

carbon and helium in faulted-seismogenic areas

SANO, Yuji^{1*}

¹Atmosphere and Ocean Research Institute, University of Tokyo

Carbon and helium have been discharging for a long time from the Earth's mantle to the atmosphere through volcanic and hydrothermal activity. In addition they are derived from faulted-seismogenic areas. It is obvious that volcanic fluxes are originated in magma source even though they may be partly contaminated by crustal material. In contrast, it is difficult to estimate how deep they are derived in non-volcanic and tectonically active regions. Irwin & Barnes [1] reported that CO₂-rich springs occur worldwide along major zones of seismicity. They further suggested that much of the CO₂ is derived from the mantle and that other important sources are the metamorphism of marine carbonate-bearing sedimentary rocks and the degradation of organic material. Carbon isotopes may provide information of the origin. When the delta13C value of spring gas in faulted-seismogenic area shows -6permil, it is explained by either mantle carbon or a mixing of marine carbonate (0permil) and sedimentary organic matter (-30permil). Thus it is difficult to estimate the origin of carbon. If the data are combined with helium isotopes, however, we can deconvolve the mantle contribution quantitatively [2]. There are several evidences of mantle carbon and helium degassing from active fault. Kennedy et al. [3] suggested the mantle helium flux in the San Andreas fault system located at boundary between the Pacific and North American plate. The bottom may extend the upper mantle. Significant CO₂ discharges were observed at the same time. A part of CO₂, up to 3.3% may be derived from the mantle [4]. Similar discharges have been observed in the North and East Anatolian fault zones [5,6]. These are examples of steady-state degassing from active fault. Non steady-state, catastrophic degassing of carbon and helium were reported in the 1995 Kobe earthquake, even though they are originated in shallow crust [7,8]. On the other hand, increase of helium isotopes in bottom seawater in the trench region after the 2011 Tohoku-oki earthquake suggested substantial input of mantle helium [9]. There may be a fluid flow induced by the earthquake, which would carry helium and methane from the mantle wedge to the trench through the entire plate boundary.

Reference [1] Irwin & Barnes, 1980. *JGR* **85**, 3115-3121. [2] Sano & Marty, 1995. *Chem Geol* **119**, 265-274. [3] Kennedy et al., 1997. *Science* **278**, 1278-1281. [4] Kulongoski et al., 2013. *Chem Geol* **339**, 92-102 [5] de Leeuw et al., 2010. *App Geochem* **25**, 524-539. [6] Italiano et al., 2013. *Chem Geol* **339**, 103-114. [7] Sano et al., 1998. *Chem Geol* **150**, 171-179. [8] Famin et al., 2008. *EPSL* **265**, 487-497. [9] Sano et al., 2014. *Nature Commun* **5**, 3084.

Keywords: Helium, Carbon, Origin, Flux, Fault

Volatiles in kimberlites:an indicator of possible deep mantle origin

KANEOKA, Ichiro^{1*}

¹Earthquake Research Institute, University of Tokyo

Kimberlites are well known to bear diamonds and their magmas are regarded to have been derived from a depth of at least more than 150km. They are found only in old continental areas and the exposed areas at the surface are quite limited to a diameter of less than 2km in most cases. Although their distributions are quite sparse, they have quite unique characteristics in their chemical and isotope compositions.

In spite of ultrabasic properties, they bear abundant volatiles such as H₂O, CO₂, halogens, sulfur and they also contain relatively abundant LIL elements. On the other hand, they show more abundant concentrations of Os and Ir compared to those of other kinds of lavas such as MORBs (mid-oceanic ridge basalts) and OIBs (oceanic island basalts). Their magmas are generally regarded to have been produced in relatively less oxidized environments compared to MORBs, OIBs and IABs (island arc basalts). Hence, it is a quite significant issue to clarify the origin of volatiles in kimberlite magmas, which might be related to the chemical circumstances of deep mantle.

Based on Sr-Nd isotope systematics, kimberlites are classified in two groups (Smith, 1983). In the ⁸⁷Sr/⁸⁶Sr-¹⁴³Nd/¹⁴⁴Nd diagram, Group I kimberlites are relatively concentrated in an area which is close to the Bulk Earth value. In contrast, Group II kimberlites are located in an area of typical enriched character and widely scattered. Most kimberlites are regarded to belong to Group I. Since Group II kimberlite magmas show the effect of recycled materials with an enriched character, volatiles in Group II kimberlites might have been also affected from them.

