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Yumi Kitayama, Emilie Thomassot, Albert Galy, Andrey Korsakov, Alexander Golovin, et al.. Geochemical evidence for carbon and chlorine enrichments in the mantle source of kimberlites (Udachnaya pipe, Siberian craton). *Geochimica et Cosmochimica Acta*, 2021, 315, pp.295-316. 10.1016/j.gca.2021.09.021 . hal-03800806

HAL Id: hal-03800806

<https://hal.science/hal-03800806>

Submitted on 5 Jan 2024

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1 **Geochemical evidence for carbon and chlorine enrichments in the mantle**
2 **source of kimberlites (Udachnaya, Siberia)**

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4

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16

17 **Keywords: kimberlite, salts, alkali-carbonate, sulfate, lithospheric mantle, Siberian**
18 **craton, chloride carbonate liquid segregation**

19

20 **Abstract**

21

22 Deep, carbonate-rich melts are key constituents of kimberlites and are crucial for
23 understanding the cycle of volatile elements in the mantle. On the Siberian craton, the
24 Udachnaya-East kimberlite hosts extremely well-preserved nodules composed of chlorides +
25 carbonates + sulfates, that do not present any relict sedimentary textures. These salty nodules
26 display textures that are commonly observed in quenched liquids and may thus represent the
27 very last stage liquid of the kimberlite. Alternatively, they could represent assimilated
28 sedimentary material, or even post-magmatic hydrothermal alteration, because kimberlites are
29 known to ascend through the lithosphere while assimilating material from their wall rocks.

30 Here we focus specifically on those chloride-carbonate nodules, which are composed
31 of 70% chloride + 30% alkali-carbonate and sulfate, and used two radiogenic systems (Rb-Sr,
32 Sm-Nd) and the isotopic composition of sulfur, in addition to their major and trace element
33 compositions (n=3). We then compared the results with the same geochemical data on host
34 kimberlites (n=4), sedimentary cover (n=3) and hydrothermal veins (n=3).

35 Taken together, our results show that the nodules are not the product of a
36 contamination by the Cambrian sedimentary cover. Trace element patterns of the nodules
37 display extreme enrichments in the same elements that are relatively depleted in the host
38 kimberlite but also in kimberlites worldwide (K, Rb, Sr, Pb), suggesting that chloride-
39 carbonate nodules are snapshots of the latest stage liquid present in the kimberlite system.
40 Their isotopic compositions (Rb-Sr, Sm-Nd and $\delta^{34}\text{S}$) are consistent with a common
41 magmatic source with their host kimberlite. We propose that chloride-carbonate nodules
42 record a missing compositional endmember, which could explain the trend towards more
43 radiogenic Sr isotope ratios at nearly constant Nd signatures observed in their host kimberlite,
44 as well as in other kimberlites worldwide. This observed trend suggests the presence of a
45 recycled component with high Rb/Sr (such as salts or terrigenous sediments) in the mantle
46 sampled by some kimberlites, either in the lithosphere or the asthenosphere. This study
47 highlights that the role of alkalis and halogens may have been underestimated in the genesis
48 of kimberlites at depths where diamonds are stable, as well as in more evolved magmatic
49 stages. Segregations of chlorides and carbonates occur specifically in sulfate-bearing
50 kimberlites, which may thus sample a mantle domain in which sulfates with $\delta^{34}\text{S} > 0\text{‰}$ are
51 dominant. The existence of such a reservoir could explain the apparent imbalance observed
52 between the chondritic value ($\delta^{34}\text{S}$ of 0‰) and the negative S isotopic compositions of mantle
53 sulfides (MORB and peridotites).

54 **1. Introduction**

55

56 Kimberlites are volatile-rich volcanic rocks of alkaline composition that contain abundant
57 olivine crystals. Their parental magma originates at great depth beneath continents, in the
58 diamond stability field (>150 km depth). Although the exact nature of their parental magma
59 does not reach a consensus yet, there is evidence for the participation of halogens and other
60 volatiles as well as alkaline elements in the genesis of kimberlites. Some key observations
61 include the presence of syngenetic phlogopite inclusion in kimberlite-hosted diamonds with
62 up to 0.5 wt% Cl (Sobolev et al., 2009), Na ± K-rich compositions of residual melts/fluids (C-
63 O-H-Cl bearing) after olivine crystallization (Golovin et al., 2007; Kamenetsky et al., 2009,
64 2014; Giuliani et al., 2017; Abersteiner et al., 2018), as well as Na ± K-chloride inclusions in
65 chromite, perovskite, apatite (Abersteiner et al., 2017), magmatic calcite and olivine from
66 Udachnaya (Tomilenko et al., 2017a, b).

67 The presence of salts at depth raises the exciting question of volatile recycling through
68 time, and its ultimate role on mantle metasomatism, especially upon the compositional
69 spectrum of mantle fluids (Izraeli et al., 2001; Klein-BenDavid et al., 2007; Weiss et al.,
70 2015; Zedgenizov et al., 2018). However, the primary origin and concentration of chlorine
71 and other volatiles in various kimberlites worldwide is difficult to unravel because: (1)
72 volatiles are often lost via exsolution during ascent and emplacement, as well as post-
73 emplacement alteration (Abersteiner et al., 2017); (2) each kimberlite composition reflects
74 some assimilation of the local lithospheric mantle directly underneath (Francis and Patterson,
75 2009; Tappe et al., 2011; Giuliani et al., 2020), and (3) the percolation of late stage fluids as
76 well as the assimilation of sedimentary or crustal xenoliths during magma ascent near the
77 surface (Kjarsgaard et al., 2009), can seriously modify the primary composition of
78 kimberlites.

79 On the Siberian craton, the Udachnaya-East kimberlite preserves a rare, dry (H₂O <0.5
80 wt%) and serpentine-free rock type with anomalously high contents of chlorine (up to 6.1
81 wt%), alkalis (Na₂O+K₂O up to 10 wt%) and sulfur (S up to 0.50 wt%), referred to as a
82 “salty” kimberlite (Kamenetsky et al., 2012; D’Eyrales et al., 2017). This salty kimberlite
83 contains nodules composed of carbonate, chloride and sulfate, whose origin is a matter of
84 debate and could be either: (1) the segregation by immiscibility from a liquid initially derived
85 from melting of the mantle (Maas et al., 2005; Kamenetsky et al., 2007, 2014), (2) the
86 assimilation of sediments or crustal xenoliths by the ascending magma (Kopylova et al.,
87 2013), or (3) a post-magmatic hydrothermal alteration (Kopylova et al., 2013). According to

88 sulfur isotopic compositions, abundant sulfates found in the salty kimberlite of Udachnaya-
89 East derive from an oxidized, sulfate-bearing mantle source (Kitayama et al., 2017). Such
90 mantle domains, if confirmed, would represent a little explored but significant reservoir in the
91 global geochemical cycle of volatile elements.

92 In this study, we investigated the genetic link between the chloride-carbonate nodules
93 and their host kimberlite, as well as their possible sources (asthenosphere, lithosphere,
94 granitic crust or sediments). For this purpose, we used a combination of two radiogenic
95 systems (Rb-Sr, Sm-Nd) and the stable isotopic composition of sulfur in chloride-carbonate
96 nodule, salty kimberlite, as well as hydrothermal salts, sulfates, a regional brine and the only
97 salt-bearing host sediment found in drill holes in the area. Our results exclude the Cambrian
98 sedimentary cover as a source of chloride-carbonate nodules and instead support a mantle
99 origin. Calculations of age-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios as well as S isotopes
100 allowed us to evaluate possible scenarios for the source of salts in nodules and kimberlites.

101

102

103

104 **2. Geological setting**

105

106 The Udachnaya-East kimberlite is located in the Daldyn kimberlite field (Aldan province) in
107 the central part of the Siberian craton (Fig. 1). At the craton scale, several kimberlite
108 emplacements from early Devonian to late Jurassic have been reported (Sun et al., 2014). In
109 the Aldan province however kimberlite emplacement ages mostly range from 340 to 360 Ma,
110 with minor occurrences in the intervals 420–400 and 600–500 Ma. The oldest recorded ages
111 (600–500 Ma) may represent older mantle material within the bulk kimberlites, rather than the
112 actual ages of kimberlite activities (Smelov and Zaitsev, 2013). The Udachnaya-East
113 kimberlite was emplaced ~365 Ma, as indicated by ^{40}Ar – ^{39}Ar (362.7 ± 3.7 Ma) and Rb–Sr
114 cooling ages (364.6 ± 4.1 Ma) from phlogopite in a kimberlitic clast (Kamenetsky et al., 2009)
115 and U–Pb age (367 ± 5 Ma) of perovskite from the host Udachnaya-East kimberlite (Kinny et
116 al., 1997).

117 The Udachnaya-East kimberlite was emplaced in a sedimentary sequence ranging in
118 thickness from 2500 m in the northeast to 3100 m in its southwestern part (Kamenetsky et al.,
119 2014 and references therein) and covering a basement of Archean-Proterozoic crustal rocks
120 (Smelov and Zaitsev, 2013). The ages of the sedimentary cover range from early to late
121 Cambrian (542 to 488 Ma). Massive salt beds of the Cambrian evaporite cover are present

122 ~400 km south of Udachnaya around the MIR and International'naya kimberlite pipes (Fig.
123 1), but are absent in sediments in the vicinity of Udachnaya (Kamenetsky et al., 2014 and
124 references therein). At Udachnaya, sediments consist mainly of shales, dolomites, marls, and
125 limestones. Dolomites of the Chukuck suite are the only host rock that contain sulfate-rich
126 veins (Fig. 2-e) and may also contain salts, although these veins are only present locally.
127 These sulfate veins could represent a Cambrian analogue of sabkha where evaporites and
128 dolomites are mixed or alternatively they could have precipitated hydrothermally from brines
129 (Kamenetsky et al., 2014; Kopylova et al., 2016). Indeed, Udachnaya is located within an area
130 of modern brines (Fig. 1), and the precipitation of halite from saline groundwaters (300 g/l)
131 has been observed in the open-pit mine (Kopylova et al., 2013 and references therein). The
132 presence of a Vendian carbonate and evaporite belt with sedimentological characteristics
133 similar to the Chukuck suite were expected just above the crystalline basement (Kopylova et
134 al., 2013 and references therein) but could not be verified, despite extensive drilling near the
135 Udachnaya-East pipe (Kamenetsky et al., 2014).

136

137

138 **3. Sample description**

139

140 Chloride-carbonate nodules were collected from stockpiles of salty kimberlite mined from
141 460-500 m depths. They are rounded or angular, range in size from 3 to 10 cm, and consist of
142 30 to 70% of carbonate, the remaining part being chlorides (Table 1). They do not present any
143 relic sedimentary textures, indicating that they were completely molten before they
144 crystallized in the kimberlite. The samples present intergrowths of randomly oriented sheets
145 of chloride and carbonates (Fig. 2-a and b). These textures are reminiscent of immiscibility
146 between alkaline-carbonate and alkaline-chloride liquids observed ~600°C in melt inclusions
147 trapped in olivine from the same kimberlite (Kamenetsky et al., 2007). Chlorides in these
148 nodules are transparent, greyish (Fig. 2-a and -b) and consist of massive halite (NaCl) with
149 sylvite (KCl) globules (Kamenetsky et al., 2007). Carbonates are opaque, white (Fig. 2-a and
150 -b) and display a wide range of alkaline-carbonate compositions ($\text{Na-Ca} \pm \text{K} \pm \text{S}$), showing a
151 positive correlation between SO_3 (up to 13 wt%) and K_2O contents (up to 14 wt%;
152 Kamenetsky et al., 2007). Among these alkali-carbonates, shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) and
153 northupite ($\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$) have previously been identified in similar samples (Kamenetsky
154 et al., 2007). Raman spectra of shortite from a chloride-carbonate nodule also show the
155 presence of SO_4 groups which are either incorporated in the carbonate structure (replacing

156 some CO₃ groups) or form very fine exsolution lamellae of aphtitalite ((K,Na)₃Na(SO₄)₂;
157 D'Eyrames et al., 2017). Finally, most sulfide were too small to be identify in hand specimen
158 and impossible to prepare in thin section due to the nature of the samples. Only one galena
159 crystal (PbS) and one djerfisherite crystal (K_{6.05}Na_{0.6}(Fe_{19.27}Ni_{0.47}Cu_{3.53})S₂₆Cl_{0.91}) have been
160 characterized.

