Survey of Finland (GTK), Espoo, Finland. Dr. O'Brien received his B.S. in 1982 from University of Minneapolis and his Ph.D. from UW in Seattle in 1988. After a short stint (1988–1991) with the GTK, he returned to Seattle for post-doctoral studies. Since 1997, he has been a Senior Research Scientist at GTK, covering diamond exploration and mantle and ore research using isotopic and electron beam methods.

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**Dr. Steven Sparks** is Professor of Geology in the School of Earth Sciences at Bristol University, Bristol, UK. His research concerns volcanic and igneous processes and he has made contributions in petrology, many physical volcanology, fundamental fluid mechanics, sedimentology, and in hazard and risk assessment methods. He has been past-President of the Geological Society of London and IAVCEI President of the Volcanology, Geochemistry and Petrology section of the American Geophysical Union 2008–2012.

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## **Roger H. Mitchell**



Roger Mitchell is one of the staunchest supporters of the kimberlite/upper mantle community. He has the distinction of being one of the 9 "Old Farts" who have attended all 10 of the International Kimberlite Conferences since their inception in Cape Town in 1973, and since 1996 has been Chairman of the International Kimberlite Conference Advisory Committee. In addition he was co-convenor, with Barbara Scott Smith, of the highly-successful 8th Kimberlite Conference held in Victoria, BC in 2003.

His first foray into kimberlite geology after graduating from the University of Manchester was on strontium isotopes when he did his Ph.D. at McMaster University. Although isotope geochemistry has long been one of his

specialities, Roger has been involved in the full spectrum of kimberlite geology ranging from field mapping (with relevance for kimberlite diatreme emplacement) and petrography to detailed mineralogy in which his studies on perovskite have made him a world authority. Early contacts in Norway had already excited his interests in carbonatites which, although perhaps subordinate to kimberlites and mantle xenoliths, have been another major aspect of his research career. After post-doctoral fellowships in Edmontonand Oslo, in 1972 Roger joined the faculty at Lakehead University where, in addition to his own research, he played a full role in the administration of his department and the university. His research has led him to being honoured by election to the Royal Society of Canada and to Fellowship of the Mineralogical Society of America.

Perhaps reflecting his upbringing, Roger has two Yorkshire characteristics of first, being a very hard worker and, second, of having a direct approach to both problems and people and the inability to suffer fools gladly. The first characteristic has resulted in over 230 papers and 5 monographs. Many papers have been written in conjunction with co-authors from Europe, Russia, China and India, being indicative of his approach to international cooperation. His second, no-nonsense trait, has been of great value in his editorships or associate editorships of various journals, and of the Proceedings Volumes of both the 6th and 8th International Kimberlite Conferences.

Roger retired from Lakehead, where he is now Emeritus Professor, in 2006 but, with the able support of his wife Valerie, he continues to be as active as ever. The word "retired" is used advisedly as he continues to research several aspects of kimberlite and carbonatite mineralogy, has recently taken on co-editorship of the Mineralogical Magazine, and is still widely consulted by mining companies. So much for retirement!

For his unstinting contributions to the International Kimberlite Conferences, it is only fitting that Roger is honoured by the co-dedication of the Proceedings of the Bangalore Conference in his name.

Barry Dawson UK

# Paragenesis and Oxygen Isotopic Studies of Serpentine in Kimberlite

Roger H. Mitchell

#### Abstract

Although serpentine is a ubiquitous mineral in kimberlites, its origin remains controversial. Some petrologists claim that all serpentine is secondary and produced by the introduction of externally derived fluids, whereas others suggest that serpentine is a primary mineral formed mainly from late-stage hydrothermal deuteric fluids. To date, the only investigations of the isotopic composition of serpentine in kimberlite have been by bulk analysis of samples that have undergone subaerial alteration, and hence undoubted interaction with meteoric water. Serpentine and chlorite in kimberlites occur as follows: (1) pseudomorphic retrograde lizardite and chlorite after primary olivine; (2) late-stage primary serpophitic serpentine; (3) prograde serpophitic serpentine replacing retrograde lizardite; and (4) serpentine-chlorite replacing magmaclast olivine and interclast phlogopite in diatreme zone rocks. Serpophitic or polygonal serpentine is a primary hydrothermal low temperature phase that common forms monomineralic segregations in the groundmass of hypabyssal kimberlites. In this study, the oxygen isotopic composition of all varieties of serpentine/chlorite was determined by ion microprobe in hypabyssal and diatreme zone kimberlites from Southern Africa, Canada and the USA. Data were acquired using the Edinburgh Cameca IMS 1270 ion microprobe and an antigorite ( $\delta^{18}O = 8.8$  ‰) standard. In Iron Mountain hypabyssal kimberlites, the  $\delta^{18}O$  of pseudomorphic marginal and vein serpentine is similar and ranges between 4.3 and 6.3 %. For compositionally zoned pseudomorphic marginal serpentines,  $\delta^{18}$ O decreases from coreto-rim (cores 6.4 to 3.8  $\% \delta^{18}$ O; rims 2.7 to 0.6  $\% \delta^{18}$ O). Prograde pseudomorphic serpophite in the Ham West kimberlite ranges in  $\delta^{18}$ O from 4.1 to -0.5 ‰, with segregationary primary serpophite  $\delta^{18}$ O ranging from 1.6 to -1.8 ‰. In diatreme zone rocks at Letseng-la-terae, the earliest pseudomorphic serpentines range in  $\delta^{18}$ O from 5.0 to 3.5 ‰, later-forming rim and marginal serpentines from 4.3 to -1.8 ‰, with interclast serpophite from 3.4 to 1.5 ‰. At Kao, the earliest pseudomorphic serpentines are relatively uniform in composition and range in  $\delta^{18}$ O from 4.9 to 4.5 ‰, later rim and marginal serpentines from 4.9 to 4.8 ‰ and interclast serpophite from 6.3 to 3.8 ‰. These data show that the kimberlites investigated have not interacted with large volumes of light meteoric waters. Similar oxygen isotopic compositions in hypabyssal and diatreme zones rocks from different localities certainly preclude the introduction of meteoritic water as a cause of serpentinization. The trends from mantle oxygen  $\delta^{18}$ O to lighter oxygen are a result of either fluid compositional evolution or very minor introduction of light water. Assuming that parental olivine has a

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primary  $\delta^{18}$ O of about +6 ‰ and that this is decreased during serpentinization by <sup>16</sup>O enrichment by reactions with isotopically lighter water (-10 to -20 ‰), at 200-300 °C, in closed or open systems, then "water/serpentine" ratios cannot exceed 0.8. These data are interpreted to suggest that there was not an influx of significant volumes of low-temperature meteoric water as a cause of serpentinization. This conclusion is supported by the absence of extremely light oxygen (i.e.  $\delta^{18}$ O < -5 ‰) in all of the serpentines investigated.

