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THE "EXCEPTIONALLY FRESH" UDACHANAYA-EAST KIMBERLITE: EVIDENCE FOR BRINE AND EVAPORITE CONTAMINATION.

Kostrovitsky SI[1]*, Kopylova MG[2], Egorov KN[3], Yakovlev DA[1], Kalashnikova TV[1], Sandimirova GP[1]

1 Institute of Geochemistry SB RAS, Irkutsk, Russian Federation, serkost@igc.irk.ru

2 Department of Earth & Ocean Sciences, University of British Columbia, Vancouver, Canada

3 Institute of the Earth's crust SB RAS, Irkutsk, Russian Federation

Introduction

The so-called "exceptionally fresh" kimberlite of the Udachnaya-East pipe was the subject of several recent publications. The composition of this serpentine-free (SFUE) kimberlite was proposed as an estimate of the deep kimberlite melt, uniquely rich in mantle chlorine and Na (e.g. Maas et al., 2005, Kamenetsky et al., 2007). We advocate a different point of view on the Udachnaya East kimberlite and show that it acquired the high Na- and Cl-contents in interaction with buried Cambrian Na-Ca-Cl brines or assimilating evaporite xenoliths (Polozov et al., 2008).

Geology and composition of Siberian kimberlites

The mineralogy and genesis of the Udachanaya kimberlite cannot be understood without geological data on Siberian kimberlites. They emplaced in 14 fields (Fig. 1); some of 5 southern fields contain economic pipes, whereas 9 northern fields are nonproductive. Siberian kimberlites erupt through carbonate-terrigeneous sedimentary rocks, in contrast to S African kimberlites that erupt through dolerites, quartz sandstones and crystalline basement. Incorporation of carbonate-rich country rock xenoliths in Siberian kimberlites (assessed as 15-20 vol%) proceeds to the extent which is uniquely high compared to other economic kimberlites. This results in the extremely high contents of CaO and CO_2 and a very broad range of $\delta^{13}C$ values and higher positive $\delta^{18}O$ (Fig. 2).

Nowhere in the world kimberlites erupt through thick sediments that contain that much deeply buried highly mineralized groundwater (>0.2-0.4 g/cm3). These ancient parental brines buried together with syngenetic sediments (Alekseev et al., 2007) in deep strata. Terrigeneous carbonate and halmeic country rocks of Mid-Paleozoic kimberlites of the southernmost kimberlite field (Mir, International'naya) rocks are saturated with groundwaters of the Yakutian artesian basin that vary in composition from ultrafresh to Na and Ca brines. All other kimberlite fields to the north are located within the Olenek artesian basin that hosts buried Cambrian saline waters and Ca-Mg chloride brines (0.24-0.3 g/cm^3). They are sealed in continuous, 1200 m-thick unit of gypsum-bearing Cambrian limestones, dolomites and halite. Among these kimberlite fields,

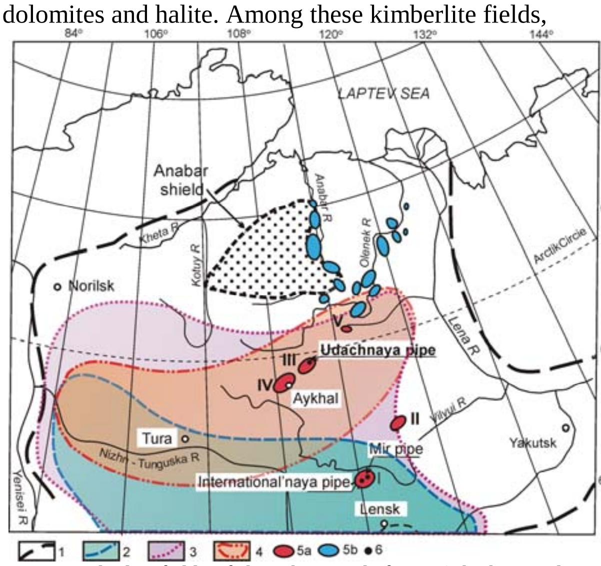

Fig. 1 Kimberlite fields of the Siberian Platform (Kharkiv et al., 1998) with occurrences of salt-bearing deposits and brines (after Alekseev et al., (2007). 1-3 – boundaries of: Siberian Platform (1), the Lower Cambrian evaporite-bearing sedimentary rocks (2), brines (3); 4 – zone of complete saturation of sedimentary cover in metamorphosed brine; 5 – kimberlite fields: a – southern diamondiferrous (I – Malobotuobinskoe, II – Nakynskoe, III – Daldynskoe, IV – Alakit-Markhinskoe, V – Verhnemunskoe), b - northern fields (without numbers); 6 – pipes.