161 To relate these nodules to kimberlite magmatism, we studied four samples of the host
162 kimberlite, carefully chosen with minimal signs of alteration or contamination. Three samples
163 have crustal contamination indices (C.I.) < 1 (Table 2, C.I. = (SiO₂ + Al₂O₃ + Na₂O) / (MgO
164 + 2*K₂O), Kjarsgaard et al., 2009), indicating little crustal contamination. Only one sample
165 (UV12-119) had C.I. = 1.6. Although this index is not relevant for quantifying the
166 contamination by surficial lithology (e.g. sediments), it gives an indication of the possible
167 incorporation of continental granitic crust. For an accurate comparison with possible sources
168 of contamination and post-magmatic alteration, we analyzed hydrothermal veins (Fig. 2-c and
169 -d), a sample of country-rock dolomite containing a sulfate-bearing vein (n=1; Fig. 2-e), a
170 sample of regional brine (n=1; Fig. 2-g) and brine precipitates (n=1; Fig. 2-f). The brine
171 sample contains sulfates and was collected from a depth of 750 m in a drill hole 1 km south of
172 Udachnaya. Brine precipitates were collected from 520 m depth in the open pit itself, where
173 they had crystallized after the evaporation of brines from host sediments. The sample of host
174 sediment (dolomite of the Chukuck suite, UV09-305 Fig. 2-e) represents the only known
175 portion of crustal material that may provide sulfate- and perhaps salt-rich xenoliths to the
176 kimberlite. It was collected at a depth of 630 m in a drill hole located between the West and
177 East kimberlite bodies of Udachnaya.

178 **4. Analytical techniques**

179

180 **4.1. Whole rock major and trace element analyses**

181

182 Pieces of chloride-carbonate nodules were selected from the interior of the nodules, to avoid
183 contamination by the surrounding kimberlite groundmass. Samples from hydrothermal veins
184 were also selected free of kimberlitic material. Samples of rock powders and brine were
185 analysed for major and trace element geochemistry by the SARM laboratory (Service
186 d'Analyses des Roches et des Minéraux, Vandœuvre-Les-Nancy, France). Major element
187 analyses were carried out using an inductively coupled-plasma optical emission spectrometer
188 (ICP OES Icap 6500, from ThermoFisher) and trace element compositions were measured
189 using an inductively coupled-plasma mass-spectrometer (ICP-MS iCapQ from
190 ThermoFisher). Chlorine concentrations were measured by ultraviolet-visible
191 spectrophotometry / potentiometric titration. For whole rock analyses, total CO₂ and S were
192 measured using an elemental analyser while H₂O+ (referring to water within mineral
193 structures) was measured by Karl-Fisher titration. Major element compositions are expressed
194 both in atomic wt.% and oxide wt.% (Table 2), because oxide wt.% is not applicable for
195 chlorides analyses (NaCl, KCl) and can lead to erroneous totals (<100 wt.% when Cl
196 concentrations are not included and >100 wt.% when included). Trace element compositions
197 are expressed in ppm (Table 3). For the brine solution, measured concentrations were
198 normalized to 100% to enable for a comparison with rock samples.

199

200 **4.2. Radiogenic isotopes**

201

202 ***Sequential chemical leaching***

203 Whole rock analyses were applied on 200 mg porphyzied powder for samples of
204 chloride-carbonate nodules, 300 mg for samples of salty kimberlites and 500 mg for the host
205 sediment. Powdered samples were digested according to a method of sequential leaching in
206 order to avoid the formation of fluorides. A series of chemical leaching separated the water-
207 soluble (mainly chlorides), acid-soluble (mainly carbonate) and residual fractions (mainly
208 silicates) of powdered samples. In order to dissolve the water-soluble phases, we started with
209 leaching the samples twice in de-ionized water (18.2 MΩ.cm) at room temperature. This was
210 followed by leaching twice in acetic acid (10 vol. %) in order to dissolve the acid-soluble
211 phases. Before and after each leaching step of this procedure, we estimated the proportions of

212 leached material by drying and weighing the solid residue. The silicate residue was then
213 digested using hydrofluoric and nitric acids, following the procedure described in Alibert et
214 al. (1983) and Michard et al. (1985). During the preparation of the silicate residue of the host
215 sediment sample, fluorides precipitated. For this sample, we thus only dissolved and analysed
216 the leachate (Table 1). For all other samples (chloride-carbonate nodules and salty
217 kimberlites), we then mixed the three isolated fractions in order to obtain material
218 representative of whole rock samples.

219 We then separated the sample solutions in separate aliquots for Sr, Rb and Sm-Nd
220 analyses. Next, we spiked the aliquots with tracers of ^{85}Rb , ^{84}Sr and mixed ^{149}Sm - ^{150}Nd
221 respectively. We equilibrated the spike and sample for more than 24 hours before separating
222 rare earth elements (REEs), Rb, Sr, Sm and Nd by column chromatography. REEs were
223 separated first using TRU-spec resin (Pin et al., 1994). For samples of chloride-carbonate
224 nodules and host sediment, Rb and Sr were then separated using AG50-X8 cation resin (e.g.
225 Alibert et al. 1983). For samples of salty kimberlites, Rb and Sr were separated using Sr-spec
226 resin (Horwitz et al., 1992). Finally, in both cases, Sm and Nd were separated using LN-spec
227 resin (Pin et al., 1997).

228

229 *Rb-Sr isotope analyses*

230 Rb concentrations were determined by isotopic dilution, measuring the isotopic
231 composition of spiked samples on an ICPMS Quadrupole (ThermoScientific X-Series 2). To
232 avoid bias related to the interference of ^{87}Sr on ^{87}Rb , we always monitored the signal of ^{88}Sr .
233 When the Rb was not sufficiently purified of Sr (e.g., in samples with extremely high Sr
234 concentration), we did not use the Rb concentrations obtained from the spiked samples. Sr
235 concentrations and isotopic compositions (^{86}Sr , ^{87}Sr , ^{88}Sr , ^{84}Sr) of spiked samples were
236 determined on TIMS (Thermal Ionization Mass Spectrometry - ThermoScientific Triton).
237 Mass-dependent fractionation was corrected to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 by the exponential
238 law and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NBS987 was 0.710248 ± 0.000025 (2σ , $n = 10$) during the
239 course of the analyses.

240 By mass, total analytical blanks represented $\leq 0.0003\%$ of the Rb and $\leq 0.01\%$ of the
241 Sr contained in the water leachates; they represented $\leq 0.004\%$ of the Rb and $\leq 0.0002\%$ of
242 the Sr contained in the acetic acid leachates; and $\leq 0.003\%$ of the Rb and 0.0015 to 0.3% of
243 the Sr contained in whole-rock material. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions of the blank were
244 0.703 ± 0.003 (2σ) for water leachates, 0.7090 ± 0.0003 for acid leachates and $0.7081 \pm$
245 0.0007 for whole-rock material. Isotopic compositions of blanks are variable but uncorrelated

246 to Rb and Sr concentrations. Rb-Sr data presented in Table 4 are corrected for blank
247 contribution. Reported uncertainties at the 2σ level correspond to error propagation of
248 individual measurements and blank correction. The analytical precision of concentrations
249 determined by isotopic dilution are $\sim 0.5\%$ for Rb and $\sim 0.2\%$ for Sr. Uncertainties on
250 $^{87}\text{Rb}/^{86}\text{Sr}$ ratios are better than 0.1% for ratios > 1 . For whole-rock kimberlite samples, Rb
251 concentrations could not be determined by isotopic dilution (incomplete purification of Rb
252 fractions), so we used the concentrations measured by ICP-MS at the SARM laboratory, with
253 larger uncertainties of 5% (Table 4). Uncertainties on the low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of these
254 samples thus appear to be significantly larger as well (10 to 25% of the values), but are highly
255 overestimated.

256

257 *Sm-Nd isotope analyses*

258 Concentrations of Sm and Nd were measured by isotopic dilution using a mixed Sm-
259 Nd spike and measuring Sm (^{146}Nd , ^{147}Sm , ^{149}Sm , ^{155}Gd , ^{148}Sm) and Nd isotopic
260 compositions (^{143}Nd , ^{146}Nd , ^{147}Sm , ^{142}Nd , ^{144}Nd , ^{145}Nd) during two separate sessions on a
261 MC-ICP MS (multi-collector inductively coupled plasma mass spectrometer - Neptune Plus).
262 For Nd isotope measurements, the instrument was equipped with an Apex HF desolvating
263 nebulizer (ESI) for increased sensitivity. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were first normalised to
264 $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ using an exponential law and then to the JNdi-1 following a pseudo (1
265 standard each 4-5 samples) standard-sample bracketing method (Yang et al., 2017).

266 Total analytical uncertainty represented 4.8 to 5.6% of the Sm mass and 1.2 to 1.3%
267 of the Nd mass contained in whole-rock material. $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic compositions of the
268 blank was 0.512231 ± 0.000577 (2σ) for water leachates, 0.511551 ± 0.000620 for acetic acid
269 leachates and 0.512137 ± 0.000578 for whole-rock material. Blanks levels are high and
270 characterized by variable isotopic compositions, which suggests that blanks are related to both
271 the long evaporation times resulting from handling large amounts of samples, and to the
272 complex procedure of subsequent leachings and recombining of solutions (designed to avoid
273 the formation of fluoride). Whole rock compositions for Sm and Nd are reported after
274 correcting for blank contribution (Table 5). Reported uncertainties at the 2σ level correspond
275 to error propagation of individual measurements and blank correction. Precisions on Sm and
276 Nd concentrations were always better than 0.2% for both Sm and Nd. Whole-rock
277 $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are estimated precise to $\sim 2\%$ for kimberlite samples and better than 0.5%
278 for chloride-carbonates samples.

279

280

281 **4.3 Stable isotopes**

282

283 *Sulfur isotope analyses by chemical extraction and gas source mass spectrometry*

284 Sulfides and sulfates were extracted by wet chemistry using the sequential extraction
285 procedure described in Kitayama et al. (2017). This sequential method (i.e. S extraction from
286 sulfides using HCl and a chromium reducing solution, followed by S extraction from sulfate
287 using a strongly reducing hydriodic hypophosphorous acid, in the same digestion flask)
288 enables us to extract sulfides and sulfates from the same powder aliquot, thus also giving a
289 measurement of their respective proportions. S isotope ratio measurements were carried out at
290 the IPGP (Institut de Physique du Globe Paris) using a fluorination line to convert the
291 extracted Ag₂S to SF₆ gas. After separation and purification, the SF₆ gas was analyzed using a
292 dual inlet ThermoFinnigan MAT 253 isotope ratio mass spectrometer (Thomassot et al.,
293 2015). Sulfur isotope measurements are reported in the δ notation with respect to V-CDT
294 (Vienna-Canon Diablo Troilite) defined as:

$$295 \quad \delta^{34}\text{S (in } \text{‰ V-CDT)} = 1000 * [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}} / ({}^{34}\text{S}/{}^{32}\text{S})_{\text{V-CDT}} - 1]$$

296 The standard deviation of the $\delta^{34}\text{S}$ values was calculated as the quadratic sum of the internal
297 and external errors. The internal standard deviation calculated for each sample ($2\sigma_{\text{int}}$) is
298 0.05‰ for $\delta^{34}\text{S}$. During our sessions, the standard IAEA-S3 was measured 12 times, giving an
299 external error ($2\sigma_{\text{ext}}$) of 0.38‰ for $\delta^{34}\text{S}$.