#### Keywords

Kimberlite • Oxygen isotopes • Serpentine • Serpophite • Chlorite

#### Introduction

Kimberlites are rocks derived from volatile-bearing magmas as indicated by the common presence in them of primary calcite and deuteric serpentine (Mitchell 1986). Their parental magma has been proposed by Brooker et al. (2011), Kjarsgaard et al. (2009), Kopylova et al. (2008), le Roex et al. (2003) and Price et al. (2000) to be a carbonated waterbearing ultrabasic silicate melt. Although the H<sub>2</sub>O/CO<sub>2</sub> ratios of the parental magmas and associated fluids are not known, Kjarsgaard et al. (2009) have emphasized that the majority of the compositions of fresh hypabyssal kimberlites are water-rich with molar  $H_2O/(H_2O + CO_2)$  ratios greater than 0.5. Calculated H<sub>2</sub>O and CO<sub>2</sub> contents of the primary magmas are estimated to range from 9.5 to 12.5 and 5.5 to 8.1 wt%, respectively (Brooker et al. 2011; Kjarsgaard et al. 2009). In contrast to hypabyssal kimberlites, diatreme zone kimberlites are poor in calcite and volatile-bearing phases are dominated by diverse serpentines and chlorites (Mitchell et al. 2009). These observations suggest that the volatiles associated with diatreme-forming events could be relatively much richer in water.

There have been few stable isotope studies of kimberlites, and of these, the majority have focussed upon the O and C isotopic composition of carbonates (Deines and Gold 1973; Kobelski et al. 1979; Kirkley et al. 1989; Wilson et al. 2007). Only, Sheppard and Epstein (1970), Sheppard and Dawson (1975), Ukhanov and Devirts (1983) and Ustinov et al. (1994) have provided data for the isotopic composition of H, C and O in silicates. These studies were undertaken on olivine, phlogopite megacrysts, serpentinized megacrysts, and bulk rock kimberlites. Samples were taken at random and included kimberlites (and orangeites) which have been subjected to significant subaerial alteration. The bulk rock data presented by Sheppard and Dawson (1975) for Southern African kimberlites represent the average of the isotopic compositions of all of the phases present in a particular sample; hence, these data are for mixtures of minerals rather than single phases, and interpretation is fraught with ambiguities. Regardless, Sheppard and

Dawson (1975) have interpreted their data to imply that "meteoritic–hydrothermal fluids" interacted with kimberlite during low-temperature (50–200 °C) serpentinization. The origins of the "fluids" were not specifically defined, although some combination of magmatic, metamorphic or exchanged meteoric waters with a range of low water/rock ratios (<0.2) was suggested. Ukhanov and Devirts (1983) provided only H isotopic data and claimed these data supported a meteoric origin for water in serpentines in the Udachnaya and Obnazhennaya kimberlites.

One of the unresolved problems in kimberlite petrology is the origin of the common serpentine and/or chlorite found in hypabyssal and diatreme zone kimberlites which have not been subjected to subaerial alteration. Commonly, serpentine is regarded by many geologists as a secondary mineral, typically resulting from the in situ serpentinization of olivine, pyroxene and/or mica by fluids not necessarily genetically related to the primary minerals. Recently, Sheppard and Dawson's (1975) conclusions have been misinterpreted by some volcanologists (Stripp et al. 2006; Cas et al. 2008; Hayman et al. 2009) to support claims that all serpentine in kimberlites is the result of alteration in pre-existing material, and therefore is entirely of secondary origin, and thus genetically unrelated to fluids present during kimberlite emplacement. In contrast, Mitchell (1986, 2008) and Mitchell et al. (2009) claim that many serpentine group minerals in kimberlites are formed from low-temperature deuteric hydrothermal fluids and are in many instances primary phases.

One approach to resolving these contradictory hypotheses is to determine the hydrogen and oxygen isotopic composition of the serpentine group minerals, as these data should indicate whether or not meteoric or deuteric fluids dominate the serpentinization process. Typically, the serpentines in kimberlites are themselves mineralogically complex, very fine grained and commonly intergrown with other minerals.(Mitchell and Putnis 1988; Mitchell 2008; Mitchell et al. 2009). Bulk analysis for H and O of samples extracted by microdrilling is possible in some instances, but unfortunately, this methodology results in a loss of paragenetic information and is not applicable to complexly zoned serpentine, and moreover, the sample can include extraneous material. In contrast, compositions determined by in situ methods such as secondary ion mass spectrometry (ion microprobe) can be directly related to spatial petrographic/paragenetic information but unfortunately do not typically provide data for hydrogen isotopes. Determination of H/D ratios by ion probe methods is subject to significant instrumental contamination problems and associated with large analytical errors (Harford and Sparks 2001). This study outlines the paragenetic types of serpentine in kimberlites and presents the results of an ion microprobe investigation of the isotopic composition of oxygen in serpentines and chlorites from some hypabyssal and diatreme zone kimberlites.

#### Serpentine in Kimberlites

#### Definitions

Primary groundmass magmatic minerals in kimberlites are those precipitated as liquidus phases from kimberlite magmas at relatively high temperatures (> 500  $^{\circ}$ C; Mitchell 1995, 1986). They include olivine; perovskite; diverse Mg-Ti-Ferich spinels; monticellite; phlogopite-kinoshitalite; apatite; and calcite. Crystallization of the magma results in increasing volatile contents in the residual melt; this being reflected in the formation of late-stage volatile-rich calcite-serpentine segregations (Mitchell 1986). There is actually a continuum from magmatic crystallization to minerals formed from hydrothermal residua (Mitchell 2008). For example, calcite can be either a primary magmatic or a primary hydrothermal phase. Some serpentines can crystallize directly from the hydrothermal fluids, commonly in association with hydrothermal primary calcite, during the later stages of crystallization, and are here defined as *primary serpentines*, that is they are not formed by the replacement of pre-existing minerals. Serpentine formed by the latter process is commonly defined as "secondary serpentine". A variety of "secondary serpentine" can be formed in kimberlites by the reaction of hydrothermal deuteric fluids with pre-existing minerals, for example serpentinization and pseudomorphing of olivine and/or monticellite. The type of serpentine (lizardite) formed is typically structurally different to late-stage primary deuteric polygonal serpentine (see below). In this work, the replacement of pre-existing primary minerals by deuteric fluid serpentine-forming reactions is termed retrograde serpentinization to distinguish it from secondary serpentine formed as a result of the introduction of external fluids (meteoric water) genetically unrelated to kimberlite magma.