On the other hand, distribution of data of Group I kimberlites on the Sr-Nd isotope diagram implies that the magma source of Group I kimberlites is less fractionated from the assumed Bulk Earth material than those of MORBs. Further, Ne isotopes in kimberlites from Russia indicates that its magma source is similar to those of OIBs isotopically and different from those of MORBs (Sumino et al. 2006). Noble gas signatures of OIBs indicate the occurrence primordial components in the OIB source (e.g.Kaneoka, 2008). The magma source of MORBs has been generally assigned to be located in the upper mantle, while those of OIBs are located at a deeper part than those of MORBs. These signatures suggest that volatiles in Group I kimberlites would probably reflect those of the deep mantle. In effect, some diamonds are regarded to have been derived from the upper part of the lower mantle. Thus, at least Group I kimberlites might contain volatiles including carbon of the lower mantle origin which has not always been recycled.

Further, kimberlite magmas are conjectured to have been erupted directly from a magma reservoir located below the thick continental lithosphere within a few hours so that captured diamonds might not be decomposed during the rise of a kimberlite magma. Hence, it is inferred that chemical contamination for a kimberlite magma might be less compared to that for a OIB magma which would take much longer time to be transported to the surface from a magma reservoir. If so, Group I kimberlites might keep more primary information on the chemical state of the lower mantle compared to OIBs.

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Keywords: volatiles, kimberlite, deep mantle, OIBs, isotopes, diamond

Carbon isotope systematics during carbonated silicate melting under upper mantle conditions

MADHUSOODHAN, Satish-kumar^{1*} ; MIZUTANI, Shogo² ; YOSHINO, Takashi³

¹Niigata University, ²Shizuoka University, ³Okayama University

Carbon isotope fractionation between graphite and carbonated silicate melt was determined at 5 GPa and in the temperature range between 1400 and 1900 °C. High pressure experiments were carried out in the carbon-saturated model harzbergite system (Enstatite-Magnesite-Olivine-Graphite), where carbonated silicate melt and graphite were the two stable carbon-bearing phases in the run products. Carbonated silicate melting resulted in an isotopic fractionation between graphite and carbon in the silicate melt, where the carbon in the melt is ¹³C enriched than co-existing graphite (Mizutani et al., 2014). ¹³C enrichment in carbonate melt were further confirmed in experiments where redox melting between olivine and graphite produced carbonate melt as well as carbonate reduction experiments to form graphite.

According to the results of carbon isotope fractionation obtained in this study between graphite and carbonated silicate melt, heavier carbon will be selectively partitioned to the melt and graphite will be lighter than the melt in the order of 1 to 2 permil. If locally oxidative or reductive domains are present or melt extraction and a Rayleigh fractionation process dominate in the upper mantle, then carbonate silicate melt-graphite carbon isotope partitioning at upper mantle conditions will have larger effect on carbon isotopic composition. It is possible that carbonate melt will progressively enrich in carbon isotopes, which corresponds to the primary igneous carbonatite values (-5 to -8 permil) and even rare carbonatites having the more enriched ¹³C (-2 to -5 permil) may be explainable in term of the existence of more reductive environment. Conversely, the graphite coexisting with such melts will have delta13C values corresponding to main mantle carbon reservoir. Recent experiments have shown that carbonate melts can be a medium for the efficient crystallization of diamonds in Earths mantle. Therefore, redox reaction at lower upper mantle is likely to yield the range of carbon isotope variation of mantle derived diamond. Moreover, carbonated mantle melting according to redox melting at upwelling mantle can be an alternative explanation for the formation of ¹²C enriched diamonds in the deep mantle

Mizutani, S., Satish-Kumar, M. and Yoshino, T., (2014) Experimental determination of carbon isotope fractionation between graphite and carbonated silicate melt under upper mantle conditions, Earth and Planetary Science Letters (in press).