300

301

302 **5. Results**

303

304 **5.1. Major and trace element compositions**

305

306 Major element compositions are reported in Table 2 and presented in Figure 3. Three salty
307 kimberlite samples have on average, 30 wt.% MgO, 8.5 wt.% CO₂, 26 wt.% SiO₂, 8 wt.%
308 FeO_{total} and their major element compositions are consistent with a mixture between olivine,
309 alkali-carbonates and chlorides. One sample (UV12-119; Table 2) deviates from the general
310 trend, indicating a possible contribution from phlogopite (Fig. 3-a, -b). Chloride-carbonate
311 nodules have from 17 to 19 wt.% CO₂, 10 to 14 wt.% CaO, 18 to 23 wt.% Na, 9 to 11 wt.%
312 K, 1 to 5 wt.% S and 17 to 31 wt.% Cl. Such major element compositions reflect the presence
313 of alkali-carbonates (e.g., shortite and/or nyerereite), chlorides (mainly halite) and alkali-

314 sulfates (e.g., aphtitalite; Fig. 3). Compared to chloride-carbonate nodules, chlorides from
315 hydrothermal veins and brine deposits have higher Na (from 36.3 to 39.4 wt.%) and lower K
316 (<0.3 wt.%) contents (Table 2, Fig. 3). In contrast, the host sediment differs from the nodules
317 in being poor in alkalis (K + Na < 0.1 wt.%) and Cl (~ 0.35 wt. %) despite S and Ca contents
318 similar to those of chloride-carbonate nodules.

319 Salty kimberlites from Udachnaya are enriched in alkalis, chlorine and sulfur
320 compared to non-salty kimberlites and other Siberian kimberlites (Figs. 3-d, -e and -f), and
321 thus record a larger contribution from alkali-carbonates and chlorides. Rb contents of
322 chloride-carbonate nodules are poorly correlated with Ca (Fig. 4-a) and CO₂ (Fig. 4-d),
323 indicating that carbonates are not the only phases containing Rb. Rb contents of nodules are
324 also inversely correlated with both Na (Fig. 4-b) and Cl (Fig. 4-e) while halite is generally
325 Rb-poor (e.g., Schock and Puchelt, 1971). The only positive correlations of Rb contents are
326 with K (Fig. 4-c) and S (Fig. 4-f), suggesting that Rb is associated to chloride (sylvite),
327 carbonate ((shortite or/and nyerereite) and sulfate (aphtitalite) phases. In salty kimberlites,
328 chloride carbonate nodules and chloride nodules, Sr is positively correlated with CO₂ (Fig. 4-
329 g) and Ca, with a trend towards alkali-carbonate compositions (Kamenetsky et al., 2007),
330 therefore Sr is largely held within carbonate minerals. Moreover, chloride-carbonate nodules
331 show a trend of decreasing Sr with increasing Cl (Fig. 4-h) and Na + K contents (Fig. 4-i)
332 indicating that Sr is not held within chloride or alkali-sulfate (aphtitalite).

333 Trace element compositions are presented in Table 3 and Figure 5. Kimberlites tend to
334 be enriched in the more incompatible trace elements compared to primitive mantle and thus
335 display steep trace element patterns, except for depletions in Cs, Rb, U, Pb and Ti (Fig. 5-a).
336 In contrast, chloride-carbonate nodules are depleted in most trace elements compared to
337 kimberlites but display marked enrichments in Rb, Pb and Sr, up to concentrations higher than
338 those of the kimberlites (Fig. 5-b). Brine salts and hydrothermal salt veins barely contain any
339 trace element (< detection limit or ≤ 1ppm) except for Ba, Cr, Pb, Rb, Sr and V (Table 3) and
340 they are enriched in Rb, Pb and Sr (Fig. 5-c). The trace element pattern of the host Chukuck
341 sediment differs from those of other samples in that its base is not subparallel to the
342 kimberlite pattern and shows enrichments in Ba, U, Pb, extremely high Sr contents and a
343 depletion in Rb (Fig. 5-d).

344

345 **5.2 Radiogenic isotopes (Rb-Sr, Sm-Nd)**

346

347 **5.2.1. Rb-Sr isotopes**

348

349 Results of Rb-Sr isotopes are reported in Table 4. Chloride-carbonate nodules have whole-
350 rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.707. Salty kimberlite samples have whole-rock $^{87}\text{Rb}/^{86}\text{Sr}$ ratios
351 ranging from 0.10 to 0.49 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.70435 to 0.70739.

352 In order to account for the difference in the Rb/Sr ratios, we have calculated the
353 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the time of kimberlite eruption ($^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$). The mean $^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$ of
354 chloride-carbonate nodules is 0.7055 ± 0.0004 (2σ , $n=2$), similar to the $^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$ of the
355 kimberlite (0.7038 to 0.7050; $n=4$; Fig. 6-a). In comparison, the brine has an $^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$ of
356 0.7088. For the host sediment, we could not dissolve the silicate residue entirely so we could
357 not obtain a whole-rock analysis. The acetic acid leachate of the host sediment, which
358 represent $\sim 71\%$ of the whole rock, has an $^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$ of 0.7088, identical to the brine
359 sample.

360 For spiked whole-rock samples of salty kimberlites, the use of Sr-spec resin for
361 column separation failed to separate Rb and Sr effectively enough and thus, no Rb
362 concentrations could be determined by isotopic dilution. Concentrations measured by isotopic
363 dilution are usually within uncertainty of those measured on a different aliquot by ICP-MS at
364 the SARM laboratory (Fig. 7). Only for whole-rock chloride-carbonate nodules, Rb
365 concentrations measured by isotopic dilution were 30-40% higher than those measured ICP-
366 MS at the SARM laboratory (Fig. 7-a). The most likely explanation is that the chemical
367 composition of the rock matrix (Rb-rich alkali-carbonate and chloride) is very different from
368 that of standard material used at the SARM laboratories, making the calibration less accurate.
369 Salty kimberlites are not as rich in alkali-carbonate and chloride as the nodules, thus, for
370 whole-rock salty kimberlites, we assume that Rb concentrations measured at the SARM
371 laboratory (Table 3) are within uncertainty of the Rb concentrations that would be measured
372 by isotopic dilution and use these values in further calculations (Table 4).

373

374 ***5.2.2. Sm-Nd isotopes***

375

376 Results of Sm-Nd isotopes are reported in Table 5 for chloride-carbonate nodules ($n=2$) and
377 salty kimberlite samples ($n=4$). Whole-rock concentrations in Sm and Nd measured by
378 isotopic dilution are within uncertainty of the concentrations measured by ICP-MS at the
379 SARM laboratory (Table 3; Fig. 7-c and -d). All epsilon Nd values are reported at the time of
380 kimberlite eruption, 365Ma.

381 Chloride-carbonate nodules have marginally radiogenic Nd isotope values, with
382 epsilon Nd values of 2.0 ± 4.7 and 5.2 ± 2.9 that overlap with those of the salty kimberlite
383 (from 3.1 ± 0.2 to 4.6 ± 0.2). The acetic acid leachate of the host sediment is less radiogenic
384 with an epsilon Nd value of -4.5 ± 3.6 .

385

386 **5.3 Sulfur abundances, speciation (sulfide, sulfate) and isotopes ($\delta^{34}\text{S}$)**

387

388 Results of sulfur contents, speciation (sulfide or sulfate) and isotopes ($\delta^{34}\text{S}$ in ‰ vs V-CDT) are
389 reported in Table 6. Chloride-carbonate nodules are the most sulfur-rich samples, with up to
390 ~3.9 wt% S, whereas salty kimberlites samples contain up to 0.30 wt% S. The veined
391 sediment also has very high sulfur content (1.7 wt% S). In contrast, only ~31 ppm of S was
392 extracted from the regional brine, which corresponds to 180 ppm if all the measured
393 elemental concentrations are normalized to 100 atomic wt.% (see notes in Tables 2 and 3).
394 Sulfur extractions were also applied to hydrothermal salt veins and salts precipitated from
395 brines, but no sulfur could be extracted. Sulfur in the salt nodules is oxidized, with sulfate
396 representing more than 99% of total sulfur while this proportion drops down to ~90% in the
397 salty kimberlites. Isotopic compositions of sulfides are similarly depleted in ^{34}S relative to V-
398 CDT in chloride-carbonate nodules (with $\delta^{34}\text{S}$ ranging from -2.7 to -1.2‰) and salty
399 kimberlites (with $\delta^{34}\text{S}$ ranging from -2.8 to -0.4‰; Fig. 8-a). Importantly, sulfates of chloride-
400 carbonate nodules ($\delta^{34}\text{S}$ ranging from 11.5 to 11.9‰) and salty kimberlites ($\delta^{34}\text{S}$ ranging from
401 11.2 to 11.9‰) have the same S isotopic compositions, significantly lower than those of the
402 host sedimentary rock (Chukuck suite) and local brine samples (with both $\delta^{34}\text{S}$ of 34‰; Fig.
403 8).

404 6. Discussion

405

406 6.1. Why the Cambrian sedimentary cover is not the source of chloride-carbonate 407 nodules

408

409 Chloride-carbonate nodules are much more enriched in alkalis ($\text{Na}+\text{K} > 20 \text{ wt.}\%$, Fig. 3-d, -e
410 and -f) and Cl (Fig. 3-e) compared to the wall-rock Chukuck sediment ($0.10 \text{ wt.}\%$ Na+K and
411 $0.35 \text{ wt.}\%$ Cl). They are also more enriched in S (1 to 5 wt.%) compared to the Chukuck
412 sediment ($1.7 \text{ wt.}\%$ S) or brine precipitates ($\text{S} \leq 0.11 \text{ wt.}\%$; Fig. 3-d), thus Cambrian Chukuck
413 suite sediments and brines cannot be their only sulfur source.

414 In terms of trace elements, hydrothermal veins and brine precipitates (Fig. 5-c) are
415 depleted in all trace elements compared to chloride-carbonate nodules (Fig. 5-b) so they
416 cannot represent a source of trace elements to the nodules. The Chukuck suite sediment is
417 more enriched in trace elements than hydrothermal vein and brine precipitates, but its pattern
418 is distinct from those of chloride-carbonate nodules in having flatter and more enriched heavy
419 rare earth elements (HREE), a larger Sr enrichment, smaller Pb enrichment, U and Ba
420 enrichments and the absence of Rb enrichment (Fig. 5-d).

421 From an isotopic point of view, $^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}}$ of bulk chloride-carbonate nodules
422 (0.7055 ± 0.0004 ; 2σ , $n=2$; Table 4, Fig. 6-a) are significantly lower than the regional brine
423 and country-rock sediment analysed in the present study ($^{87}\text{Sr}/^{86}\text{Sr}_{365\text{Ma}} = 0.7088$, Table 4, Fig.
424 6-a) or reported in previous works (Zaitsev et al., 1985 in Kopylova et al., 2013). Just like Sr
425 isotopes, sulfur signatures are significantly different in the country-rocks and in the chloride-
426 carbonate nodules. Sulfates extracted from the nodules have $\delta^{34}\text{S}$ from 11.5 to 11.9‰, within
427 the compositional range of their host salty kimberlites ($\delta^{34}\text{S}_{\text{sulfate}}$ from 9.2 to 12.0‰; Kitayama
428 et al., 2017; Fig. 8-a). These sulfate compositions are lower than those of the Chukuck suite
429 sediment (33.5‰), regional brine (33.7‰), hydrothermal sulfate minerals (15.6 to
430 34.3‰; Kitayama et al., 2017), and much lower than any country-rock sediment of the
431 Siberian platform ($\geq 25\%$; Kitayama et al., 2017 and Vinogradov and Ilupin, 1972 in
432 Kopylova et al., 2013; Fig. 8). Taken together, Sr and S isotopes indicate that chloride-
433 carbonate nodules are neither xenoliths of Cambrian sediments nor precipitates from
434 hydrothermal fluids.