two southern (containing Udachnaya and Aykhal pipes, among others) fields (3, 4 on Fig. 1) are situated within the zone of complete saturation of sedimentary cover in metamorphosed brines (Alekseev et al., 2007). In contrast to the southern kimberlite fields, the northern kimberlites erupt through buried low-mineralized waters (0.03-0.05 g/cm^3) (Khar'kiv et al., 1991).

Kimberlite pipes are commonly localized at the intersection of faults (Kharkiv et al., 1991). The faults and pipes penetrate the brine-sealing strata and act as drainage systems. The drainage, however, is eventually blocked if carbonate precipitation from the brines is intensive (Pavlov and Ilupin, 1973). It was shown experimentally that even short (2-6 days) contact of kimberlite with brines changes its composition (Khar'kiv et al., 1991). This observation explains a marked difference between compositions of the northern and southern Siberian kimberlites at depths where they cut through brine-bearing strata. Southern Siberian pipes (fields 1-4 in Fig. 1) are unique in high Na, Cl and S contents. For example, sulfur is elevated in Mir, Udachnaya and International'naya kimberlites (0.8 – 5.3 wt%), but is low (0-0.3 wt%) in northern Siberian pipes

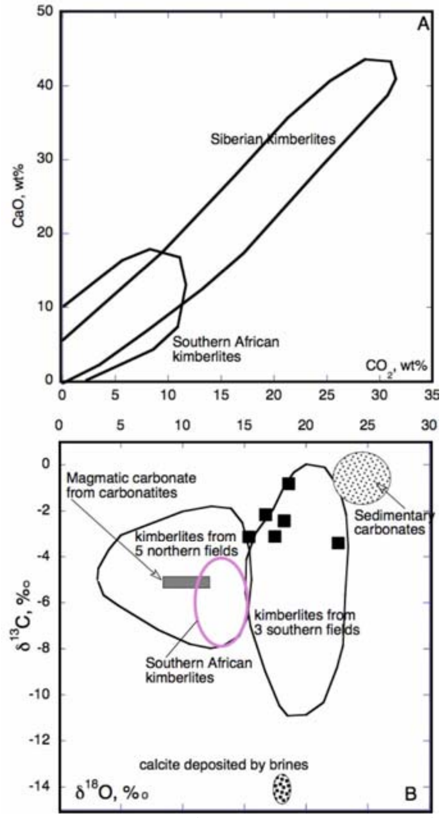

Fig. 2. Compositions of Siberian kimberlites, modified after Kharkiv et al., (1991). A: CaO-CO_2 (wt%) plot. B: Plot of O-C isotopes in SFUE kimberlite (black squares, Egorov et al., 1986) in comparison with data on Siberian and Southern African kimberlites and carbonates in various rock types.

(Kharkiv et al., 1991), as it is typical of kimberlites worldwide. The studies of sulfur isotopes in sulfate minerals in the Southern Siberian kimberlites proved its sedimentary origin (Ilupin, 1990). In Mir and International'naya pipe, there is a significant increase of Na_2O, Cl and SO_3 contents with depth (Kharkiv et al., 1991). The Mir kimberlite contains 0.11-0.29 wt% Cl at 75-506 m, but at deeper horizons (600-1170 m) Cl content gradually increases to 1.4-1.9 wt%. In Udachnaya–West, Cl content increases from 0.3 wt% at 24 m to 1.2-1.7 at 224-914 m. In these pipes, the elevated concentrations of Cl and Na are restricted to depths where country rocks that carry buried brines. This contrasts with the average Cl content of 0.03-0.06 wt% in Indian and African kimberlites (Ilupin, 1990). Upper parts of the pipes were not flushed with brines and were instead in contact with meteoric fresh waters before formation of the Cenozoic permafrost. Sodium, Cl and S reside in a suite of minerals rarely observed in kimberlites, such as halite, zemkorite, shortite, sodalite, gypsum, anhydrite and other alkali carbonates (Khar'kiv et al., 1991). It was estimated that, on average, Mir and Udachnaya kimberlites contain at least 1.5 vol% halite throughout the entire depth of pipes below 200 m (Pavlov and Ilupin, 1973) irrespective of whether the serpentine abundance in the kimberlite is high or low. The halite abundance and spatial distribution matches the lithology of country rocks at the corresponding levels. For example, the maximal (8 vol%) abundance of halite are restricted to levels of the diatremes from southern fields where they cut through halite evaporite. This is also true of gypsum and anhydrite. (Khar'kiv et al., 1991). The textural positions of S-, Na- and Cl-rich minerals in thin sections demonstrate their crystallization in the sequence serpentine -> anhydrite+ carbonate->halite (Pavlov and Ilupin, 1973).

