[Petrogenetic evidence and FTIR constraints on the origin of diamonds in xenoliths from Yubileynaya and Komsomolskaya pipes, Yakutia]

[Z.V. Spetsius[1], I.N. Bogush[1], W.L. Griffin[2], S.Y. O'Reilly[2] and A.S. Ivanov**]**

[[1]*Geo-Scientific Investigation Enterprise, ALROSA PJSC, Mirny, 678170, Russia, spetsiuszv@alrosa.ru*
[2]*ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS/GEMOC), Macquarie University, NSW 2109, Australia, bill.griffin@mq.edu.au*]

[Introduction]

[Mantle eclogites make up an important component in mantle xenolith suites and are transported to the surface by kimberlite magmas; diamondiferous eclogites represent one of the main diamond reservoirs on Earth. Although peridotitic xenoliths are dominant in kimberlites and P-type diamonds are more abundant than E-type, recovered diamondiferous eclogite xenoliths are significantly more abundant world-wide than are diamondiferous peridotites and are present in all industrial kimberlite deposits of the Yakutian province (Kostrovizky et al., 2015). Despite the relative rarity of eclogitic xenoliths sampled by kimberlites, they offer key constraints on the formation of thickened Archean cratonic lithosphere, as well as the extent of modification resulting from interaction with melt or fluids in mantle environments and during kimberlite transport (e.g., Pearson et al., 2003). Studies of eclogites are important for refining models of global crust–mantle evolution and provide constraints on the origin of diamondiferous mantle as eclogites represent significant diamond reservoirs in some portions of SCLM of Siberian Craton (e.g., Spetsius et al., 2008).

The late Devonian Komsomolskaya and Yubileynaya pipes are located in the center of the Yakutian province, within the Alakit-Marhinsky kimberlite field. The diamond grade of Yubileynaya kimberlites (0.90 ct/t) is higher than Komsomolskaya (0.36 ct/t) but the diamond value of the latter is twice as high. The aim of this study is to petrologically characterize the Yubileynaya and Komsomolskaya xenoliths and their diamonds in order to place robust constraints on the differences in origin of diamonds within the SCLM beneath these pipes. Examination of these diamondiferous eclogites can also have important implications for understanding of diamond genesis and lithosphere evolution within the Siberian Platform, in general. These xenoliths present the opportunity to investigate a unique collection of diamond-bearing xenoliths that will permit constraints on their source materials and on diamond-forming processes. Here, we present major- and trace-element data on garnet and clinopyroxene minerals along.

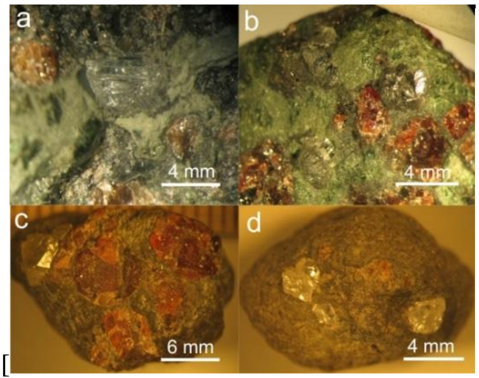
Samples and Methods

35 diamondiferous xenoliths from the Komsomolskaya and Yubileynaya pipes of Yakutia comprise bimineralic eclogites, rare kyanite eclogites and some garnet megacrysts. Most xenoliths contain two or more diamond crystals (0.5-8.0 mm) with predominantly octahedral or transitional forms (Fig.1). Coated diamonds were found in two xenoliths from the Yubileynaya pipe. The distribution of crystals in xenoliths is irregular and does not coincide with the specimen surfaces. Mineral inclusions are rare and represented by sulfides, garnet, clinopyroxene and very rare rutile. Fine-grained interstitial metasomatic mineral assemblages and partial melting phases have also been identified in these xenoliths; this is a characteristic feature of most of the specimens, and a specific feature of diamondiferous eclogites. Samples from Yubileynaya are more intensively metasomatised and altered.

Major element compositions of garnets and clinopyroxenes in the xenoliths were determined with a Superprobe JXA-8800R electron microprobe at the "ALROSA" OJS Company (Mirny, Yakutia). Natural minerals and synthetic were used as standards. Analytical conditions included an accelerating voltage of 15 keV, a beam current of 20 nA, beam size of 5 µm, and 20 seconds counting time for all elements. All analyses underwent a full ZAF correction.