Low-temperature hydrothermal residual fluids can also permeate throughout pre-existing magmatic assemblages, resulting in the replacement of the minerals by deuteric polygonal serpentine with in some instances concomitant destruction and replacement of retrograde serpentine. This style of *deuteric replacement* is termed here *prograde serpentinization*.

#### Serpentine Paragenesis in Kimberlites

Serpentine group polymorphs and their polytypes occur in kimberlites in the following parageneses:

- 1. Pseudomorphic retrograde vein serpentine formed by the direct conversion of macrocrystal and phenocrystal forsteritic olivine to lizardite-1T (Jago and Mitchell 1985). Such serpentine forms anastomosing thin veins within the parental olivine and typically shows relatively coarse-grained mesh textures with pronounced (or flamboyant) anisotropy (Figs. 1 and 2). In some instances, the serpentine comprising the veins is a pale yellow Fe-poor variety containing small crystals of magnetite. In other cases, the serpentine is pale brown, Fe-rich, lacks magnetite and contains Ni-sulphides (millerite, heazlewoodite). The difference between the magnetitebearing and sulphide-bearing serpentines depends upon whether the serpentine is produced under relatively oxidizing or reducing conditions, respectively (Mitchell 1986). The serpentinizing fluids are in hypabyssal kimberlites considered to be of deuteric origin.
- Pseudomorphic retrograde marginal serpentine formed by the direct conversion of forsteritic olivine to compositionally diverse "serpentines", together with the replacement of earlier vein serpentine. Typically, these serpentines occur as mantles on, or as complete replacements of, olivine macrocrysts and phenocrysts (Fig. 1). Some pseudomorphed olivines exhibit several



**Fig. 1** Retrograde vein serpentine and pseudomorphic marginal serpentine replacing olivine macrocrysts in the Iron Mountain (USA) hypabyssal kimberlite. Plane polarized light image. Numbers indicate analytical points (see Table 1)



**Fig. 2** Retrograde vein serpentine replacing olivine microphenocrysts in the Wesselton W7 hypabyssal kimberlite (South Africa). Plane polarized light image. Numbers indicate analytical points (see Table 1)

(1–4) discrete mantles of differing colour and composition. All are relatively coarse grained and exhibit "flamboyant" anisotropy. The "serpentines" range in character from lizardite to mixed layer serpentine– chlorites. The textures and compositions indicate that several discrete stages of serpentinization must have occurred subsequent to the formation of vein serpentine.

3. Non-pseudomorphic, segregationary serpentine (Figs. 4 and 5) is characteristic of hypabyssal kimberlite (Mitchell 1986, 2008). Typically, segregations occur as discrete amoeboid areas within the groundmass of the kimberlite and consist of serpentine alone or serpentine plus calcite. Some segregations contain marginal calcite, acicular phlogopite and/or acicular apatite. There is no textural evidence to suggest that these serpentines are pseudomorphing earlier-formed olivine or phlogopite. Calcite, apatite and mica in the segregations can be partially replaced or completely pseudomorphed by segregationary serpentine.

Segregationary serpentine can be pale yellow to light brown in colour, is characteristically extremely fine grained and, depending on grain size, can be isotropic or near-isotropic. In the latter case, it appears as an aggregate of tiny spheres with a texture rather like that of frogspawn. Such serpentines have commonly been termed "Povlen-type serpentine" or "serpophite" (Lodochnikov 1933). The latter name is a useful descriptive term but has no strict mineralogical meaning, as Wicks and Zussman (1975) initially showed the material is not amorphous and consists of finegrained identifiable phases. Subsequent studies have shown that serpophitic serpentine consists primarily of polygonal (Middleton and Whittaker 1976; Mitchell and Putnis 1988; Baronnet et al. 1994) and polyhedral (Baronnet et al. 2007;



**Fig. 3** Core-to-rim variations in the isotopic composition of oxygen (\*<sup>18</sup>O) versus FeO<sub>T</sub> content of serpentine replacing olivine microphenocrysts in Wesselton W7 hypabyssal kimberlite (South Africa). Note that very light oxygen ( $\delta^{18}$ O < -5 ‰) is not present and that the cores of the crystals contain oxygen with isotopic compositions similar to those of mantle oxygen ( $\delta^{18}$ O = + 5 to + 6 ‰)

Andreani et al. 2008) serpentine with lesser very thin chrysotile fibres; and not platy lizardite or antigorite.

Baronnet and Devourard (1996) and Devouard et al. (1997) have shown that polygonal serpentine can be synthesized from hydrous Mg-silicate gels at 300 °C and 0.07 GPa. Polygonal serpentine formation in these experiments does not require a precursor phase; consequently, polygonal serpentines in kimberlites can be regarded as primary phases (Mitchell 2008). Primary in this context, as noted above, implies crystallization directly from a residual deuteric hydrothermal fluid. Andreani et al. (2008) consider that polyhedral and polygonal serpentines are always the last type of serpentine to form in ultramafic rocks; their formation requiring open space, relatively low temperatures (<200-300 °C) and small amounts of Al (0.06-0.22 apfu). On the basis of these observations, Mitchell (2008) has regarded segregation polygonal serpentine to be a product of low-temperature transformation of a Mg-Si-bearing gel formed from residual deuteric fluids in the final stages of crystallization of hypabyssal kimberlite.

4. Pseudomorphic polygonal serpentine is produced when the residual hydrothermal sols or gel-forming fluids do not form discrete segregations (Fig. 4). In this case, the fluids migrate and permeate throughout the pre-existing kimberlite mineral assemblage, and replace both fresh and/or previously altered minerals. Thus, retrograde pseudomorphic lizardite–chlorite which initially replaced olivine can be in turn replaced by very finegrained polygonal serpentine. Mitchell (1986) and Jago



**Fig. 4** Near-isotropic prograde serpophitic serpentine replacing olivine and near-isotropic primary hydrothermal serpophitic serpentine occurring as segregations in the Ham West (Canada) hypabyssal kimberlite. Crossed polarized light image. Numbers indicate analytical points (see Table 1)

and Mitchell (1985) have termed this process "prograde serpentinization". Replacement of pre-existing minerals by calcite can also accompany this low-temperature serpentinization event. Kimberlites which have been extensively replaced by prograde polygonal serpentine and calcite can consist essentially of serpentine and calcite with relict spinels and rutile (after perovskite). Although at first sight, such rocks might be considered to be the products of subaerial secondary alteration by meteoric waters. However, the preserved igneous textures indicate their real origins, as secondary replacement typically results in the eradication of primary igneous textures by replacement with massive aggregates of secondary phases. It should be noted that polygonal serpentine does not form in the subaerialweathering environment (Baronnet, pers. comm. 2006).