Geology and mineralogy of the Udachnaya East

The 353-367 Ma Udachnaya pipe emplaced through the Lower to Upper Cambrian sedimentary rocks (limestones, dolomites, argillites, sandstones and conglomerates) and Lower Ordovician carbonates over 2 km thick. The pipe at 400-500 m depth cuts through an aquifer of the Olenek artesian basin characterized by high concentrations of Na and Cl, 0.3 g/cm^3 (Drozdov et al., 2008).

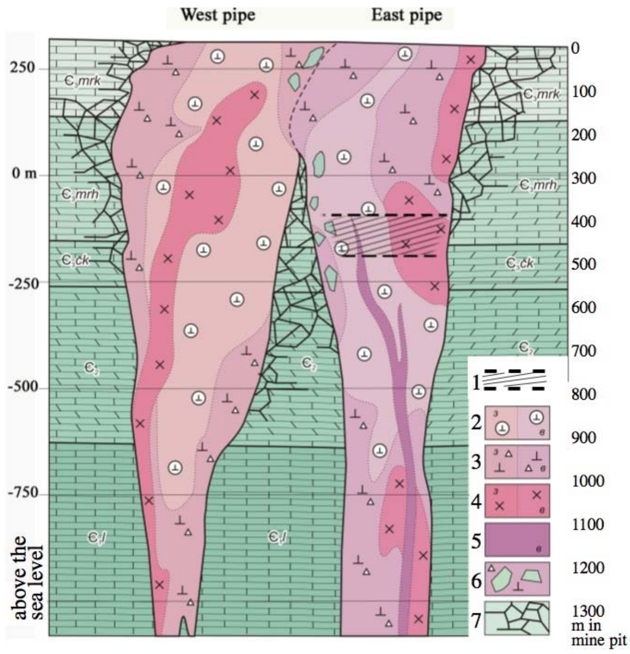

Fig. 3. Geological cross-section of the Udachnaya kimberlite. 1 – SFUE kimberlite, 2- Phase 2 volcaniclastic kimberlite breccia; 3- Phase 3 massive volcaniclastic kimberlite breccia; 4 – Phase 1 hypabyssal kimberlites; 5 – Phase 5 of hypabyssal dyke kimberlites; 6 – large blocks of country rocks in kimberlite; 7 – zone of fracturing in the country rocks.

The Udachnaya kimberlite comprises two separate pipes, older West and younger East, that merge at 250 m below the present surface. Each of the Udachnaya pipes formed through 3-5 eruptive phases (Kharkiv et al., 1991) (Fig 3). The Udachnaya East kimberlite includes early hypabyssal diopside-phlogopite kimberlite found as clasts in the later breccia (Egorov et al., 1986), several phases of volcaniclastic kimberlite breccia and dykes of hypabyssal monticellite kimberlite (Kornilova et al., 1998). The Udachnaya West kimberlite hosts serpentinized olivine down through entire explored depth (1200 m), whereas the profile of olivine serpentinization of the Udachnaya East kimberlite is complex. In the upper 400 m of the kimberlite, olivine is 80-95% serpentinized, at 400-500 m it is fresh, and below the degree of serpentinization gradually increases to 100% at 700-1200 m. Fresh olivine and serpentine-free matrix are observed in all 3 magmatic phases of Udachnaya East at 400-500 m depth (Fig 3). The predominant serpentine-free Udachnaya East (SFUE) kimberlite is fragmental, containing 1-30% xenoliths of country rocks, mantle xenoliths and clasts of early hypabyssal kimberlite.