Keywords: carbonated mantle melting, carbon isotopes, graphite, fractionation

$^3\text{He}/^4\text{He}$ distributions near the Tancheng-Lujiang faults zones, at Liaoning, NE China

ZHENG, Guodong^{1*} ; XU, Sheng¹ ; NAKAI, Shun'ichi² ; WAKITA, Hiroshi³ ; WANG, Xianbin¹

¹Institute of Geology and Geophysics, Chinese Academy of Sciences, ²Earthquake Research Institute, The University of Tokyo,

³Faculty of Science, The University of Tokyo

Chemical and isotopic compositions have been measured for natural gases near the NNE trending Tancheng-Lujiang Fault Zones (TLFZ) at Liaoning Province, NE China, including hydrocarbon-rich natural gases from Liaohe basin (121°E-124°E, 40.5°N-42°N) and nitrogen-rich geothermal gases from the eastern Liaoning Mountains. Observed $^3\text{He}/^4\text{He}$ ratios show two orders of magnitude variability from 0.04 RA to 3.5 RA where RA is atmospheric $^3\text{He}/^4\text{He}$ ratio 1.4×10^{-6} . The following geochemical observations are noted: (1) at Liaohe basin and the adjacent geothermal fields, $^3\text{He}/^4\text{He}$ ratios show positive correlations with He contents; (2) in Liaohe basin, the $^3\text{He}/^4\text{He}$ ratios are largely variable (0.04-3.5 RA), generally high in the eastern depress and low in the western depress; (3) in the eastern Liaoning mountains, geothermal $^3\text{He}/^4\text{He}$ ratios are generally low (0.2-0.7 RA) but have closed relationship with distribution of seismic activity and heat flow; and (4) overall there is a spatial distribution pattern that $^3\text{He}/^4\text{He}$ ratios gradually decrease from the TLFZ eastwards and westwards. Such a $^3\text{He}/^4\text{He}$ distribution feature shows strong evidence that the TLFZ played an important role on mantle-derived helium transform from mantle upwards and groundwater circulation along the deep major faults.

Keywords: helium, fault, china, isotopes

Heterogenous carbon reservoir in sublithospheric mantle: variations of carbon isotopic composition in diamonds from Sao-

ZEDGENIZOV, Dmitriy^{1*}; KAGI, Hiroyuki²; SHATSKY, Vladislav³; RAGOZIN, Alexey²

¹V.S.Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia, ²University of Tokyo, Tokyo, Japan,, ³A.V.Vinogradov Institute of Geochemistry, Irkutsk, Russia

The Juina kimberlite field in Brazil is a well-known source of alluvial sublithospheric diamonds as identified by their properties and mineral inclusions. Taking advantage of the rather common occurrence of superdeep mineral inclusion assemblages in diamonds from Sao-Luis river alluvial deposits (Juina, Brazil), we carried out a study of variations of C isotope in diamonds from this locality.

Diamonds from Sao-Luis are characterized by rough morphologies and have complex growth histories. Episodic growth, plastic deformation and breakages are visible in these crystals and most diamonds have experienced a final episode of resorption before exhumation. Total nitrogen content in studied diamonds reach 1200 ppm and more. Only several studied diamonds are nitrogen-free (type IIa). Some diamonds consist of domains that are also nitrogen-free but other parts may contain nitrogen. Many diamonds have very low (>10 ppm) but still detectable nitrogen impurity. Extremely high nitrogen aggregation state and overall platelet degradation detected in the majority diamonds from Sao-Luis are suggested they have stored at considerably higher temperatures that are typical for continental lithosphere.

Syngenetic inclusions in 59 diamonds from Sao-Luis were represented by phases of superdeep paragenesis as it was described previously. The dominated inclusions are majoritic garnets, ferropericlases, CaSi- and CaSiTi-perovskites, MgSi-perovskites, TAPP, SiO₂ phases, kyanites, AlSi-phases, olivines and Fe-sulfides. Rare inclusions of clinopyroxenes, KFsp (K-hollandite?), CF, NAL, grossular, native iron, magnesite, CaCO₃+CaMgSi₂O₆ (composite inclusions) have been found in separate diamonds. All majoritic garnets we found are of metabasic affinity and in some cases associated with omphacitic clinopyroxenes.

The studied diamonds from Sao-Luis display wide variations of carbon isotopic compositions ($\delta^{13}\text{C}$) ranging from 2.7 to -25.3 ‰. The diamonds with inclusions of ferropericlase have very narrow range of $\delta^{13}\text{C}$ values from -2.1 to -7.7 ‰, which are closely similar to the normal mantle values [Cartigny, 2005; Stachel et al., 2009]. From this observation, it may be suggested that their formation may proceed from isotopically homogeneous mantle reservoir that do not support the model of large primordial isotopic variability of carbon isotopes in primitive Earth's mantle with a predicted pyrolite composition. Diamonds with inclusions of majoritic garnet and CaSi- and CaSiTi-perovskites in many cases show marked differences from the expected normal mantle values of $\delta^{13}\text{C}$ values. Low $\delta^{13}\text{C}$ values (-10 to -25 ‰) have been observed exclusively in a series of superdeep diamonds with calcic-majorite garnets, Ca-silicates, aluminous silicates and SiO₂ from Sao-Luis.