5. Interclast "serpentine" (Figs. 6, 7, 8) is a characteristic of diatreme zone Kimberley-type pyroclastic kimberlite (or KPK; Scott Smith et al. 2013) a.k.a. tuffisitic kimberlites. This material is commonly intimately intergrown with microlitic diopside (e.g. see Figs. 28 and 69 of Mitchell 1997); polygonal serpentine appears to be absent. Although considered to be "serpentine sensu lato", there have been no modern TEM or XRD investigations of this material. Mitchell et al. (2009) on the basis of SEM-BSE-morphological and compositional data suggest that this "serpentine" is a mixed layer serpentine-chlorite phyllosilicate, formed by the deuteric hydrothermal alteration in primary phlogopite. It should be noted that olivine in magmaclasts in KPK is commonly pseudomorphed by retrograde lizarditechlorite that was formed in a different serpentinization



**Fig. 5** Near-isotropic primary hydrothermal serpophitic serpentine occurring as segregations in the Ham West (Canada) hypabyssal kimberlite. Crossed polarized light image. Numbers indicate analytical points (see Table 1)

event to that which produced the interclast serpentine, that is there is typically no pervasive "prograde serpentinization" of clasts and interclast matrix (Mitchell et al. 2009).

#### **Experimental Methods**

In this work, the oxygen isotopic composition of all of the above varieties of serpentine was determined in hypabyssal and diatreme zone kimberlites from Southern Africa, Canada and the USA. Data were acquired in two analytical sessions (February 2007 and January 2010) at the University of Edinburgh (Scotland, UK) with a Cameca IMS 1270 (#309) ion microprobe, using a  $\sim$  5-nA primary <sup>133</sup>Cs<sup>+</sup> beam. All data were collected on Au-coated polished thin sections on material located near the centre of the section. Secondary ions were extracted at 10 kV, and <sup>16</sup>O  $(\sim 3.0 \times 10^9 \text{ cps})$  and <sup>18</sup>O  $(\sim 4.0 \times 10^6 \text{ cps})$  were monitored simultaneously on dual Faraday cups (L<sup>2</sup> and H<sup>2</sup>). Each analysis involved a pre-analysis sputtering time of 50 s, followed by automatic secondary beam and entrance slit centring, and finally data collection in two blocks of five cycles, amounting to a total count time of 40 s. The internal precision of each analysis is <0.2 ‰, and the external precision, calculated from multiple analyses of the standard, that is assumed to be homogeneous is estimated at <0.3 ‰.

The analytical standard used was a sample of antigorite (Royal Ontario Museum acquisition #M8571) whose bulk isotopic composition had been determined by standard fluorination methods at Queen's University (Kingston, Ontario), that is  $\delta^{18}O = 8.8$  ‰. Secondary analytical controls included lizardite-1T (Royal Ontario Museum

acquisition #M19804;  $\delta^{18}$ O = 9.9 ‰). Lacking a chlorite standard, it was assumed that chlorite behaves like serpentine with respect to ionization characteristics and can be analysed with the antigorite standard. Because of significant compositional differences, with respect to Al content, between chlorite and serpentine, the use of the antigorite standard for chlorite analyses means that the accuracy of these data is likely to be significantly less than that obtained for serpentine, and the values should be taken as "indicative" only. The O isotopic composition of the antigorite standard was routinely measured multiple times during each analytical session. Analytical results are presented in Tables 1 and 2 as  $\delta^{18}$ O ‰ relative to SMOW.

#### **Experimental Results**

#### **Hypabyssal Kimberlite**

Figures 1 and 2 illustrate the locations of analytical points and types of serpentines analysed (Table 1) in hypabyssal kimberlites. For Iron Mountain (Coopersmith et al. 2003) and Wesselton W3 (Shee 1985; Mitchell et al. 2009) kimberlites, it is apparent that the  $\delta^{18}$ O of pseudomorphic retrograde marginal and vein serpentine is similar and ranges between 4.3 and 6.3 ‰. Figure 3 illustrates coreto-rim compositions ( $\delta^{18}$ O vs. FeO<sub>T</sub>) of Wesselton W7 kimberlite (Shee 1985) compositionally zoned pseudomorphic marginal serpentines. Core serpentines range from 6.4 to 3.8 ‰  $\delta^{18}$ O, and rims from 2.7 to 0.6 ‰  $\delta^{18}$ O, indicating that  $\delta^{18}$ O decreases from core-to-rim of these pseudomorphed olivines and is correlated with decreasing FeO<sub>T</sub> content of the serpentine.

Prograde pseudomorphic serpophite (Fig. 4) in the Ham West HW20 and HW11 kimberlites (Jago and Mitchell 1985) ranges in  $\delta^{18}$ O from 4.1 to -0.5 ‰, with segregationary primary serpophite  $\delta^{18}$ O ranging from 1.6 to -1.8 % (Figs. 4 and 5). These data suggest that later-stage serpophite-forming fluids are isotopically light relatively to those that form retrograde marginal pseudomorphic serpentine. The relatively heavy isotopic composition of prograde pseudomorphic serpophite in HW11 (Table 1) must represent that of a re-equilibrated mixture between that of pre-existing retrograde pseudomorphic serpentine and the residual primary serpophite-forming fluid, as all serpophite has probably crystallized from late-stage fluids. Non-pseudomorphic segregation serpophite, coexisting with calcite and apatite, in the Lac de Gras kimberlite ranges in  $\delta^{18}$ O from 3.0 to 2.0 % (Table 1).