435 To further test the possible contribution (even minimal) of Cambrian surficial material
436 in the bulk composition of the nodules, one can use mixing calculations. In Fig. 8-b, mixing
437 between the sulfate-rich wall-rock sediment of the Chukuck suite and the salty kimberlite

438 endmember would lead to a concave mixing trend (because $[Sr]/[S]$ is 3 times higher in the
439 kimberlite than in the sediment). However, in such a diagram as presented in Fig 8-b, salty
440 kimberlite and chloride-carbonate samples display a horizontal trend of increasing $^{87}Sr/^{86}Sr$
441 ratios at a constant $\delta^{34}S$, unlike this mixing trend.

442 Similarly, we have considered a possible contribution from the local brine. Mixing
443 calculations of kimberlite material with $\leq 30\%$ of this brine produce a horizontal trend of
444 increasing $^{87}Sr/^{86}Sr$ ratios at a constant $\delta^{34}S$. If true, the nodule should have an intermediate
445 composition lying between the brine and the kimberlite endmembers, in all compositional
446 spaces. This is not consistent with the trend observed in $\delta^{34}S$ vs $1/[S]$ (Fig 8-c). In this
447 graphical space, kimberlites are the samples with intermediate composition. Based on this
448 observation, we can rule out a contribution from any known surficial reservoir in the genesis
449 of chloride-carbonate nodules. Their sulfates represent the endmember compositions of
450 kimberlitic sulfates observed in the salty kimberlites of the Udachnaya-East pipe.

451 These kimberlitic sulfates must come from a source that has yet to be identified, below
452 the Cambrian sedimentary cover. In the absence of a known crustal component with such a
453 signature, we further explore the interpretation that these characteristics are derived from the
454 mantle source of kimberlites.

455
456

457 **6.2. A late-stage chloride-carbonate liquid, segregated from the evolving kimberlite**

458

459 One of the most remarkable features of kimberlites worldwide is their very similar trace
460 element patterns (Khazan & Fialko, 2005, Giuliani et al., 2020). This similarity is interpreted
461 to reflect that even kimberlites with highly variable major element compositions had a
462 broadly similar parental melt before lithosphere assimilation. They would either derive from
463 similar sources or have equilibrated with a common mantle component (Tappe et al., 2018;
464 Giuliani et al., 2020). If the broad similarity between all kimberlites is accepted, the origin
465 and the nature of their mantle source remain unclear. In particular, trace element patterns of
466 kimberlites worldwide display some systematic depletions in K, Rb, Pb and Sr (Khazan &
467 Fialko, 2005), which have yet to be fully discussed and explained.

468 Chloride-carbonate nodules from the Udachnaya-East kimberlite display extreme
469 enrichments in Rb, Pb and Sr, while the distribution of other trace elements is subparallel to
470 that in salty kimberlites, with the same base-line trend of trace element enrichments albeit at
471 ~ 2 orders of magnitude lower in abundances compared to kimberlite samples (Fig. 5-b). Only

472 carefully chosen portions from the core parts of the nodules were analyzed, in order to
473 minimize the effect of a possible contamination by the host kimberlite. Chloride-carbonate
474 nodules are extremely enriched in K, Rb, Pb and Sr. In fact, they appear as the perfect
475 counterparts of their host kimberlite, which are depleted in K, Rb, Pb and Sr. This suggests
476 that the chloride-carbonate nodules may be linked to their host kimberlite by a process that
477 led to the selective fractionation of these specific elements. To explain the subparallel base-
478 line, as well as the marked enrichments in Rb, Pb and Sr in the chloride-carbonate nodules
479 (Fig. 5-b), we propose that they were formed by the segregation of a chloride-carbonate
480 liquid. The nodules are essentially composed of chloride and carbonates, and they are much
481 more enriched in alkalis (Na + K), Cl and S compared to salty kimberlites (Fig. 3-d and -e).
482 Rb is compatible in chloride, alkali-carbonate and perhaps also sulfur-bearing phases (Fig. 4-a
483 to -f), whereas Sr is compatible in alkali-carbonate (Fig. 4-g, -h and -i) and Pb is a soluble and
484 chalcophile element that also fits well into carbonates (as Pb^{2+}). Therefore, the striking
485 enrichments of the chloride-carbonate nodules in Rb, Sr and Pb above the contents observed
486 in kimberlites (Fig. 5-b) as well as the slight depletions of the same elements in kimberlites
487 (Fig. 5-a) are consistent with the chloride-carbonate nodules being a late-stage liquid,
488 segregated from the evolving kimberlite.

489 This scenario is in agreement with the major element composition of salty kimberlites
490 all falling within the mixing range of olivine (mantle or early liquidus), phlogopite (liquidus
491 or metasomatized mantle) and chloride-carbonates (Fig. 3). The peculiar texture of chlorides
492 and carbonates, reminiscent of immiscibility between alkaline-carbonate and alkaline-
493 chloride liquids observed $\sim 600^{\circ}\text{C}$ in melt inclusions trapped in olivine from the same
494 kimberlite (Kamenetsky et al., 2004, 2007), suggests that chloride-carbonate nodules are
495 snapshots of a liquid that was quenched $\sim 600^{\circ}\text{C}$ at the closure of the kimberlite magma
496 evolution. The convex pattern shaped by the relative abundances of light REE (from La to
497 Sm) in Figure 9 as well as the smooth rise with increasing atomic number towards heavy REE
498 is best explained by the crystallization of a phase enriched in light REE, such as apatite or
499 perovskite, before the chloride-carbonate liquid exsolved. This is also consistent with a very
500 late-stage segregation of the chloride-carbonate liquid from the kimberlite itself.

501 We propose that the trace-element patterns of kimberlites worldwide (Giuliani et al.,
502 2020 and references therein) may also reflect the segregation a late-stage chloride-carbonate
503 liquid. This hypothesis, however, is challenged by the apparent lack of "salty nodules" in most
504 kimberlite-hosted deposits where major diamond mining operations retrieve very fresh and
505 unaltered rocks (e.g., Siberia, Slave, Superior, Kaapvaal, Tanzania, Congo). Weathering and

506 dissolution of the nodules may explain that chloride-carbonate materials are missing in other
507 localities. We did observe that alkali-carbonates and chlorides are extremely soluble and
508 sensitive to changes in air moisture, even in the controlled environment of the laboratory.
509 Nonetheless, some few kimberlite localities do have a coexisting discrete carbonate phase that
510 can be interpreted as a product of kimberlite-carbonatite immiscibility at depth, or even as the
511 coexistence of such distinctive components as primary liquids (Tappe et al., 2017; Howarth et
512 al., 2019; Tappe et al., 2020a). These examples partially support our preferred model. If true
513 this would imply a wider occurrence of chlorides and alkali-carbonates in kimberlites than
514 previously thought.

515 At the time of kimberlite emplacement, chloride-carbonate nodules have epsilon Nd
516 that overlap with those of their host salty kimberlites (Table 4, Fig. 6-b), kimberlitic
517 perovskite from the same pipe/field (Kamenetsky et al., 2009; Sun et al., 2014) and more
518 generally with other Siberian kimberlites (Carlson et al., 2006; Sun et al., 2014; Agashev et
519 al., 2018) and Group I kimberlites from Southern Africa (Nowell et al., 2004; Smith, 1983;
520 Tappe et al., 2020b; Fig. 6-b). Unlike Nd, it is generally accepted that Sr isotopes of
521 kimberlites are easily overprinted during magma cooling in the presence of fluids and
522 volatiles. This is best illustrated when comparing groundmass perovskite (with less radiogenic
523 $^{87}\text{Sr}/^{86}\text{Sr}$, Fig. 6-a) to their host kimberlite (whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratios extend to more radiogenic
524 values at more or less unchanged epsilon Nd values, Fig. 6-b). A similar trend is observed in
525 kimberlites from Western Greenland kimberlites (Fig. 4 in Tappe et al., 2012). It is worth
526 noticing that the Sr isotope range in salty kimberlites is bracketed on one side by the
527 perovskite composition (Kamenetsky et al., 2009), and on the other side by the chloride-
528 carbonate nodule composition (Fig 6). We thus suggest that chloride-carbonate nodules
529 represent the endmember fluid composition that stretches the range of Sr isotopic
530 compositions in kimberlites to more radiogenic values. The aim of the following section is to
531 explore the possible source(s) for the radiogenic isotope composition of these chloride-
532 carbonate nodules.

533

534

535 **6.3. A high Rb/Sr component in the mantle sampled by kimberlites**

536

537 Pearson et al. (1995) have shown that peridotite xenoliths of the lithospheric mantle below the
538 Udachnaya-East kimberlite pipe have heterogeneous radiogenic isotope composition (e.g.,
539 epsilon Nd from -39.2 to + 8.2, Fig. 6-b). It seems unlikely then, that assimilation of dry

540 lithospheric material had a dominant impact in the clustered compositions found in salty
541 kimberlites and associated nodules. Similarly, the continental crust of the Northeastern
542 Siberian craton (Fig. 6-b; epsilon Nd = -22 ± 4 and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7126 \pm 0.0045$, both
543 recalculated at 365Ma; Rosen et al., 2006) is very distinct from the signatures observed in our
544 samples and is thus not a likely source for the chloride-carbonate nodules. Instead, epsilon Nd
545 of kimberlites and chloride-carbonate nodules (from +2 to +5.2) as well as their $^{87}\text{Sr}/^{86}\text{Sr}$
546 ratios (from 0.7038 to 0.7056), are both consistent with a moderately depleted mantle. These
547 signatures may reflect a source in the ambient convecting upper mantle from which minor
548 recycled components would be oversampled during low-degree partial melting. Although we
549 cannot precisely define the specific type of sediments involved, they must have high Rb/Sr
550 ratios in order to yield radiogenic Sr compositions over time. Such geochemical flavor with
551 radiogenic Sr composition is comparable to what is found in some modern ocean island
552 basalts (OIB) classified as enriched mantle 2 (EM2, e.g., Samoa, Hofmann, 2003; Fig. 6-b).
553 The high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of EM2 basalts has been interpreted by some authors as the recycling
554 of terrigenous sediments (high Rb/Sr, Chauvel et al., 1992; Hofmann, 2003 and references
555 therein), whereas the recycling of pelagic/carbonate-rich sediments (low Rb/Sr ratios) would
556 lead over time to less radiogenic Sr-compositions such as observed in EM1-type basalts (Fig.
557 6-b). The recycling of salts with very high Rb/Sr ratio, could also well explain the radiogenic
558 Sr composition of salty kimberlites and chloride-carbonate nodules.

559 If not from the asthenosphere, the enrichment seen in kimberlites could have been
560 acquired from alkalies, chlorine and sulfur-rich fluids that were percolating within the
561 lithospheric mantle before being assimilated by the parental magma of the kimberlite (Francis
562 and Patterson, 2009; Tappe et al., 2011; Guilianni et al., 2020). Metasomatism of the base of
563 the lithospheric mantle, which would then initiate kimberlite magmatism, could have been
564 fueled by the many subduction zones surrounding the Siberian continent in Neoproterozoic-
565 Cambrian times, enriching the lithospheric mantle in volatile elements such as H₂O and CO₂
566 (Kolesnichenko et al., 2017). This alternative hypothesis is supported by the presence of
567 secondary melt inclusions in olivine from sheared peridotites at Udachnaya that equilibrated
568 from 230 to 180 km depth (Golovin et al., 2018, 2020). These inclusions have trace element
569 patterns with marked enrichments in Cs, Rb, Pb and Sr (Golovin et al., 2018) much like the
570 chloride-carbonate nodules (Fig. 5-b).

571 Both scenarios (involving either an asthenospheric or lithospheric source of chlorides
572 in kimberlite) are strongly supported by positive $\delta^{37}\text{Cl}$ signatures recently reported in West
573 Greenland kimberlite samples (Hoare et al., 2021) and by large quantities of halogens found

574 in the lithospheric mantle beneath the Udachnaya-East kimberlite (Broadley et al., 2018).
575 These evidences support our hypothesis for the presence of a salt-rich component in the
576 mantle sampled by kimberlites.