The $\delta^{13}\text{C}$ measurements in core to rim traverses within some individual crystals varied substantially, indicating multi-stage growth histories. The variations in $\delta^{13}\text{C}$ within individual diamonds may be attributed to either different source of carbon or fractionation effect during diamond growth. No correlation of carbon isotope composition and nitrogen content has been found in individual diamonds. It therefore appears that the cores and rims of the Sao-Luis diamonds precipitated from different fluids/melts with variable N/C ratios and/or under different growth conditions. The highly negative $\delta^{13}\text{C}$ values in the core (-20 to -25 ‰) potentially represent organic matter in sediments or altered basalts, and the lower $\delta^{13}\text{C}$ values may represent mixing trends towards normal mantle compositions [Schulze et al., 2004; Harte, 2011]. In this study, we have also described a series of diamonds which show opposite trend of change carbon source from primordial mantle to subducted/crustal (either biotic or abiotic carbon).

Keywords: carbon, diamond, sublithospheric mantle, subduction

Chemical composition of nano-inclusions in supe-deep diamonds and implications to the growth condition

KAGI, Hiroyuki^{1*} ; ISHIBASHI, Hidemi² ; OHFUJI, Hiroaki³ ; ZEDGENIZOV, Dmitry⁴ ; SHATSKY, Vladislav⁴ ; RAGOZIN, Alex⁴

¹Graduate School of Science, University of Tokyo, ²Graduate School of Science, Shizuoka University, ³Geodynamic Research Center, Ehime University, ⁴Russian Academy of Science

Superdeep diamonds originating from the mantle transition zone and the lower mantle were found from alluvial deposits of Sao-Luis river (Juina, Brazil). We investigated carbon isotopic variations and chemical compositions of nano-inclusions in the superdeep diamonds which can give a clue for the growth condition.

We found syngenetic inclusions of superdeep paragenesis from 59 diamond samples from Sao-Luis. The dominant inclusions in diamonds from studied here are CaSi-perovskite and AlSi-phases. MgSi- and CaTi-perovskites, ferropericlase, native iron, coesite and zircon have also been found. Our SIMS analysis showed the wide variations of carbon isotopic compositions ranging from 2.7 to -25.3 ‰ in $\delta^{13}\text{C}$. The details on the carbon isotopic analysis will be reported by Zefgenizov et al. in this session.

Some samples contained microinclusions and FTIR analyses showed that water and carbonates were not major components of these tiny inclusions. To identify the microinclusions, TEM observations were carried out on a foil of carbonado (0.1 micron thick) made from a polished diamond specimen after Au-coating. The foil was fabricated with a Ga ion beam using a focused ion beam (FIB) instrument (JEOL JEM-9310FIB). The foil was observed with a TEM (JEOL JEM-2010) under an accelerating voltage of 200 kV. We found that the microinclusions were euhedral inclusions of several tens nanometers in size. The TEM observations revealed that the nano-inclusions have a negative crystal shape suggesting the syngenetic origin directly related to the diamond growth. In this study, chemical composition of the nano-inclusions were conducted by synchrotron X-ray fluorescence analysis using X-ray micro-beam as an incident light at BL-4A, Photon Factory, KEK. The obtained results clarified that the nano-inclusions contain S, Cr, Mn, Fe, Co, Ni, Cu Zn, and so on. The present study suggests that the growth media of the superdeep diamonds are composed of sulfide melt.