#### **Diatreme Zone Kimberlites**

Figures 6, 7, 8, 9 illustrate the locations of analytical points and types of serpentines analysed (Table 2) in diatreme zone kimberlites from Letseng-la-terae (Bloomer and Nixon 1973), Kao (Clement 1973) and Lethlekane (Field et al. 2008). The pseudomorphic serpentine analysed in all cases is lizardite-chlorite after olivine macrocrysts located within magmaclasts (formerly termed "pelletal lapilli"; see Scott Smith et al. 2013; Mitchell et al. 2009). At Letseng-la-terae (Fig. 6), the earliest pseudomorphic serpentines range in  $\delta^{18}$ O from 5.0 to 3.5 ‰, later-forming rim and marginal serpentines from 4.3 to -1.8 ‰, with interclast serpophite from 3.4 to 1.5 ‰. Figure 9 illustrates core-to-rim compositions ( $\delta^{18}$ O vs. FeO<sub>T</sub>) of Letseng-la-terae pseudomorphic serpentines and shows that although there is no correlation between  $\delta^{18}$ O and FeO<sub>T</sub>, marginal serpentines are all enriched in light oxygen. At Kao (Fig. 7), the earliest pseudomorphic serpentines are relatively uniform in composition and range in  $\delta^{18}$ O from 4.9 to 4.5 ‰, later rim and marginal serpentines from 4.9 to 4.8 % and interclast serpophite from 6.3 to 3.8 ‰. The limited data for Lethlekane (Fig. 8) indicate that pseudomorphic serpentine is relatively uniform in isotopic composition and enriched in <sup>18</sup>O relative serpentines at Letseng and Kao.

#### Discussion

The oxygen isotopic composition of the earliest-formed retrograde pseudomorphic serpentine after olivine is remarkably similar (4–6 ‰  $\delta^{18}$ O) in all hypabyssal kimberlites from diverse localities. This cannot be fortuitous as the kimberlites investigated are of different ages and emplaced in very different geological and hydrological environments. In all examples, oxygen isotopic compositions are seen to evolve in the late-stage segregationary serpentines towards lighter oxygen ( $\delta \sim 0.0$  ‰) from these initial values.

In the diatreme zone kimberlites, interclast serpophite at Letseng-la-terae is lighter than pseudomorphic serpentine and appears to continue the light isotope enrichment trend. In contrast, interclast serpophite at Kao is of variable composition but relative to pseudomorphic serpentine is slightly enriched in <sup>18</sup>O; this could imply that the fluids forming these particular serpentines were unrelated.

For later-forming zoned and mantled pseudomorphic serpentine, isotopic evolution in hypabyssal and diatreme environments is towards <sup>16</sup>O enrichment ( $\delta$  <sup>18</sup>O = 3.5–0.5 ‰), suggesting that the light isotope enrichment

 Table 1 Oxygen isotopic composition <sup>18</sup>O ‰ of serpentines in hypabyssal Kimberlites

Location	Analysis	<sup>18</sup> O	Location	Analysis	<sup>18</sup> O
Iron Mountain (Wyoming, USA)			Ham West (Canada)		
Hypabyssal Kimberlite (Jan. 2010)			HW20 Hypabyssal Kimberlite (.	Jan. 2010)	
Pseudomorphic serpentine	1	4.2	Pseudomorphic serpophite	1	1.9
Pseudomorphic serpentine vein	2	4.3	Pseudomorphic serpophite	2	1.2
Pseudomorphic serpentine	3	4.6	Pseudomorphic serpophite	3	1.0
Marginal serpentine	4	5.3	Pseudomorphic serpophite	4	1.0
Pseudomorphic serpentine	5	4.7	Pseudomorphic serpophite	5	1.5
Pseudomorphic serpentine	6	4.2	Pseudomorphic serpophite	10	3.2
Pseudomorphic serpentine	7	4.8	Pseudomorphic serpophite	11	2.5
Marginal serpentine	8	5.7	Pseudomorphic serpophite	12	2.4
Pseudomorphic serpentine matrix	9	6.3	Pseudomorphic serpophite	13	2.5
			Pseudomorphic serpophite	14	2.5
Wesselton Mine (South Africa)			Pseudomorphic serpophite	15	-0.5
W3 Hypabyssal kimberlite (Jan. 2010)			Segregation serpophite	6	-1.3
Pseudomorphic serpentine vein	1	4.9	Segregation serpophite	7	-1.6
Pseudomorphic serpentine vein	2	4.9	Segregation serpophite	8	-1.8
Pseudomorphic serpentine vein	3	4.7	Segregation serpophite	9	-1.8
Marginal serpentine	4	5.1	Segregation serpophite	16	-0.1
			Segregation serpophite	17	0.1
Wesselton Mine (South Africa)			Segregation serpophite	18	-0.5
W7 Hybabyssal kimberlite (Feb. 2007)			Segregation serpophite	19	-0.1
Pseudomorphic serpentine core	1	3.8			
Pseudomorphic serpentine rim	2	2.5	Ham West (Canada)		
Pseudomorphic serpentine matrix	3	3.4	HW11 Hypabyssal kimberlite (Jan.2010)		
Pseudomorphic serpentine rim	4	1.6	Segregation serpophite	1	1.5
Pseudomorphic serpentine core	5	4.2	Segregation serpophite	2	1.2
Pseudomorphic serpentine rim	6	0.6	Segregation serpophite	3	1.6
Pseudomorphic serpentine core	7	4.6	Segregation serpophite	4	1.3
Pseudomorphic serpentine rim	8	1.7	Pseudomorphic serpophite	5	4.1
Pseudomorphic serpentine rim	9	2.7	Pseudomorphic serpophite	6	3.3
Pseudomorphic serpentine rim	10	3.6	Pseudomorphic serpophite	7	3.7
Pseudomorphic serpentine rim	11	2.2			
Pseudomorphic serpentine core	12	3.7	Lac De Gras (Canada)		
Pseudomorphic serpentine core	13	5.8	93T33 Hypabyssal kimberlite (Jan. 2010)		
Pseudomorphic serpentine rim	14	2.9	Segregation serpophite	1	2.6
Pseudomorphic serpentine rim	15	2.9	Segregation serpophite	2	2.0
Pseudomorphic serpentine core	16	6.4	Segregation serpophite	3	2.9
Pseudomorphic serpentine rim	17	2.9	Segregation serpophite	4	3.0
Pseudomorphic serpentine matrix	18	1.7	Segregation serpophite	5	2.6
Pseudomorphic serpentine rim	19	2.8	Segregation serpophite	6	3.0
Pseudomorphic serpentine rim	20	3.6			

trend is either a feature of fluid compositional evolution or a influx of light meteoric water. Local alteration in situ by either present day or paleo-meteoric waters is very unlikely to produce such similarities, as the isotopic composition of meteoric water would certainly be very different at each locality. For example, it seems unreasonable to expect the

 Table 2
 Oxygen isotopic composition
 <sup>18</sup>O ‰ of serpentines in diatreme zone Kimberlites