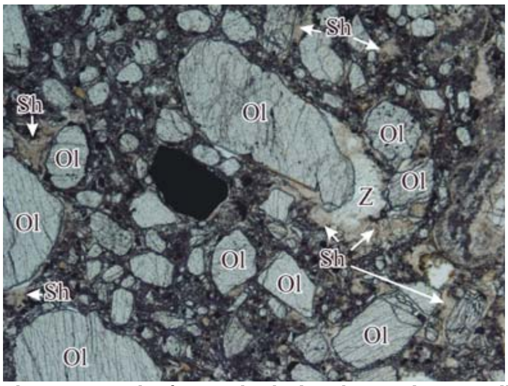

Fig. 4. Photomicrograph of SFUE kimberlite showing late crystallization of zemcorite (Z) and shortite (Sh) in rims around olivine macrocrysts.

The matrix of SFUE is composed of phenocrystal olivine and calcite, with varied abundances of interstitial shortite, zemkorite, halite, sylvine, phlogopite, apatite, perovskite, Ti-magnetite (Fig. 3). The kimberlite is carbonatized; recrystallization of calcite makes it more coarse-grained and forms monomineral calcite veins. SFUE kimberlite is also cut by late fine-grained gypsum veinlets along rock fractures and coarse gypsum zones in places reaching thickness 20 m. The kimberlite often host geodes with carbonate-chloride minerals precipitated in late leached cavities. SFUE kimberlite carries large angular xenoliths of carbonate-halide compositions with thermally-metamorphosed selvages (Fig. 5A, B).

Bulk composition

The main trend in the major element composition of the SFUE kimberlite is the inverse correlation of CaO with SiO_2 and MgO, typical of all worldwide kimberlites. The content of Na_2O (0.07 - 3.1 wt %, 0.97 wt. % on average) is higher than that of a typical kimberlite (0.16 wt% Na_2O in Group I Southern African kimberlite, Becker and Le Roex, 2006). Sodium content does not correlate with H_2O content controlled by the serpentine mode. Moreover, Na content in the kimberlite breccia, clasts of early hypabyssal

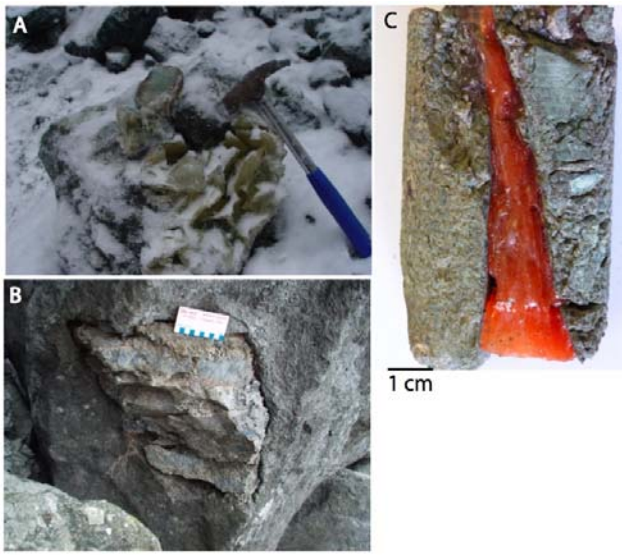

Fig. 5. A: Coarse grained gypsum from a geode formed in a late leached cavity in the SFUE kimberlite. B: A xenolith of halite with thermally-metamorphosed blue upper selvage (Polozov et al., 2008). C: A vein of halite in the International'naya pipe.

kimberlite and late hypabyssal dykes are similar (Fig. 5) suggesting the secondary origin of Na minerals. The absence of H_2O-Na_2O correlation is supported by findings of kimberlite with serpentinized olivine that contains halite xenoliths and halite in the groundmass. There is a threshold concentration of 9 wt% CO_2, above which Na_2O content in kimberlite cannot exceed 0.5 wt%. We ascribe this eventual sealing of kimberlite to brine by carbonate precipitation from Ca-rich brines. High concentrations of Cl is analyzed in Udachnaya East below 160 m. They reache 9 wt%, in SFUE kimberlite (Kamenetsky et al., 2007) and 2.2- 4.2 wt% at 760-860 m (Pavlov and Ilupin, 1973).