577

578

579 **6.4. A mantle domain in which sulfates are dominant**

580

581 Sulfides of chloride-carbonate nodules (with $\delta^{34}\text{S}$ ranging from -2.7 to -1.2‰) and salty
582 kimberlites (with $\delta^{34}\text{S}$ ranging from -2.8 to -0.4‰) have S-isotopic compositions consistent
583 with mantle sulfides (MORB compositions of $\sim -1\%$, Labidi et al., 2013 and $0 \pm 1.65\%$ for
584 peridotitic sulfides from Udachnaya-East, Rudnick et al., 1993; Fig. 8-a). Similarly, sulfates
585 of these nodules ($\delta^{34}\text{S}$ ranging from 11.5 to 11.9‰) have the same S-isotopic compositions as
586 sulfates from the salty kimberlite ($\delta^{34}\text{S}$ ranging from 11.2 to 11.9‰), within the range of
587 kimberlitic sulfates proposed by Kitayama et al., 2017; Fig. 8-a). These sulfate isotopic
588 compositions correspond to the composition of sulfate in isotopic equilibrium with sulfide
589 ($\delta^{34}\text{S}$ of -1‰) at a temperature between 460°C and 570°C (Ohmoto and Rye, 1979; Miyoshi
590 et al., 1984). Just like major, trace elements and radiogenic isotopes, S isotope systematics
591 indicate that the chloride-carbonate nodules and salty kimberlites share a common mantle
592 source, which retains mantle signatures instead of a signature contaminated by the Cambrian
593 sedimentary cover.

594 The dominance of sulfate over sulfide in these nodules, as well as their S-isotopic
595 composition provide some insights into the S-isotope composition of the mantle. Globally in
596 the mantle, the isotope budget for reduced sulfur is not balanced: sulfides in mantle xenoliths,
597 mid-ocean ridge basalts (Labidi et al., 2013, 2014) and in ocean island basalts (HIMU, Cabral
598 et al., 2013; EM1, Delavault et al., 2016) all have $\delta^{34}\text{S} < 0\%$, when we expect balance to be
599 achieved around the chondritic value of 0‰ (Canon Diablo Troilite). To explain this
600 imbalance, it has been proposed that the depleted mantle itself has strictly negative $\delta^{34}\text{S}$ ($\sim -$
601 1‰, Labidi et al., 2013, 2014). According to Labidi et al. (2013), this would result from
602 isotopic fractionation during core-mantle segregation: ^{34}S would have been preferentially
603 dissolved in the core, leaving behind an excess of ^{32}S in the mantle. Alternatively, sulfates
604 with $\delta^{34}\text{S} > 0\%$ stored in the mantle source of kimberlites could represent the missing ^{34}S
605 reservoir needed to achieve mass balance at the planetary scale. Labidi et al. (2015) have
606 suggested that oxidized sulfur in EM2-type lavas (from the ocean island of Samoa) could be
607 the product of the interaction between magmatic water and reduced sulfur from the magma,

608 following the reaction: $S^{2+} + 4H_2O = SO_4^{2-} + 4H_2$. Although it is beyond the scope of this
609 study, a similar reaction happening in the sulfur pool of the Udachnaya-East kimberlite,
610 where most reduced sulfur becomes oxidized in a reaction with water, could be used to
611 explain both the isotopic compositions of sulfates and the absence of water in the sulfate-rich,
612 salty kimberlites.

613

614

615 **7. Conclusions**

616

617 *Chloride-carbonate nodules derived from the kimberlitic mantle source.*

618 The combination of major, trace element, Rb-Sr, Sm-Nd and S-isotopes indicates that
619 chloride-carbonate nodules are magmatic products derived from a moderately depleted mantle
620 source. Our results exclude the possibility that these chloride-carbonate nodules are xenoliths
621 from the Cambrian sedimentary cover or crystallized from Cambrian brines infiltrating the
622 kimberlite. They support the hypothesis that alkali-carbonates and their associated chlorides
623 and sulfates in salty kimberlites have a mantle origin (either lithospheric or asthenospheric),
624 tied to the genesis of their host kimberlite. Radiogenic isotope compositions indicate that a
625 recycled component with high Rb/Sr (such as salts or terrigenous sediments) may be present
626 in the mantle sampled by the salty kimberlite of Udachnaya-East, and perhaps of some other
627 kimberlites as well. Such a component is consistent with the abundance of sulfates in the salty
628 kimberlite and associated chloride-carbonate nodules.

629

630 *Segregation and preservation of the last-stage chloride-carbonate liquid of kimberlite.*

631 The trace element signatures of chloride-carbonate nodules can be explained by a
632 magmatic fractionation during the segregation of a late-stage chloride-carbonate liquid from
633 the rest of the kimberlite. This late-stage carbonate-chloride liquid was then quenched,
634 resulting in a texture of intertwined chlorides and carbonates. Although most kimberlites
635 worldwide are free of such distinct chloride-carbonate nodules, we propose that their
636 strikingly similar trace element patterns (Khazan & Fialko, 2005, Giuliani et al., 2020) – in
637 particular, their depletions in K, Rb, Pb and Sr – reflect the ghost signatures of such nodules
638 and attest for their past existence in kimberlites worldwide.

639

640

641

Furthermore, in kimberlites worldwide, Sr isotopes display a range that extends to
radiogenic Sr compositions at nearly constant Nd isotope values. The origin of such a range is
most often interpreted as the result of overprint during magma cooling in the presence of

642 fluids (Tappe et al, 2012). However, in the absence of any sample of these hypothetical fluids,
643 this interpretation has remained highly speculative. Based on their Nd-Sr isotope composition,
644 here we propose that chloride-carbonate nodules are actually snapshots of these fluids,
645 recording a missing compositional endmember.

646

647 ***An alternative hypothesis for the global imbalance of mantle sulfur.***

648 A mantle domain in which sulfate are dominant could partly explain why mantle
649 sulfides do not match the chondritic value. Sulfate compositions in the chloride-carbonate
650 nodules point toward a S isotope composition enriched in ^{34}S ($\delta^{34}\text{S}$ of +11‰) that correspond
651 to the composition of sulfates in isotopic equilibrium with mantle sulfides ($\delta^{34}\text{S}$ of -1‰) at the
652 temperature at which nodules crystallized (~570°C). Such a ^{34}S -enriched domain may explain
653 the apparent imbalance observed between the chondritic value ($\delta^{34}\text{S}$ of 0‰) and the negative
654 compositions of both MORBs ($\delta^{34}\text{S}$ of -1‰, Labidi et al., 2013, 2014) and peridotites ($\delta^{34}\text{S}$ of
655 -1‰, e.g., Rudnick et al., 1993).

656

657

658 **Acknowledgements**

659 The authors would like to thank Sebastian Tappe and two anonymous reviewers for their time
660 and the quality of their critical comments that helped us improving the initial version of our
661 manuscript, as well as Jeffrey G. Catalano and Rajdeep Dasgupta for the editorial handling.
662 We are grateful to Catherine Zimmerman, Aimeryc Schumacher, Laurie Reisberg, Christiane
663 Parmentier and Damien Cividini for their help in the clean lab and radiogenic isotope analyses
664 at CRPG. Equally, we would like to thank Pierre Cartigny for granting us full access to the
665 fluorination line and gas source mass-spectrometer for S-isotope measurements at IPGP while
666 the CRPG fluorination line was not installed "yet". This work benefitted from the financial
667 support of Agence Nationale de la Recherche to ET (ANR Dear-Sir; ANR-15-CE31-0005).
668 Fieldwork at the Udachnaya mine, carried out by AVG and AVK, was supported by the
669 Russian Federation state assignment of IGM SB RAS. This is contribution 2800 from CRPG.

670

671

672 **Research data:**

673 Research Data associated with this article can be accessed at:

674 <https://doi.org/10.24396/ORDAR-70>

675 Otelo research data repository (ORDaR) has been used for this contribution.

676

677

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943 **Figure captions: (9 figures, provided as independent files)**

944

945 **Figure 1:** Map showing the distribution of kimberlite fields on the Siberian craton and the
946 location of the Udachnaya-East kimberlite pipe relative to the extent of brine-bearing
947 sediments and Cambrian saliferous sediments (modified after Sharygin et al., 2011).

948

949 **Figure 2:** Photographs of salt-bearing samples from the Udachnaya-East kimberlite pipe and
950 area. Chloride-carbonate nodules and their host kimberlite, samples UV11-201 (a) and
951 UV11-203 (b). Chloride-carbonate nodules show an intricate network of alternating chloride
952 and carbonate sheets, interpreted as immiscibility textures formed during quenching. (c) Grey
953 halite from a hydrothermal vein. (d) Hydrothermal vein with blue and clear halite showing
954 smooth weathered surfaces, cutting through the kimberlite. (e) Country rock sediment of the
955 Chukuck suite with a sulfate-rich vein, sample UV09-305. (f) Brine precipitates collected from
956 520m depth in the open pit, where they have crystallized after the evaporation of brines,
957 sample UV09-720 (pen for scale). (g) Brine collected at a depth of 750 m from a drill hole 1
958 km south of Udachnaya (0.5 L bottle).

959

960 **Figure 3:** Major element compositions of samples from the Udachnaya-East kimberlite pipe
961 and area, showing the contributions of silicate (e.g., olivine, phlogopite), carbonate (e.g.
962 calcite, northupite, shortite, nyerereite), sulfate (e.g. aphtitalite) and chloride (e.g. halite,
963 sylvite) compositions to the whole-rock compositions. (a, b, c) Olivine, phlogopite, chloride
964 and carbonate (the mineral endmembers connected by grey lines) are the main constituents of
965 kimberlites (red squares and white circles) from Udachnaya-East. (d, e, f) Aphtitalite, halite,
966 and shortite (the alkali-minerals connected by grey lines) are the main constituents of
967 chloride-carbonate nodules (purple diamonds with black rims). Other Siberian kimberlites
968 are also shown for comparison (small grey circles).

969 *References:* [1] Kamenetsky et al., 2008; [2] Kamenetsky et al., 2009; [3] Kamenetsky et al.,
970 2007; [4] This study, D'Eyrammes et al., 2017 and Kamenetsky et al., 2012; [5] Agashev et al.,
971 2018.