Location	Analysis	<sup>18</sup> O	Location	Analysis	<sup>18</sup> O
Letseng-le-terae (Lesotho) (Jan. 2010)			Kao (Lesotho)		
K1 Main Pipe sample #1			K1 (Jan. 2010)		
Pseudomorphic serpentine core	1	5.0	Pseudomorphic serpentine core	1	4.5
Pseudomorphic serpentine core	2	4.9	Pseudomorphic serpentine core	2	4.9
Pseudomorphic serpentine rim	3	3.9	Pseudomorphic serpentine rim	3	4.9
Marginal serpentine	4	2.4	Marginal serpentine	4	4.8
Pseudomorphic serpentine core	5	3.5	Pseudomorphic serpentine core	5	4.9
Pseudomorphic serpentine rim	6	3.1	Pseudomorphic serpentine core	6	4.6
Marginal serpentine	7	4.3	Marginal serpentine	7	4.8
Marginal serpentine	9	4.0	Interclast serpophite	8	3.8
Pseudomorphic serpentine rim	10	4.3	Interclast serpophite	9	6.3
Pseudomorphic serpentine core	11	3.5	Interclast serpophite	10	5.3
Pseudomorphic serpentine core	12	4.2			
Interclast serpophite	13	2.1	Lethlekane (Botswana)		
Interclast serpophite	14	1.5	(Jan. 2010)		
Pseudomorphic serpentine core	15	4.4	Pseudomorphic serpentine core	1	8.1
Pseudomorphic serpentine rim	16	1.7	Pseudomorphic serpentine core	2	7.8
Interclast serpophite	17	1.7	Pseudomorphic serpentine core	3	7.5
Interclast serpophite	18	3.4	Marginal serpentine	4	9.1
Letseng-le-terae (Lesotho)					
K1 Main Pipe sample #2 (Feb. 2007)					
Pseudomorphic serpentine core	1	4.2	Pseudomorphic serpentine rim	16	5.2
Pseudomorphic serpentine core	2	3.9	Pseudomorphic serpentine core	17	4.0
Pseudomorphic serpentine core	3	4.0	Pseudomorphic serpentine core	18	3.7
Pseudomorphic serpentine rim	4	3.8	Pseudomorphic serpentine rim	19	4.8
Pseudomorphic serpentine rim	5	3.2	Pseudomorphic serpentine rim	20	4.3
Pseudomorphic serpentine rim	6	3.9	Marginal serpentine	21	2.3
Pseudomorphic serpentine vein	7	2.5	Pseudomorphic serpentine core	22	4.6
Marginal serpentine	9	1.2	Pseudomorphic serpentine rim	23	2.3
Marginal serpentine	10	1.3	Pseudomorphic serpentine rim	24	2.4
Marginal serpentine	11	1.7	Pseudomorphic serpentine core	25	4.1
Pseudomorphic serpentine core	12	4.6	Pseudomorphic serpentine rim	26	1.7
Pseudomorphic serpentine core	13	4.8	Pseudomorphic serpentine vein	27	1.4
Pseudomorphic serpentine rim	14	2.8	Pseudomorphic serpentine core	29	3.9
Marginal serpentine	15	-1.8	Marginal serpentine	30	1.8

Cretaceous local groundwater/rainfall at Letseng-la-terae (a kimberlite emplaced in basalt) to be similar to that of Devonian groundwater at the Iron Mountain kimberlite emplaced in granite.

From these data, it is also clear that there cannot be simple permeation of an externally derived fluid throughout these kimberlites, otherwise all isotopic compositions regardless of paragenesis would be similar, and trends such as those shown in Figs. 3 and 9 would not be preserved. These observations argue against any *significant* amounts of meteoric water being involved in the serpentinization events and are at variance with the hypotheses of Hayman et al. (2009) that interclast serpentine in KPK is merely a replacement of pre-existing material.

Figure 10 shows how the oxygen isotopic compositions of pseudomorphic serpentine might change as a function of water/serpentine ratios in open and closed systems (Sheppard et al. 1969; Wenner and Taylor 1973). It is assumed that parental olivine has a primary  $\delta^{18}$ O of about +6 ‰, that is similar to that of fresh olivine in kimberlite



**Fig. 6** Letseng-la-terae (Lesotho) diatreme zone KPK (Main Pipe) consisting of serpentine–chlorite pseudomorphs after olivine set in a chlorite–diopside interclast matrix. Back-scattered electron image. Numbers indicate analytical points (see Table 2; sample #1)



**Fig. 8** Lethlekane (Botswana) diatreme zone KPK consisting of serpentine–chlorite pseudomorphs after olivine set in a chlorite–diopside interclast matrix. Back-scattered electron image. Numbers indicate analytical points (see Table 2)



Fig. 7 Kao (Lesotho) diatreme zone KPK (K1) consisting of serpentine-chlorite pseudomorphs after olivine set in a chlorite-diopside interclast matrix. Back-scattered electron image. Numbers indicate analytical points (see Table 2)

(Ustinov et al. 1994) and mantle-derived ultramafic rocks (Taylor and Sheppard 1986), and that this is reduced by <sup>16</sup>O enrichment as a consequence of mixing and reaction with isotopically lighter water. Figure 10 is based upon the serpentine–water fractionation factor ( $\Delta^{18}$ O) determined by Wenner and Taylor (1973). Minor revisions to this fractionation factor by Früh-Green et al. (1996) do not change the conclusions given below. Chlorite–water fractionation factors determined by Cole and Ripley (1998) are essentially identical to those of serpentine–water, suggesting that isotopic fractionation between chlorite and water can be described by the same parameters as those for serpentine–water. Figure 10 indicates that for serpentinization at

200-300 °C in closed systems with initial water compositions ranging from -10 to -20 ‰, "water/serpentine" ratios cannot exceed 0.8. Low-temperature (<100 °C) serpentinization (Evans 2004) is considered to be an unlikely process with respect to the probable serpentinization temperatures of kimberlites (200-400 °C: Mitchell 1986; Evans 2004; Stripp et al. 2006; Andrani et al. 2007), and effectively rules out high ( $\gg$ 1) "water/serpentine" ratios as a cause for the isotopic trend observed. Thus, these data are interpreted to suggest that there was not an influx of significant volumes of low-temperature meteoric water as a cause of serpentinization. This conclusion is supported by the absence of extremely light oxygen (i.e.  $\delta^{18}O < -5 \%$ ) in all of the serpentines occurring in the kimberlites investigated. Similar conclusions can be drawn for open systems (Fig. 10).