The trace elements have been measured by laser Ablation ICP-MS (LAM) in the Geochemical Analysis Unit at Macquarie University, with NIST 610 glass as external standard and Ca as internal standard; pit diameters were 40 –50 mm and partly at Virginia Polytechnic and State University, and details are given in (Pernet-Fisher et al, 2014).

The morphology of about 300 crystals from eclogite xenoliths of both pipes diamonds was studied, and selected diamonds Komsomolskaya (102) and Yubileynaya (167) were analyzed by micro-Fourier transform infrared (FTIR) spectroscopy to determine both nitrogen content (N_{FTIR}) and nitrogen aggregation state. IR spectra were obtained over the range of 370-4200 cm^{-1} with the use of Vertex 70 FTIR spectrometer and Hyperion 2000 microscope. The spectra resolution was 2 cm^{-1}. Errors in nitrogen content (N_{FTIR}) and nitrogen aggregation state are estimated to be better than 20% and 5% respectively.



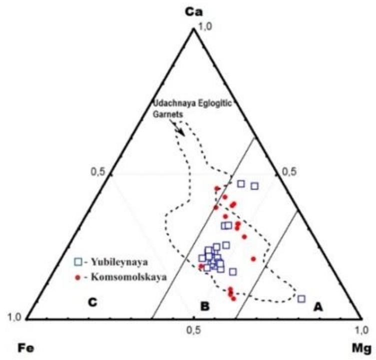


Figure 1: Examples of diamondiferous xenoliths from the Komsomolskaya (a, b) and Yubileynaya (c, d) pipes.
Figure 2: Compositions of garnets of Yubileynaya and Komsomolskaya diamondiferous xenoliths.

Analytical Results

Investigations of 35 xenoliths with diamonds from Yubileynaya and Komsomolskaya pipes allowed to confirm the petrology of these unique rocks and provide new results on the properties of diamonds. Data on major- and trace elements in minerals of 35 diamondiferous xenoliths from the Komsomolskaya and Yubileynaya kimberlites are summarized. Garnets and clinopyroxenes typically plot within the Group B eclogite classification field (Fig. 2). One sample from the Yubileynaya pipe is a high-magnesian chromian harzburgite-dunite garnet megacryst (Cr_2O_3 =9.85 wt%) that contains inclusions of octahedral diamond. Two samples from Komsomolskaya pipe correspond to Group C eclogite (one of these contains minor amounts of kyanite). Minerals in eclogites from this study display no zonation in their chemistry; as such, the major-element compositions can be used to estimate the equilibration temperatures of these samples. We adopted the thermometer of Ellis and Green (1979), which is based on Mg–Fe^{2+} exchange between clinopyroxene and garnet. The results suggest equilibration at 1000–1225 °C at 4 GPa and integrated residence temperatures of ~1160-1200 ºC for diamond growth with slightly lower temperatures for Yubileynaya eclogites.

Garnets in Yubileynaya eclogites are generally characterized by low Cr_2O_3 <0.2 wt% and TiO_2 (0.15-0.45 wt%) at a near-constant MgO of 11.2-13.4 wt%; in contrast CaO and FeO contents show large variations, respectively (7.2-17.7 wt%) and (4.4-16.4 wt%) defining two different groups (Fig. 2). Eclogitic garnets of this pipe also define two obviously different groups with low and high LREE (Fig. 3). Komsomolskaya eclogitic garnets have variable Cr_2O_3 extending up to 1.2 wt%, low TiO_2 (0.10-0.39 wt%), and a range of FeO (9.0-17 wt%) and CaO (3.6-17.2 wt%) contents. Garnets of Group B and C eclogites from Komsomolskaya pipe generally have Mg# >60 and convex-upward REE profiles. Most clinopyroxenes and some garnets in xenoliths from both pipes display LREE and MREE enrichments, consistent with cryptic metasomatism. The REE variation in garnets and clinopyroxenes suggests that some of the xenoliths were formed by subduction. The presence of Eu-anomalies suggests a plagioclase-rich cumulate protolith for some eclogites. Subducted oceanic crust is suggested by garnets of some xenoliths from both pipes.