972

973 **Figure 4:** Rb concentrations with respect to CaO (a), Na (b), K (c), CO₂ (d), Cl (e) and S (f)
974 and Sr concentrations with respect to CO₂ (g), Cl (h) and Na + K (i) in mineral and whole
975 rock compositions of samples from the Udachnaya-East kimberlite and area. The host

976 *sediment is outside the displayed range of Sr compositions. Other Siberian kimberlites are*
977 *also shown for comparison.*

978 *References: [1] Kamenetsky et al., 2008; [2] Kamenetsky et al., 2007 – CO₂ contents were*
979 *not included in the analyses of alkali-carbonate sheets so we estimated them assuming only*
980 *CO₂ was missing from a total oxide wt.% of 100; [3] Kamenetsky et al., 2004; [4] This study,*
981 *D'Eyrames et al., 2017 and Kamenetsky et al., 2012; [5] Agashev et al., 2018.*

982

983 **Figure 5:** *Trace element concentrations normalized to primitive mantle (McDonough and*
984 *Sun, 1995), for salty kimberlites compared to kimberlites worldwide (a), chloride-carbonate*
985 *nodules (b), hydrothermal salt veins and brine salts (c) and host sediment (d).*

986 *Reference: [1] Giuliani et al., 2020.*

987

988 **Figure 6:** *(a) ⁸⁷Sr/⁸⁶Sr ratios calculated at 365 Ma chloride-carbonate nodules and salty*
989 *kimberlites (both whole-rock compositions) from the Udachnaya-East pipe, compared to*
990 *those of the Cambrian host sediment (acid leachate) and regional brine, as well as other*
991 *ranges from the literature including Siberian sediments, Siberian kimberlites, kimberlitic*
992 *perovskite and clinopyroxene from the Udachnaya-East pipe and the Daldyn kimberlite field,*
993 *silicate residue of salty kimberlite from the Udachnaya-East pipe, peridotite xenoliths from*
994 *the Udachnaya-East pipe, depleted mantle and enriched mantle. (b) Epsilon Nd vs ⁸⁷Sr/⁸⁶Sr*
995 *(at 365 Ma) of salty kimberlites (whole-rock and silicate residue) and chloride-carbonate*
996 *nodules (whole-rock) of the Udachnaya-East pipe, as well as the Chukuck suite sediment of*
997 *the Cambrian sedimentary cover (acetic acid leachate). Kimberlitic perovskite and*
998 *clinopyroxene from the Udachnaya-East pipe and the Daldyn kimberlite field, peridotite*
999 *xenoliths from Udachnaya-East, other Siberian kimberlites, Group I and Group II kimberlites*
1000 *from Southern Africa are shown for comparison (the values displayed correspond to the*
1001 *initial isotopic compositions, calculated at the time of each kimberlite eruption). Endmember*
1002 *compositions of modern basalts (Hofmann, 2003), including the depleted MORB mantle*
1003 *(DMM, epsilon Nd = +11 and ⁸⁷Sr/⁸⁶Sr = 0.703 at 365 Ma) and enriched mantle (EM1,*
1004 *epsilon Nd = -2 and ⁸⁷Sr/⁸⁶Sr = 0.705 and EM2, epsilon Nd = +2 and ⁸⁷Sr/⁸⁶Sr = 0.706, both*
1005 *at 365 Ma), as well as the average continental crust from the Northeastern Siberian craton*
1006 *(epsilon Nd = -22 ± 4 and ⁸⁷Sr/⁸⁶Sr = 0.713 ± 0.005 at 365 Ma, outside the graphical range,*
1007 *Rosen et al., 2006) are also shown for comparison.*

1008 *References: [1] Kostrovitsky et al., 1986 in Kopylova et al., 2013; [2] Nowell et al., 1998;*
1009 *Agashev et al., 2018; Carlson et al., 2006; Sun et al., 2014; [3] Maas et al., 2005; [4]*

1010 Kamenetsky et al., 2009; Sun et al., 2014; [5] Pearson et al., 1995; [6] Zindler and Hart,
1011 1986; Hofmann 2003; [7] Smith, 1983; Nowell et al., 2004; Tappe et al., 2020a; [8] Rosen et
1012 al., 2006.

1013

1014 **Figure 7:** Rb (a), Sr (b), Sm (c) and Nd concentrations (d) of whole-rock samples measured
1015 by acid digestion and isotopic dilution (ID) compared to the concentrations measured by
1016 fusion and ICP-MS at the SARM laboratory. Concentrations obtained by the two methods are
1017 within uncertainty, except for the Rb-contents of chloride-carbonate nodules due to their non-
1018 conventional matrix compositions (Rb-rich alkali-carbonate).

1019

1020 **Figure 8:** Sulfur isotopic compositions ($\delta^{34}\text{S}$) measured in sulfides and sulfates from salt-
1021 bearing samples of the Udachnaya-East pipe: with respect to 1/[S] in wt.% (a) and with
1022 respect to their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at 365 Ma (b). Literature ranges for Siberian sediments (pale
1023 yellow area), primitive mantle (black cross), MORB and peridotitic sulfides from the
1024 Udachnaya-East pipe (green area) are shown for comparison. (a) Sulfides from chloride-
1025 carbonate nodules (filled diamonds) and salty kimberlites (filled squares) are all within the
1026 mantle range, whereas sulfates from chloride-carbonate nodules (open diamonds) and salty
1027 kimberlites (open squares) define kimberlitic sulfate compositions. In plots of $\delta^{34}\text{S}$ vs 1/[S],
1028 binary mixing between two endmember compositions produces linear correlations between
1029 them. Sulfates from chloride-carbonate nodules represent the endmember composition found
1030 in salty kimberlites. They cannot be explained by mixing between other known sulfur sources.
1031 (b) Sulfates dominate the sulfur budget of all samples, thus, only the sulfur isotopic
1032 compositions of sulfates are represented. In plots of $\delta^{34}\text{S}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, binary mixing
1033 between two end-member compositions produces non-linear correlations between them. The
1034 curvature of the mixing lines depends on the endmembers' relative S and Sr concentrations.

1035 References: [1] Kitayama et al., 2017; [2] Labidi et al., 2013, 2014; [3] Rudnick et al., 1993;
1036 [4] McDonough and Sun, 1995; [5] Kostrovitsky et al., 1986 and Vinogradov and Ilupin,
1037 1972 in Kopylova et al., 2013.

1038

1039 **Figure 9:** Rare Earth Element (REE) concentrations in the chloride-carbonate nodules
1040 normalized to the average composition of salty kimberlites. The smooth rise in these ratios
1041 with increasing atomic number of the REEs suggests either that chloride-carbonate nodules
1042 equilibrated after the crystallization of a phase enriched in light REE (apatite being a good
1043 candidate as we did observe it in kimberlite samples).

1044 **Table captions: (6 tables + 1 supplementary material, provided in an independent file)**

1045

1046 **Table 1:** Chloride fraction (in wt.%) estimated from major element compositions compared to
1047 weighed proportions (in wt.%) of the water leachates, acid leachates and residual solids of the
1048 leached samples.

1049

1050 **Table 2:** Major element compositions of salty kimberlites and chloride-carbonate nodules
1051 from the Udachnaya-East pipe, as well as hydrothermal veins from the same pipe and salt-
1052 bearing samples from the sedimentary cover.

1053

1054 **Table 3:** Trace element compositions of salty kimberlites and chloride-carbonate nodules
1055 from the Udachnaya-East pipe, as well as hydrothermal veins from the same pipe and salt-
1056 bearing samples from the sedimentary cover.

1057

1058 **Table 4:** Rb and Sr concentrations and isotopic compositions of nodules and samples from
1059 the Udachnaya-East kimberlite pipe and area.

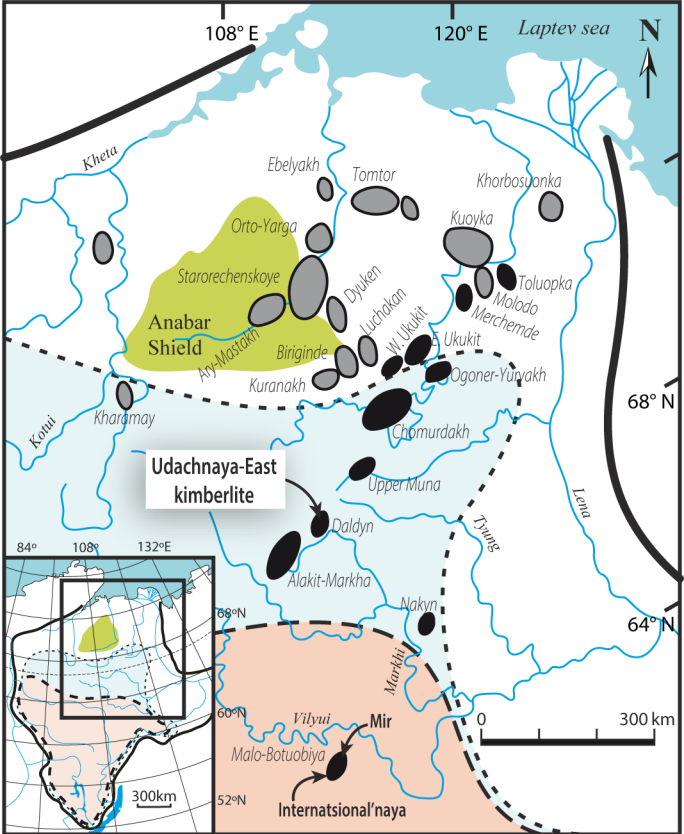
1060

1061 **Table 5:** Sm and Nd concentrations and isotopic compositions of nodules and samples from
1062 the Udachnaya-East kimberlite pipe and area.

1063

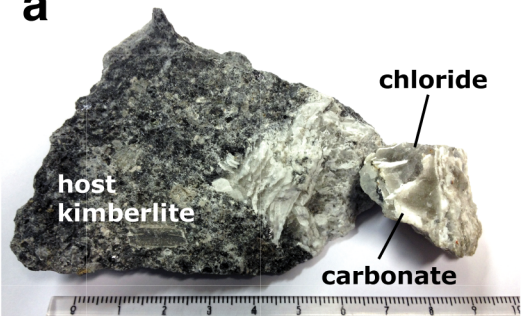
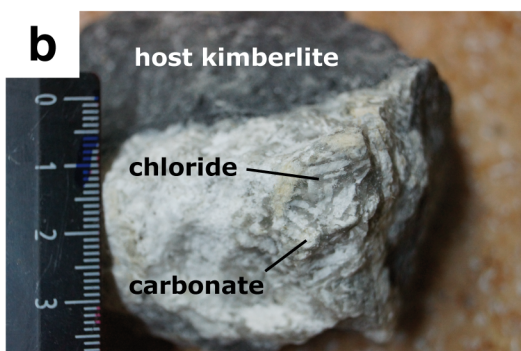
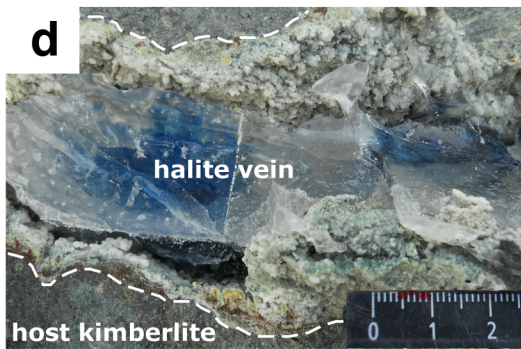
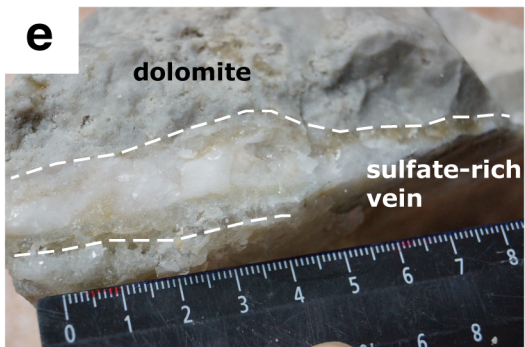
1064 **Table 6:** S concentrations and isotopic compositions (as sulfide and sulfate) of nodules and
1065 other samples from the Udachnaya-East kimberlite and area.