Figure 10 should be taken as an illustrative "end-member" case, as the  $H_2O/(H_2O + CO_2)$  ratios of the fluids involved are unity and equilibrium is assumed. In reality, as noted above, fluids in kimberlites are undoubtedly mixtures of H<sub>2</sub>O and CO<sub>2</sub>, with dominant H<sub>2</sub>O (Kjarsgaard et al. 2009) and equilibrium, especially in diatreme zone rocks, might not be realized. The effects of varying the composition of the fluids on the oxygen isotopic composition of carbonates in kimberlites have been discussed by Wilson et al. (2007). It was shown that  $\delta^{18}$ O values can vary significantly (2-17 ‰) and depend not only on temperature, but strongly upon the assumed CO<sub>2</sub>/H<sub>2</sub>O ratio of the fluid. Hence, the observed isotopic trend towards enrichment in <sup>16</sup>O could simply result from changes in the fluid composition during crystallization. Calculation of such changes is beyond the scope of this preliminary investigation.



Fig. 9 Core-to-rim variations in the oxygen isotopic composition of oxygen ( $\delta^{18}$ O) versus the FeO<sub>T</sub> content of pseudomorphic serpentinechlorite replacing olivine macrocrysts in diatreme zone kimberlite from Letseng-la-terae (Lesotho)

The calculated low water/serpentine ratios and <sup>16</sup>0 enrichment trends, in themselves, do not rule out some influx of meteoric water, although they clearly demonstrate that this is not a volumetrically important process in the formation of serpentine in kimberlite. However, this observation does not imply that such a secondary process is the primary cause of serpentinization. This is because petrographic observations (Mitchell 1986, 2008; Mitchell and Putnis 1988) together with O and C isotopic data for carbonates (Wilson et al. 2007) have provided conclusive evidence that serpophite-carbonate segregations in kimberlites are of deuteric origin and not post-emplacement secondary replacement features as advocated, for example, by Hayman et al. (2009) and Cas et al. (2008). Such processes cannot produce the complex textural and paragenetic relationships actually observed and would result in pervasive uniform serpentinization with or without secondary calcite. It is unreasonable to expect that post-emplacement secondary serpentinization would produce similar petrographic and mineralogical features in kimberlites of diverse age and emplacement conditions in different groundwater regimes. Note that Andreani et al. (2007) have shown that serpentinization is a dynamic process and controlled by reaction kinetics rather than by P or T conditions; hence, equilibria of the type utilized by Stripp et al. (2006) are not relevant to the crystallization of serpentine from deuteric Mg-Si sols. Andreani et al. (2007) show that the sequence of serpentine formation with decreasing temperature in serpentine veins in oceanic peridotites is as follows: lizardite; polygonal serpentine; chrysotile; conical serpentine, that is essentially the same sequence as observed in kimberlites from vein and marginal pseudomorphic lizardite to serpophitic segregation serpentine. This sequence cannot



**Fig. 10** Isotopic composition of "serpentine" ( $\delta^{18}$ O) calculated for open and closed systems as a function of (water/"serpentine") ratios, temperature and isotopic composition of external fluids (meteoric water) characterized by isotopically light oxygen. Serpentine–water fractionation factors are from Wenner and Taylor (1971).  $\delta R_i = initial \delta^{18}$ O of olivine;  $\delta W_i = initial \delta^{18}$ O of water

originate from post-emplacement serpentinization. Consequently, it is concluded here that the water involved in vein and marginal serpentinization and formation of serpophite– calcite segregations is also principally of deuteric origin. On the basis of petrographic criteria, the serpentine–chlorite of the interclast matrices of PKP is considered to result from the alteration in pre-existing phyllosilicates by deuteric fluids (Mitchell et al. 2009). These fluids on the basis of the O isotopic data presented here are considered also to be of deuteric origin. However, fluids which resulted in the marginal and pseudomorphic serpentinization of olivine in magmaclasts might (e.g. Letseng-la-terae) or might not (e.g. Kao) be the same as those forming the interclast matrix serpentine chlorite.

#### Conclusions

The oxygen isotopic composition of serpentine and serpentine–chlorite replacing olivine in diverse hypabyssal and diatreme zone kimberlites ranges from about + 5 to  $-1.7 \delta^{18}$ O ‰. These data are interpreted to indicate that early-forming retrograde serpentine replacing olivine (and/or mica) had near-mantle oxygen isotopic compositions. Subsequent isotopic evolution of these deuteric fluids to lower temperatures (200–300 °C) resulted in slight enrichment in <sup>16</sup>O. This oxygen isotopic variation can be modelled using experimentally derived water–serpentine fractionation factors and diverse externally derived water/serpentine ratios. The observed isotopic variations can be

interpreted to indicate that serpentine compositions must reflect low water/serpentine ratios (< 0.8) at the time of their formation. An alternative explanation of these data is that the isotopic trends observed reflect changes in the  $CO_2/H_2O$  ratio of the serpentine-forming fluids.

These isotopic data coupled with petrographic observations suggest that pervasive replacement of kimberlites by large volumes of low-temperature externally derived (meteoric) water has not occurred. Similar trends in oxygen isotopic evolution regardless of facies or location imply that internal deuteric processes are dominant in the formation of the observed serpentine–chlorite assemblages.

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# Wyoming Craton Mantle Lithosphere: Reconstructions Based on Xenocrysts from Sloan and Kelsey Lake Kimberlites