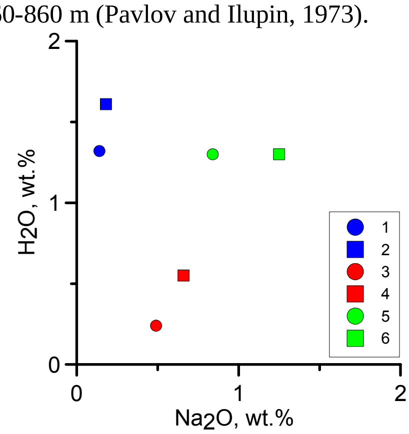

Fig. 6. A Na_2O-H_2O plot for SFUE kimberlite. 1 – late dyke of macrocrystal hypabyssal kimberlite; 2, 4, 6 – volcaniclastic breccia; 3, 5 – clasts of hypabyssal kimberlite in the breccias.

Isotope systematics

The systematics of stable and radiogenic Sr isotopes in SFUE kimberlite constrains its origin, but can be fully understood only in the broad regional context. C isotopic ratios in SFUE kimberlite plot among the highest values in the field of contaminated Siberian kimberlites (Fig. 2B). The contamination by heavy crustal carbon is the most significant at the depth where SFUE kimberlite occurs. The Udachnaya East kimberlite has ™^{13}C equal to -3.4 -2.7%$_o$ at 20-400 m, -1.6 –1.3%$_o$ at 400-600 m, and -1.5 - -2.1%$_o$ at 600-900 m (Khar'kiv et al., 1991).

The $^{87}Sr/^{86}Sr_i$ values in SFUE kimberlite is 0.70438-0.709 (Kostrovitsky, 1986, Kornilova et al., 1998, Kostrovitsky et al., 2007; Maas et al., 2004), which is higher than that for Group I kimberlites. The highest $(^{87}Sr/^{86}Sr)_i$ ratio of 0.709 is observed in the sample with the most intense development of secondary carbonate. Salts deposited in the Udachnaya East open pit has $(^{87}Sr/^{86}Sr)_i$ of 0.708348, whereas extreme values of Sr initial ratio (0.712052) are measured in coarse halite in geodes (Tab 1).

The Sr isotope systematics reflect the mixture of the kimberlite with Udachnaya brines $(^{87}Sr/^{86}Sr)_i$ = 0.7088-0.7092, Alekseev et al., 2007) or with halite xenoliths (0.707871, Table 1). εNd of the SFUE kimberlite is 2-4 (Maas et al., 2005), typical of the asthenospheric magmas, including Group I kimberlites. It was shown that contamination by sedimentary xenoliths and alteration of Siberian kimberlites due to brines do not affect Nd isotopes (Kostrovitsky et al., 2007).

Table 1. Composition and radiogenic isotopes of salts in the SFUE kimberlite.

	Salt recently deposited in the open pit	Halite xenoliths	Geode with coarse halite and sylvine in SFUE
Sample No	08-21	10-10 Na	10-22
Mg, wt%	0.287	0.36	0.215
Al	0.0073	0.039	0.033
Si	0.12	0.241	0.171
NaCl	99.25	98.18	95.66
K	0.0459	0.03	3.41
Ca	0.246	0.616	0.224
Fe	0.0154	0.0578	0.0753
Br	0.0283	0.0342	0.041
S		0.386	0.0011
Sr, ppm	21	140	11
Rb, ppm	4	4	14.2
$^{87}Rb/^{86}Sr$	0.55113	0.08267	3.74353
$(^{87}Sr/^{86}Sr)_i$	0.708348	0.707871	0.712052
εSr_i	54.6	53.9	113.3
Age (Ma)	0	360	360

Chlorine isotopic ratios of halite in SFUE kimberlite (-0.25 to 0.4%$_o$ δ^{37}Cl, Sharp et al., 2007) also collaborate its origin in evaporates (-0.5 to 0.5%$_o$ ™ ^{37}Cl) or in Udachnaya brines (-0.33 to 0.52%$_o$, Alekseev et al., 2007).

Discussion

The secondary origin of Na-, Cl- and S-rich minerals in the Udachnaya East kimberlite is supported by the following evidence.

1. The broad regional distribution of the Na-Cl-S mineralization that develops in all ~ 150 pipes of the Southern kimberlite fields independently of how much serpentine the kimberlites contain;

2. The spatial correlation between the geology and cryohydrogeology of the local country rocks and the mineralogy of Siberian kimberlites, in particular the difference between Southern and Northern Siberian kimberlites (Fig. 2A).