FTIR data display differences in total nitrogen content and aggregation state in diamonds of xenoliths from these two pipes. About 80% of the crystals from xenoliths of Yubileynaya pipe have high total contents of nitrogen (600-1500 at.ppm) with low aggregation state (20-30%) and 20% of crystals have total nitrogen content < 500 at.ppm with high aggregation states (30-80%). Two obvious trends are

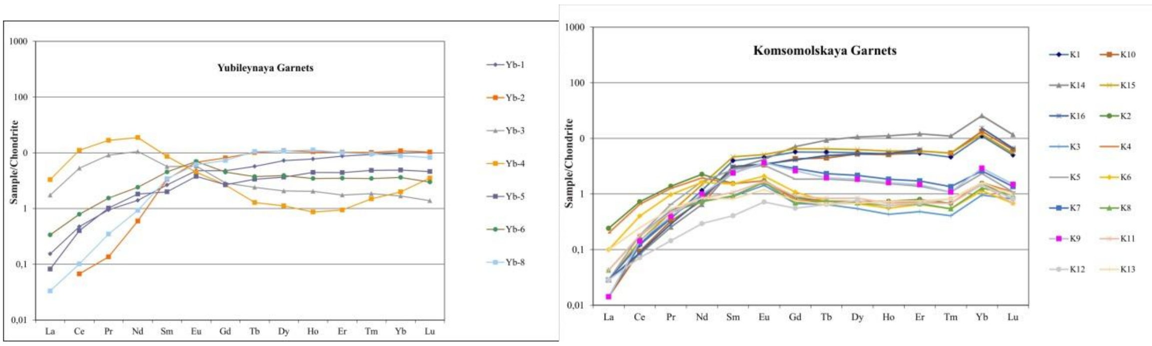


Figure 3: Chondrite-normalized REE abundances of Yubileynaya and Komsomolskaya xenolith garnets. All normalization factors from McDonough and Sun (1995).

evident on the plot of total nitrogen *vs* aggregation state that confirms the presence of two diamond populations in xenoliths from this pipe. Crystals in xenoliths from Komsomolskaya pipe have moderate nitrogen contents (200-900 at.ppm) and predominantly 20-50% aggregation. Diamonds with different nitrogen aggregation state occur in individual xenoliths from both pipes. FTIR data confirm the multistage growth of the diamonds.

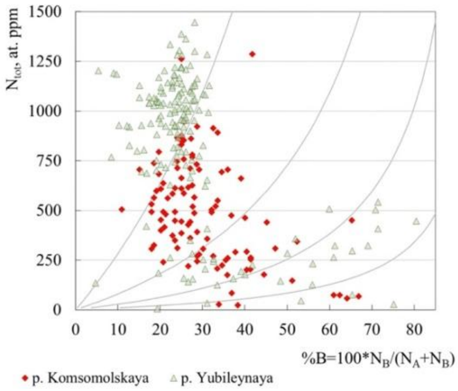


Figure 4. Distribution of total nitrogen and aggregation state in diamonds from Yubileynaya and Komsomolskaya eclogitic xenoliths.

Conclusions

The distribution of diamonds in the xenoliths, the presence of diamonds with different nitrogen aggregation state in the same xenolith and other evidence suggest multistage diamond growth from metasomatic fluids. Diamonds in eclogites may precipitate directly from water-rich melts/fluids. In addition, metasomatic fluids that may themselves originate from subducted crust potentially play an important role in the modification of primary mantle eclogites and may be linked to diamond formation.]

References

[Ellis DJ, Green DH (1979) An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contrib Mineral Petrol 71:13-22.

Kostrovizky SI, Spetsius ZV, Yakovlev DA, Fon-der-Flaas GS, Suvorova LF, Bogush IN (2015) Atlas of primary diamond deposits of Yakutian kimberlite province. Mirny, OOO MGT, 480 p. (in Russian).

McDonough WF, and S.-S. Sun (1995) The composition of the Earth, Chem. Geol., 120, 223-253.

Pearson DG, Canil D, Shirey SB (2003) Mantle samples included in volcanic rocks: xenoliths and diamonds. Treatise Geochem 2:171-275.

Pernet-Fisher JF, Howarth GH, Liu Y, Barry PH, Carmody L, Valley JW, Bodnar RJ, Spetsius ZV, Taylor LA (2014) Komsomolskaya diamondiferous eclogites: Evidence for oceanic crustal protoliths. Contrib Mineral Petrol 167(3):1-17.]