I. V. Ashchepkov, H. Downes, R. Mitchell, N. V. Vladykin, H. Coopersmith, and S. V. Palessky

#### Abstract

The structure of the lithospheric mantle of the Wyoming craton beneath two Paleozoic kimberlite pipes, Sloan and Kelsey Lake 1 in Colorado, was reconstructed using single-grain thermobarometry for a large data set (>2,600 EPMA analyses of xenocrysts and mineral intergrowths). Pyrope compositions from both pipes relate to the lherzolitic field (up to 14 wt% Cr<sub>2</sub>O<sub>3</sub>) with a few deviations in CaO to harzburgitic field for KL-1 garnets. Clinopyroxene variations (Cr-diopsides and omphacites) from the Sloan pipe show similarities with those from Daldyn kimberlites, Yakutia, and from kimberlites in the central part of the Slave craton, while KL-1 Cpx resemble those from the Alakit kimberlites in Yakutia that sample metasomatized peridotites. LAM ICP analyses recalculated to parental melts for clinopyroxenes from Sloan resemble contaminated protokimberlite melts, while clinopyroxenes from KL-1 show metasomatism by subduction fluids. Melts calculated from garnets from both pipes show peaks for Ba, Sr and U, and HFSE troughs, typical of subduction-related melts. Parental melts calculated for ilmenites from Sloan suggest derivation from highly differentiated melts, or melting of Ilm-bearing metasomatites, while those from Kelsey Lake do not display extreme HFSE enrichment. Three P-Fe# (where Fe# = Fe/(Fe + Mg) in atomic units) trends within the mantle lithosphere beneath Sloan have been obtained using monomineral thermobarometry. At the base, the trends reveal melt metasomatized (possibly sheared) peridotites (Fe# = 13-15 %), refertilized peridotites (Fe# = 10–11 %) and primary mantle peridotites (Fe# = 7–9 %). Anomalous heating was found at depths equivalent to 4.0 and 3.0-2.0 GPa. The mantle section beneath KL-1 is widely metasomatized with several stages of refertilization with dispersed IIm–Cpx trends. The step-like subadibatic heating in the mantle column beneath the Sloan pipe is strong in the

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D. G. Pearson et al. (eds.), *Proceedings of 10th International Kimberlite Conference*, Volume 1, Special Issue of the Journal of the Geological Society of India, DOI: 10.1007/978-81-322-1170-9\_2, © Geological Society of India 2013 base and the middle part and weaker within 2–3 GPa. Heating beneath the KL-1 pipe is more evident in the base and middle part from 7.0 to 3.0 GPa.

#### Keywords

Mantle lithosphere • Thermobarometry • Colorado • Wyoming craton • Pyrope • Cr-diopside • Ilmenite • Chromite

#### Introduction

Information about the composition and structure of the mantle beneath North America is mainly available from the Slave craton (Aulbach et al. 2004; Kopylova and Caro 2004). Less is known about the Wyoming craton, despite the rather long history of investigation of its kimberlites, mantle mineralogy, and petrology (McCallum et al. 1975; Eggler et al. 1979; Hearn 1984; Ater et al. 1984; Hausel 1998; Smith et al. 1979; Ashchepkov et al. 2001; Smith and Griffin 2005; Usui et al. 2007; De Stefano et al. 2009; Carlson et al. 2004; Schulze et al. 2008 etc.). The more productive kimberlites in the Slave and Superior cratons have attracted more attention from mantle petrologists (Menzies et al. 2004; Schmidberger et al. 2007; Smart et al. 2009; MacKenzie and Canil 1999; Kopylova et al. 1999; Kopylova and Caro 2004; Heaman et al. 2003, 2004, 2006; Kjarsgaard et al. 2004; Schmidberger and Francis 1999; Meyer et al. 1994; Eccles et al. 2010 etc.).

The Wyoming craton is a unique example in which to study the evolution of the upper mantle because kimberlites were emplaced from Late Proterozoic through Late Paleozoic to Eocene and Miocene times (Lester and Larson 1996; Griffin et al. 2004; Hausel 1998; Hearn 2004). Earlier studies of xenocrysts and xenoliths from the Wyoming craton (McCallum and Eggler 1976; Eggler et al. 1979; Ater et al. 1984; Downes et al. 2004; Davies et al. 2004; Schulze et al. 1992, 1995; Hearn 2004; Hausel 1998; Coopersmith et al. 2003; Carlson et al. 2004) revealed general variations of mineral chemistry and compositions of mantle minerals and xenoliths, as well as information about the transformation of the Wyoming craton keel. Petrologic reconstructions suggest continuous destruction of the craton by subduction tension, tectonic and plume forces with reduction in the cratonic keel (Coopersmith et al. 2003; Carlson et al. 2004; Carlson and James 2011) accompanied by extreme variations in mantle isotopic compositions (Carlson et al. 1999, 2004; Rudnick et al. 1999). We present new information for samples from the Sloan and Kelsey Lake-1 (KL-1) pipes (Ater et al. 1984; Coopersmith et al. 2003 and references therein; Carlson et al. 2004). Using mainly monomineral thermobarometry and geochemical features of minerals, we show reconstructions of the subcratonic lithospheric mantle (SCLM) beneath the Wyoming craton and its possible evolution.

#### Location and Geology

The Wyoming craton has experienced mantle-derived volcanism over a long period of time, including kimberlites (Vendian to Eocene), lamproites (Mitchell and



Fig. 1 Location of kimberlite pipes in Wyoming craton in state line district and surrounding area

Bergman 1991), minettes (Macdonald et al. 1992), and alkaline basalts (O'Brien et al. 1995), and most of these contain deep-seated xenoliths. The Paleozoic Sloan and Kelsey Lake kimberlite groups are located in the southern part of the Wyoming craton in the State Line kimberlite district, in northern Colorado (Fig. 1). They both consist of several kimberlites bodies (5 in Sloan and 8 in Kelsey Lake) (Hausel 1998; Coopersmith et al. 2003; Schulze et al. 2008), some of them relatively large (up to 400 m) which contain diamonds. Most of them carried abundant xenocrysts which are more frequent and fresher in the Sloan pipes. Large peridotite xenoliths are rare, and in KL-1 pipe, they are mostly altered.

#### **Data Set and Methods**

The samples from two pipes were analyzed in the Institute of Mineralogy and Petrology SD RAN Novosibirsk by Electron Microprobe (EPMA) (Lavrent'ev and Usova 1994) from KL-1 pipe (H. Coopersmith collection) and Sloan (H. Downes samples) as separate grains and mineral intergrowths (758 and 1,150 analyses, respectively). In addition, 14 mineral grains from KL-1 and 21 from Sloan were analyzed by inductively coupled mass spectrometry with laser ablation system (LAM ICP). The method and precision were described by Ashchepkov et al. (2010, 2013, 2012).

#### **Mineralogy of Xenocrysts**

Megacrysts and xenocrysts from Sloan and Kelsey Lake-1 (KL-1) pipes were analyzed by EPMA and LAM ICP-MS in the Analytic Centre IGM SB RAS (Novosibirsk). We also investigated a smaller number of xenocrysts from the Vendian Chicken Park and Ordovician Iron Mountain kimberlites.

*Garnets* (Gar) from Sloan (Fig. 2) mainly fall in the lherzolite field (Gr9) (Sobolev et al. 1973a, 1977; Gurney 1984) with up to 12.5 wt%  $Cr_2O_3$ . In contrast, the KL-1 garnets reach 14 wt%  $Cr_2O_3$  and 5 % of them show



Fig. 2 Variations of major element compositions from garnets from Sloan and Kelsey Lake 1