Keywords: diamond, nano inclusion, X-ray fluorescence analysis, super deep diamonds

High-pressure melting experiments on magma genesis in Hawaiian plume: effect of volatiles

GAO, Shan^{1*} ; TAKAHASHI, Eiichi¹ ; IMAI, Takamasa¹ ; SUZUKI, Toshihiro¹

¹Earth and Planetary Sciences, Tokyo Institute of Technology

Introduction: Compared with OIB, Hawaiian tholeiitic basalt is thought to be relatively drier (about 0.5 wt.% H₂O content; Muenow, 1979). In front of the plume core, overlying mantle is metasomatized by hydrous partial melts derived from the Hawaiian plume. Downstream from the plume core, lavas tap a depleted source region similar to enriched Pacific mid-ocean ridge basalt (Dixon & Clague, 2001). Magma genesis model has been proposed by some authors (Hauri, 1996; Takahashi & Nakajima; 2002; Sobolev et al., 2007) that magma produced near the axis of the plume head may be mixtures of two types of melts 1) basaltic andesite melt formed by melting of eclogite and 2) picritic melts formed by the reactive melting of eclogite and peridotite. A series of high temperature high pressure experiments were conducted to explore the genesis of tholeiitic magma from Hawaiian plume and investigate the role of volatiles in magma genesis.

Experiments: A series of experiments were conducted under dry and slightly hydrous conditions at 2.85GPa for 1, 3 to 9 hours and from 1460 to 1520C with a piston cylinder by making basalt peridotite sandwich which using MgO-rich CRB72-180 (Takahashi et al 1998) and a fertile peridotite KLB-1 (Takahashi 1986) as starting materials.

Results: Three factors that might affect melting progress and chemical reaction among minerals – temperature, duration and water content – were examined, respectively.

1) Temperature: (1460~1520C and every 20C as an interval.)

Basalt went partial molten at 1460C and completely molten when temperature went above 1500C. Orthopyroxene reaction rim formed on the border area due to the reaction between high Si-rich melt and olivine in the peridotite matrix. The opx film becomes more visible and thicker with the increasing of temperature. Partial melting degree of peridotite is also related to the increasing of temperature but the change is not very sensitive when 20C as an interval. The higher temperature, the more peridotite molten. The area of the peridotite near the opx film has a higher degree of partially melting than areas away from the boundary.

2) Duration: (1, 3 and 9 hours.)

Longer time do accelerate the speed of chemical reaction between basalt and peridotite in this study. Basalt molten completely as the running time longer than 3 hours. The orthopyroxene reaction rim on the boundary between peridotite and basalt becomes thicker. Large clinopyroxene crystals formed on the border (the minerals on the border from melt to peridotite are cpx, opx, garnet) momentarily yet faded away as the chemical reaction went on with time. Partial melting of peridotite is also positively related to duration. When the melt of peridotite is too much and unable to support the weight of basalt and it would get rid of the crack and finally went to the basalt side and mixed with the basalt melt.

3) Water content

Basalt layer melted completely, and large orthopyroxene crystallized in the basalt side. Peridotite layer also melted considerably at the same time than its anhydrous counterparts owing to the reason that the join of water could lower the peridotite liquidus line and finally made it more partial melted than in hydrous condition.

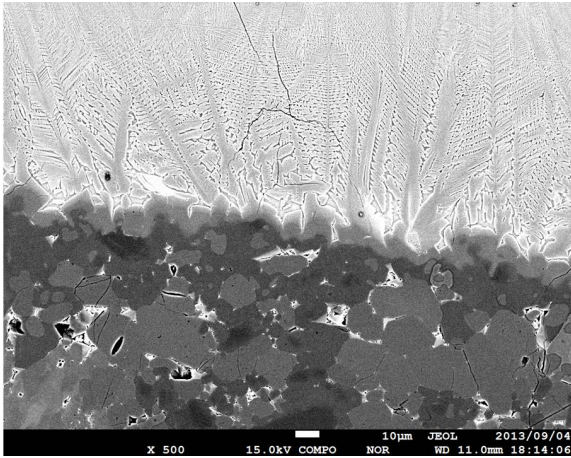
Discussion: Under dry conditions below peridotite solidus, melting is limited in eclogite layers and chemical reactions with ambient peridotite is hindered by opx film. On the other hand, under slightly wet conditions, water could accelerate the melting process of both eclogite and peridotite layer. As a result, melts formed under wet conditions are saturated with oliv+opx whereas those formed under dry conditions could be saturated with only opx. Changing nature of Hawaiian magma during the shield building stage will be discussed in the light of present melting experiments.