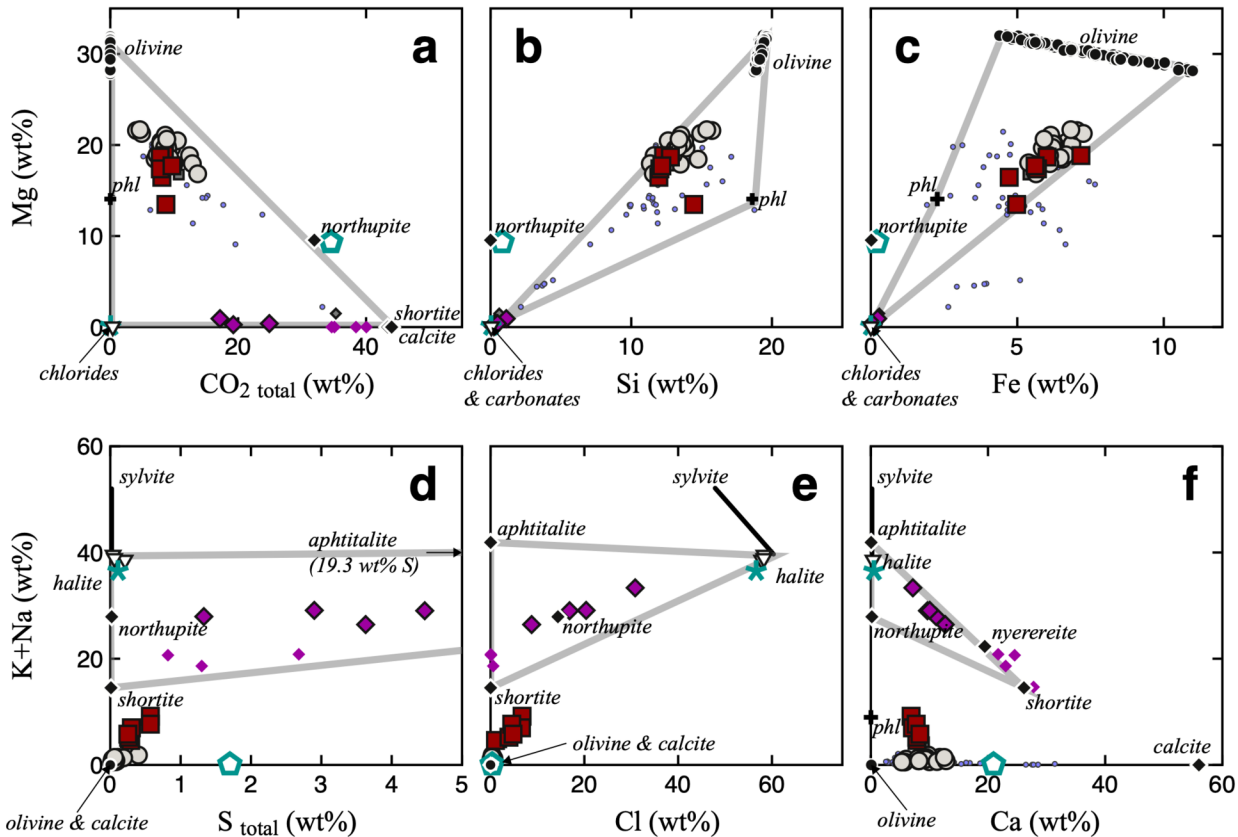
1066



- Boundaries of the Siberian platform
- Exposed basement of the Siberian craton
- Cambrian saliferous sediments
- Area of modern brines

- Kimberlite fields:**
- Mesozoic (251 - 65.5 Ma)
 - Paleozoic (542 - 251 Ma)

a**b****c****d****e****f****g**

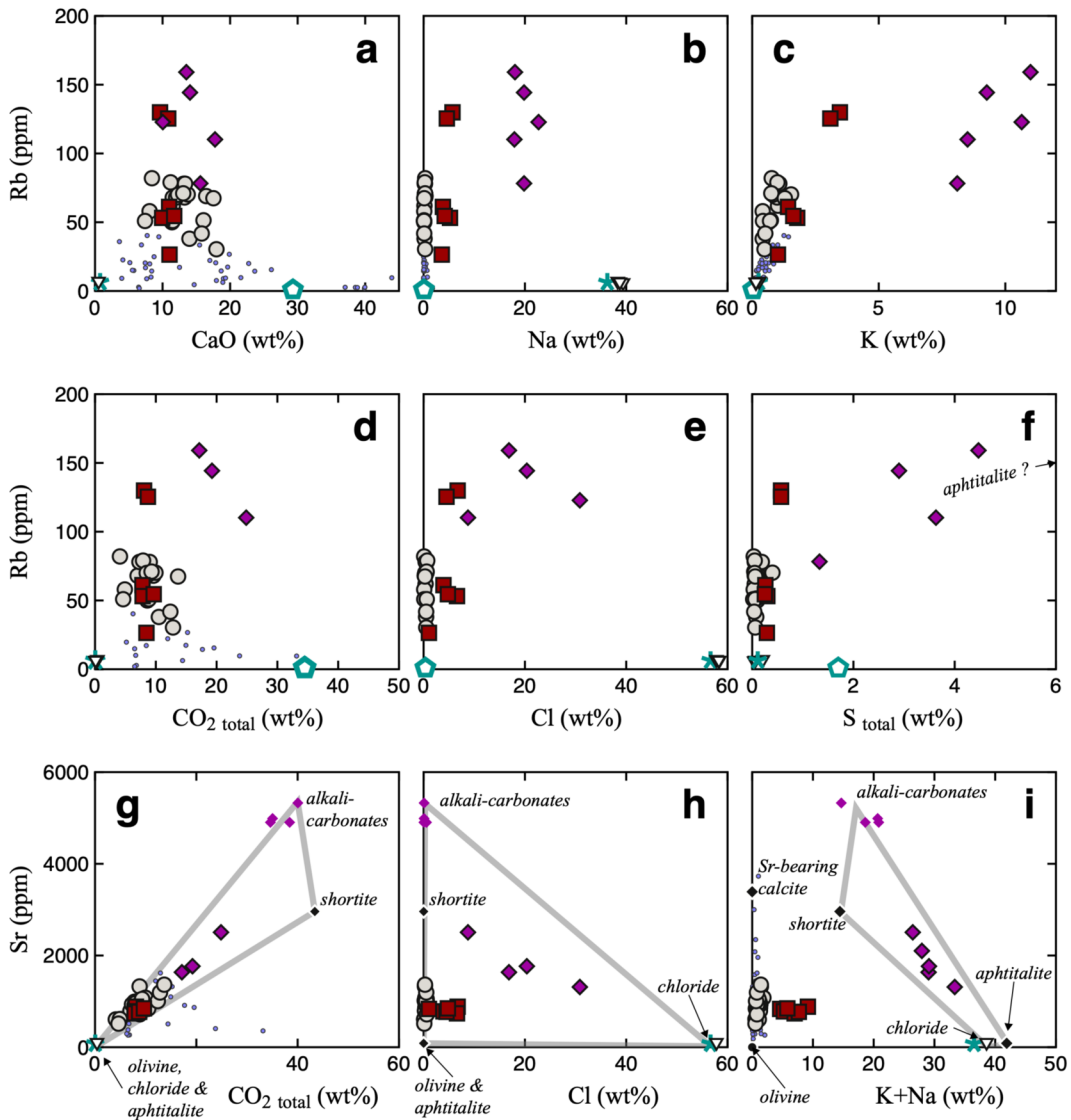


Mineral compositions:

- olivine ^[1]
- ◆ carbonate (calcite, shortite ^[3], northupite ^[3]) and sulfate (aphtitalite ^[3]) compositions
- ◆ alkali-carbonate sheets ^[3]
- ◆ carbonates (calcite, shortite ^[3], northupite ^[3]) and sulfate (aphtitalite ^[3]) compositions
- ◆ chloride (halite to sylvite)
- mixing

Whole-rock compositions:

- ◆ chloride-carbonate nodule
- salty kimberlite ^[4]
- non-salty kimberlite ^[4]
- siberian kimberlites ^[5]
- ▽ hydrothermal veins
- * brine precipitates
- ◇ host sediment