3. Chemical and isotopic evidence for crustal contamination in Southern Siberian kimberlites.

4. A restriction of halite or gypsum mineralization in the Mir and International'naya pipes to certain depth horizons of the pipes where they cut through country rock strata with the similar mineralogy.

5. The localization of the highest abundances of Na-Cl-S-bearing minerals in the Udachnaya East kimberlite at a certain depth interval that transcends 3 magmatic phases of kimberlites formed at different times (Fig. 3).

6. Veins of halite (Fig. 5C), gypsum and carbonate cutting through kimberlite and xenoliths alike;

7. The textural position of halite and alkali carbonate as secondary after serpentine and other groundmass minerals as observed in thin sections.

The contamination of the SFUE kimberlite and other Southern Siberian kimberlites by Na-Cl-S crustal material occurred, in our mind, in two different ways. The kimberlites have been contaminated by buried brines. The origin of Na-Cl-S-bearing mineralization by interaction with buried brines is supported by modern halite precipitation from brines in the Udachanaya East open pit. Furthermore, a reaction of solid, fully-crystallized kimberlite with brines is evidenced by the zones of leaching, cavities and geodes associated with Na-Cl-S minerals. Besides the brine contamination, the kimberlites assimilated carbonates and lagoon sulfate-chloride rocks. Despite the lack of evaporite beds in the local drill core around Udachnaya, large xenoliths of halite are found in the kimberlite. They cannot be late chloride-rich segregations from residual kimberlite melt (Kamenetsky et al., 2007b) as they have thermally-metamorphosed margins and angular shapes (Fig. 5B). These evaporites may have come from the depth not intersected by local drilling. Evaporite beds were inferred to had been deposited around Udachnaya in the Middle Cambrian, in an area 200 by 50 kms (Fig. 1), in a 1 km thick sequence that formed in a supratidal arid coastline and lagoon environment in between carbonate reefs (Polozov et al., 2008). The assimilation of the xenoliths occurs at relatively high, magmatic temperatures producing hybrid melt with elevated contents of Na, K, Cl and S. This melt is trapped as Cl-rich fluid inclusions in secondary fractures of olivine (Golovin et al., 2003); compositions of these inclusions contrast to primary deep-seated CO_2 inclusions (Sobolev et al., 1987). Alkali-, sulfur- and chlorine-rich minerals may have crystallized from this late hybrid melt, and may be "comagmatic" with kimberlite, as found by Maas et al. (2005). The possibility of crustal contamination is implied by ubiquitous presence of diopside and phlogopite in early hypabyssal SFUE kimberlite (Egorov et al., 1986). The presence of these minerals in Group I kimberlite is usually a sign of hybridization and assimilation of crustal xenoliths with SiO_2 contents higher than that of the kimberlite melt (Caro et al., 2004).

A reason for the serpentine-free character of some International'naya and Udachnaya East kimberlite rich in Na-, Cl- and S minerals is not fully understood. It is possible that serpentine-free rocks form only in zones of especially intense contamination. This view is supported by the spatial restriction of SFUE kimberlite to strata with the most mineralized buried brines at Udachnaya and the most contaminated $\delta^{13}C$ signatures in SFUE kimberlite (Khar'kiv et al., 1991). Serpentine in kimberlites form on several stages, magmatic (serpentine of the groundmass). deuteric (serpentine replacing monticellite and olivine rims) and post-emplacement, related to meteoric groundwaters (serpentine replacing large olivine). Experiments on interaction between solid kimberlite and meteoric waters with elevated Na and Cl contents demonstrated that such waters cannot serpentinize olivine (Lashkevich and Egorov, 1998). This effect is also observed on abyssal peridotites whose serpentinization is inhibited by marine waters. This effect, however, cannot explain the absence of magmatic serpentine that crystallizes as late groundmass mineral in fresh kimberlites. The only explanation to the lack of this interstitial serpentine is the hybrid composition of the residual kimberlite melt, in which the H_2O solubility is lowered by increased halogen and alkali abundances. This could only happen if brines or evaporite xenoliths were assimilated by partly molten kimberlite melt.

We conclude that the source of chlorine, S and Na in the Udachnaya-East kimberlite is shallow sedimentary marine rather than the deep mantle. SFUE kimberlites therefore cannot be used to constrain compositions and physical properties of ultra-fresh primary kimberlite melts (Kamenetsky et al., 2007) or be a new standard for mantle chlorine isotopes (Sharp et al., 2007).