Keywords: Hawaiian plume, high-pressure, magma, volatiles

SCG09-07

Room:315

Time:April 28 15:06-15:21



Partitioning of carbon between metallic- and silicate-liquids in magma ocean of differentiated planetesimals

ASAHARA, Yuki^{1*} ; OHTANI, Eiji¹

¹Tohoku University

Partitioning behavior of carbon has not been determined well though it is one of the strong candidates for light element in the earth's core. We investigated partitioning of carbon with sulfur and oxygen between metallic- and silicate liquids at 6 GPa and 2073 K in carbonaceous chondrite composition (Allende meteorite; CV3). High pressure experiments were conducted with multi-anvil high pressure apparatus. Graphite was used as capsule material. Composition of coexisting metallic- and silicate liquids were measured by electron microprobe with wavelength dispersion type spectrometer except for carbon in silicate liquid. To estimate carbon concentration in silicate liquid, carbon concentration of bulk recovered sample was measured by elemental analyzer. Present result suggests that in oxidized carbonaceous chondrite composition, partitioning coefficient of carbon [$D_{Metallicliquid/Silicateliquid} = C_{Metallicliquid} / C_{Silicateliquid}$; C is concentration of carbon in wt.%] is close to 1, and it increases with increasing the Fe^{metal}/Fe^{oxide} ratio of the bulk carbonaceous chondrite composition.

Experimental study of Group-I kimberlite: evidences for carbonatite primary melt and implication to mantle plumes

LITASOV, Konstantin^{1*} ; SHARYGIN, Igor² ; SHATSKIY, Anton² ; OHTANI, Eiji³

¹Novosibirsk State University, Novosibirsk, Russia, ²V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia, ³Department of Earth and Planetary Materials Science, Tohoku University, Sendai, Japan

The experiments on the origin of Udachnaya-East kimberlite (UEK) have been performed using a Kawai-type multianvil apparatus at 2-6.5 GPa and 900-1500 °C. The studied composition represented exceptionally fresh Group-I kimberlite containing (wt.%): SiO₂ = 25.9, TiO₂ = 1.8, Al₂O₃ = 2.8, FeO = 9.0, MgO = 30.1, CaO = 12.7, Na₂O = 3.4, K₂O = 1.3, P₂O₅ = 1.0, Cl = 0.9, CO₂ = 9.9, and H₂O = 0.5. Super-solidus assemblage consists of olivine (Ol), Ca-rich garnet (Gt), Al-spinel (Sp), perovskite (Pv), CaCO₃ (calcite or aragonite), and apatite at 4-6.5 GPa with an addition of clinopyroxene at 3-4 GPa and Na-Ca carbonate with molar ratio of (Na+K)/Ca ~ 0.44 at 6.5 GPa and 900 °C. The apparent solidus was established between 900 and 1000 °C at 6.5 GPa. In the studied P-T range, melt has Ca-carbonatite composition (Ca/(Ca+Mg) = 0.6-0.8) with high alkali and Cl contents (2.8-6.7 wt.% K₂O, 7.3-11.6 wt.% Na₂O, 1.2-3.7 wt.% Cl). The K, Na and Cl contents and Ca/(Ca+Mg) value decrease with temperature. It is argued, that the primary kimberlite melt at depth >200 km was essentially carbonatitic (<5 wt.% SiO₂), however, evolved toward carbonate-silicate composition (with 15-20 wt.% SiO₂) during ascent. The absence of orthopyroxene among the run products indicates that xenogenic orthopyroxene was preferentially dissolved into kimberlite melt. The obtained subliquidus phase assemblage (Ol + Gt + Sp + Pv) at P-T condition of UEK source region differs from lherzolite lithology of this source. Both petrological observations and experiments indicate that kimberlite magma lost substantial amount of CO₂ at shallow depths.

Our study combined with earlier experiments on carbonate-silicate systems at pressures to 30 GPa implies that liquid phase of thermo-chemical plume generated at the core-mantle boundary is represented by alkali-carbonatite melt. This conclusion has broad geodynamic implication providing insight into fluid regime of mantle melting under hotspots along margins of African large low-shear-wave-velocity province. We conclude that the long term activity of rising hot mantle plume and associated carbonatite melt (i.e. proto-kimberlite melt) causes thermo-mechanical erosion of the subcontinental lithosphere mantle (SCLM) roots and creates hot, oxidized, and deformed metasomatic layer at lower parts of initially depleted SCLM, which corresponds to depths constrained from the sheared Gt-lherzolites. The sheared Gt-lherzolites undoubtedly represent the samples from this layer.

Keywords: mantle, kimberlite, carbonatite, plume, melting