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References:

Alekseev SV, Alekseeva LP, Borisov VN, Shoukar-Stash O, Frape SK, Chabaux F, Kononov AM (2007) Isotopic composition (H, O, Cl, Sr) of ground brines of the Siberian Platform. Russian Geology and Geophysics 48:225-236.

Becker M, Le Roex AP (2006) Geochemistry of South African on- and off-craton, Group I and Group II kimberlites: Petrogenesis and source region evolution. J Petrol 47(4):673-703.

Caro, G., Kopylova, MG., Creaser. R. (2004) The hypabyssal 5034 kimberlite of the Gahcho Kue cluster, Southestern Slave craton, Northwest Territories, Canada: A granite-contaminated Group-I kimberlite. Can. Mineralogist, 42, 183-207.

Drozdov AV, Iost NA, Lobanov VV (2008) Criohydrogeology of diamond mines of Western Yakutia, vol. Irkutsk State Technical University, Irkutsk, p 508. (In Russian)

Egorov KN, Kornilova VP, Safronov AF, Filippov ND (1986) Micaceous kimberlite from the Udachanaya-East pipe. Transactions of the Russian Academy of Sciences 291(1):199-202. (In Russian)

Golovin AV, Sharygin VV, Pokhilenko NP, Malkovets VG, Kolesov BA, Sobolev NV (2003) Secondary melt inclusions in olivine of unalteres kimberlites of the Udachnaya-East. Transactions of the Russian Academy of Sciences 388(3):199-202. (In Russian)

Ilupin, IP, Vaganov, VI, Prokopchuk, BI (1990). Kimberlites. Moscow, NEDRA, 245 p. (in Russian).

Kamenetsky VS, Kamenetsky MB, Sharygin VV, Golovin AV (2007a) Carbonate-chloride enrichment in fresh kimberlites of the Udachnaya-East pipe, Siberia: A clue to physical properties of kimberlite magmas? Geophysical Research Letters 34(9).

Kamenetsky VS, Kamenetsky MB, Sharygin VV, Faure K, Golovin AV (2007b) Chloride and carbonate immiscible liquids at the closure of the kimberlite magma evolution (Udachnaya-East kimberlite, Siberia). Chemical Geology 237(3-4):384-400.

Khar'kiv AD, Zuenko VV, Zinchuk NN, Kruchkov AI, Ukhanov VA, Bogatykh MM (1991) Kimberlite Petrochemistry vol. TCNIGRI, Yakutsk, p 302. (in Russian)

Khar'kiv AD, Zinchuk NN, Kruchkov AI, (1998) Primary diamond depisits of the world. Moscow, NEDRA p 556. (in Russian)

Lashkevich VV, Egorov KN (1988) Theoretical modeling of hydrothermal-metasomatic processes in the kimberlites. In the book: Thermodynamics in the Geology. Abstracts of reports II All-Union Simposium. V. 1. Miass. 139-141. (in Russian)

Maas, R , Kamenetsky, MB, Sobolev, NV, Kamenetsky, VS and Sobolev, AV (2005) Sr, Nd, and Pb isotope evidence for a mantle origin of alkali chlorides and carbonates in the Udachnaya kimberlite, Siberia. Geology, 33 (7). pp. 549-552.

Pavlov, DI, and Ilupin IP (1973) Halite in Yakutian kimberlite, its relations to serpentine and the source of its parent solutions, Dokl. Acad. Sci. USSR, Earth Sci. Ser., Engl. Transl., 213, 178–180.

Polozov AG, Sukhov SS, Gornova MA, Grishina SN. (2008) Salts from Udachnaya-East kimberlite pipe (Yakutia, Russia): occurrences and mineral composition. Extended Abstracts of 9IKC-A -00247.

Sharp, ZD., Barnes, JD., Brearley, AJ., Chaussidon, M., Fischer, TP., Kamenetsky, VS. (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. Nature, 446, 5, 1062- 1065.

Sobolev AV, Sobolev NV, Smith CB, Dubessy J. (1989) Fluid and melt compositions in lamproites and kimberlites based on the study of inclusions in olivine. Proceedings of the 4th IKC. Kimberlites and related rocks. GSA Spec. Publ. V. 1. N 14. P. 220-240.