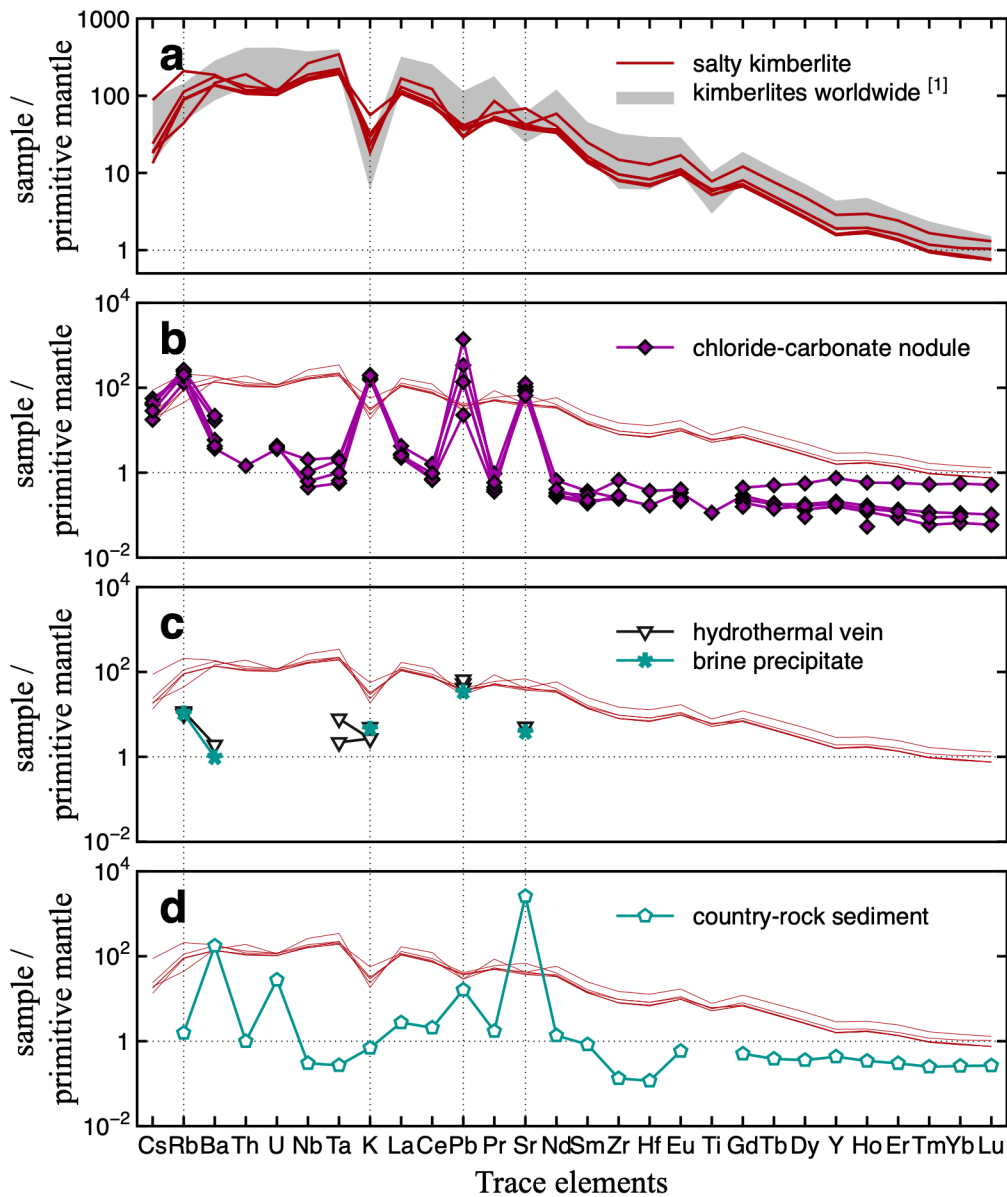


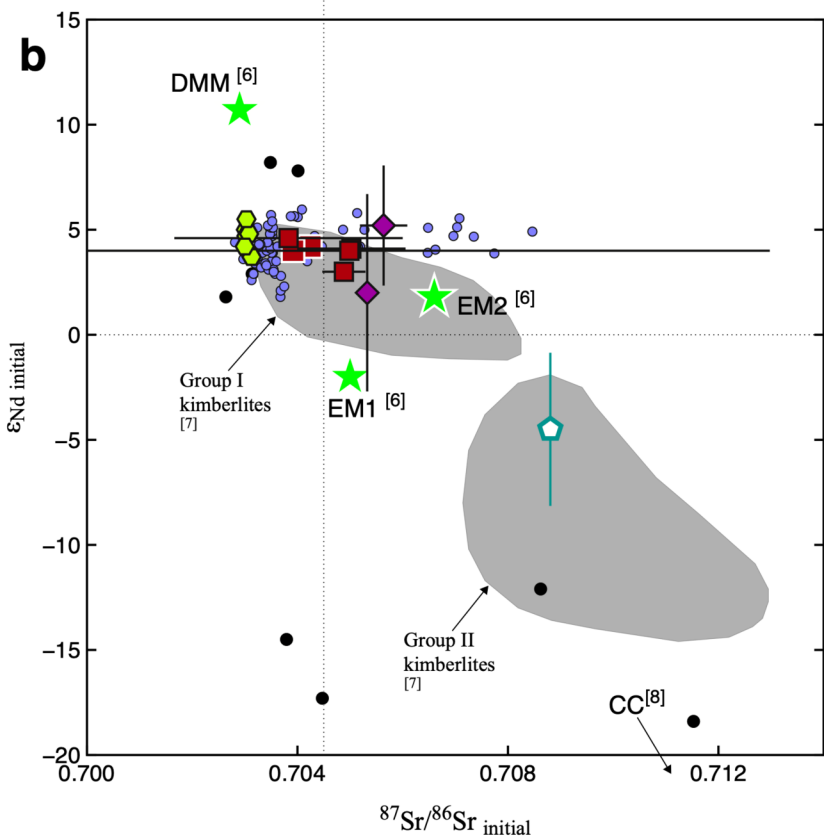
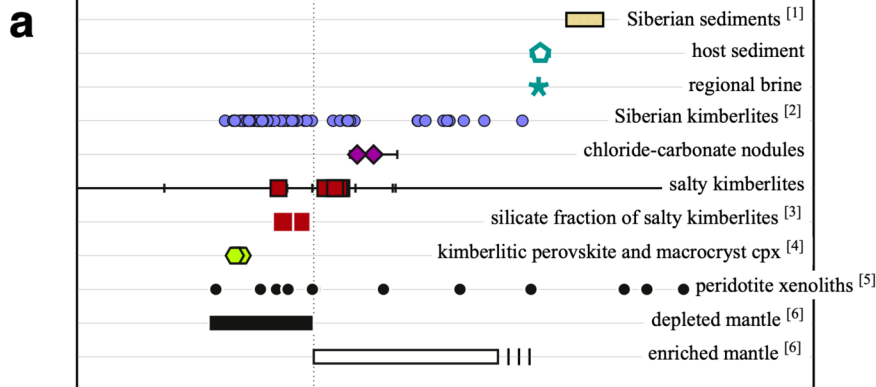
Mineral compositions:

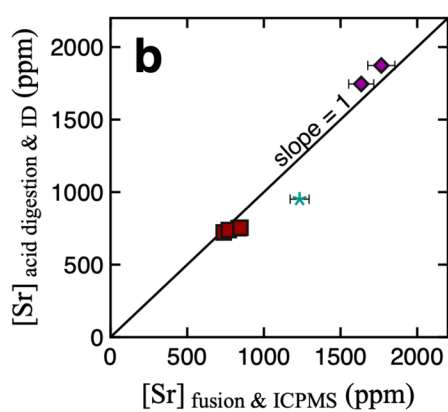
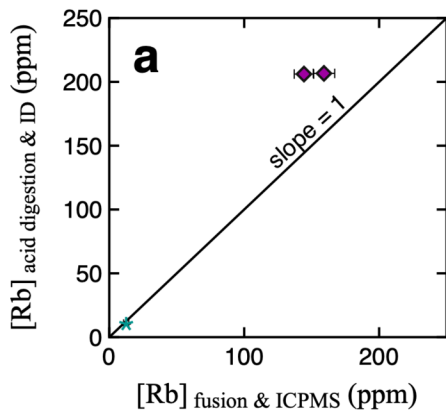
- olivine ^[1]
- ◆ alkali-carbonate sheets ^[2]
- ◆ carbonate (Sr-bearing calcite ^[3], shortite ^[2] and sulfate (aphitalite ^[2]) compositions
- chloride (halite to sylvite)
- mixing (sulfate - alkali-carbonate - chloride)

Whole-rock compositions:

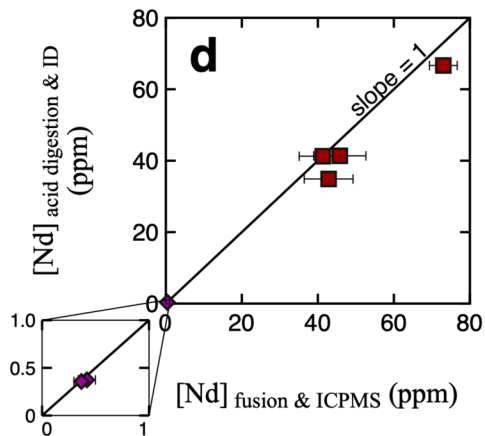
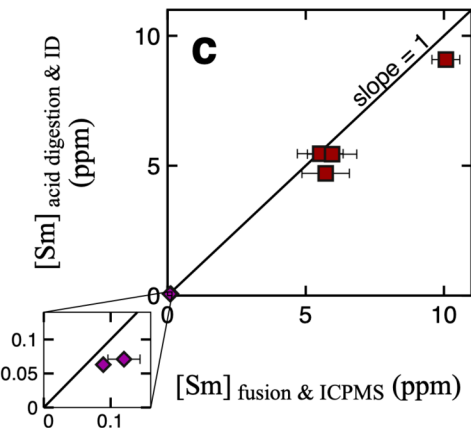
- ◆ chloride-carbonate nodule
- non-salty kimberlite ^[4]
- Siberian kimberlites ^[5]
- ▽ hydrothermal veins
- ★ brine precipitates
- ◇ host sediment



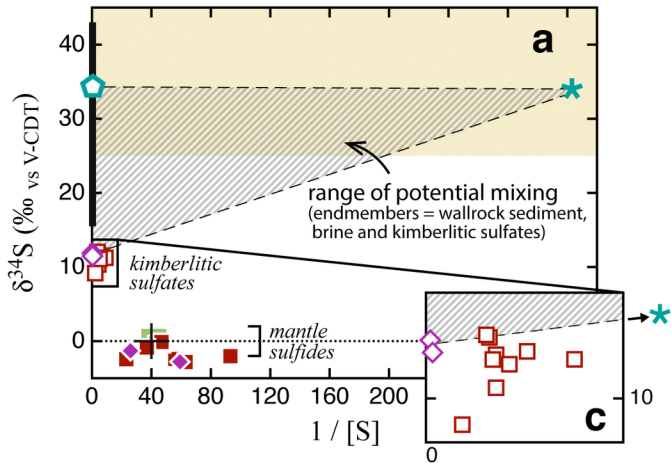




whole-rock:
■ salty kimberlite
◆ chloride-carbonate
nodule
* regional brine



whole-rock:
■ salty kimberlite
◆ chloride-carbonate
nodule

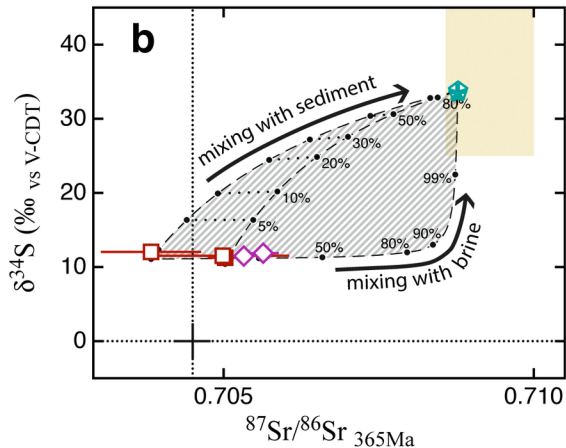


chloride-carbonate: ◆ sulfide ◇ sulfate

salty kimberlite: ■ sulfide ^[1] □ sulfate ^[1]

mantle range: ■ MORB ^[2] and peridotitic sulfides ^[3]

+ primitive mantle ^[4]



sedimentary cover: Siberian sediments & brines ^[5]

⬠ wallrock sediment

✱ regional brine

hydrothermal veins: — sulfates and sulfides ^[1]

mixing line and range

sample / salty kimberlite

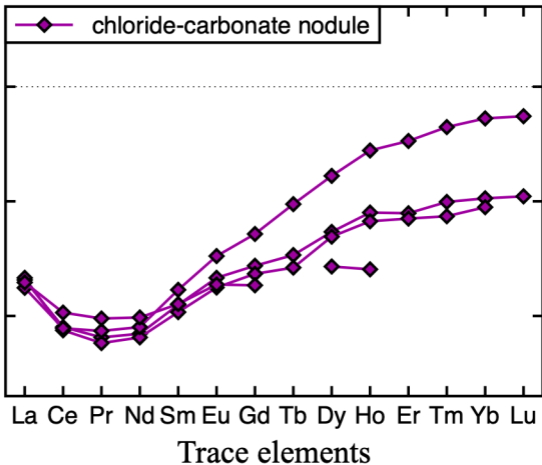


Table 1: Chloride fraction (in wt.%) estimated from major element compositions compared to weighed proportions (in wt.%) of the water leachates, acid leachates and residual solids of the leached samples.

Sample	Rock type	estimated chloride fraction ^[1]	water leachate ^[2]	acetic acid leachate ^[2]	solid residue ^[2]
UV11-201	chloride-carbonate nodule	28%	71%	26%	3%
UV11-203	chloride-carbonate nodule	34%	73%	26%	1%
UV09-305	host sediment	1%	5%	71%	24%

Notes:

[1] Percentage in the sample estimated from the major element composition of bulk powder assuming all Na and Cl form NaCl or KCl.

[2] Percentage in the sample estimated as the difference in weight before and after each leaching step.

Table 2: Major element compositions of salty kimberlites and chloride-carbonate nodules from the Udachnaya-East pipe, as well as hydrothermal veins from the same pipe and salt-bearing samples from the sedimentary cover.

Sample:	salty kimberlites				Chloride-carbonate nodules ^[1]				Hydrothermal salt veins ^[1]			Sedimentary cover ^[1]		
	UV04-24	UV11-70	UV12-119	UV12-120	UV11-180	UV11-201	UV11-203	UV11-203 picked carbonate	UV14-111 grey halite	UV14-111 colorless clear halite	UV14-111 clear blue halite	UV09-720 brine precipitate	UV14-brine regional brine [5]	UV09-305 host sediment
Note:														
Major element compositions in oxide wt. %														
SiO ₂	26.3	25.8	30.9	26.1	0.3	2.39	0.69	1.06	0.12	< L.D.	< L.D.	0.08	na	1.76
TiO ₂	1.56	1.24	1.23	1.05	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	na	< L.D.
Al ₂ O ₃	2.08	1.55	4.36	1.60	< L.D.	0.37	0.12	0.295	< L.D.	< L.D.	< L.D.	< L.D.	na	0.11
FeO total	9.23	7.32	6.40	7.21	0.079	0.300	0.089	0.063	< L.D.	< L.D.	< L.D.	< L.D.	na	0.259
MnO	0.191	0.133	0.105	0.135	0.0023	0.017	0.0049	0.0044	0.0008	< L.D.	< L.D.	0.0045	na	0.02
MgO	31.2	28.8	22.3	29.4	0.256	1.54	0.44	0.638	0.071	< L.D.	< L.D.	0.191	na	15.5
CaO	11.0	9.9	10.8	11.7	10.0	13.5	14.1	17.8	0.523	< L.D.	< L.D.	0.75	na	29.3
Na ₂ O	4.84	7.02	6.18	5.61	30.6	24.3	26.7	24.2	51.6	53.1	52.2	48.9	na	0.08
K ₂ O	1.23	2.14	3.72	1.96	12.8	13.2	11.2	10.3	0.331	0.178	0.178	0.303	na	0.046
P ₂ O ₅	0.73	0.39	0.47	0.41	< L.D.	0.14	0.17	0.23	< L.D.	< L.D.	< L.D.	< L.D.	na	< L.D.
LOI	11.6	20.2	14.4	18.2	nd	nd	nd	nd	nd	nd	nd	nd	na	40.9
Total ^[2]	100.0	104.5	100.9	103.3	54.1	55.8	53.5	54.5	52.7	53.3	52.4	50.2	na	87.9
CO ₂ total	8.46	7.83	8.7	9.65	nd	17.2	19.2	24.9	0.39	0.11	0.1	0.04	nd	34.5
H ₂ O+ total	0.27	0.56	0.18	0.38	nd	nd	nd	nd	nd	nd	nd	nd	na	nd
Major element compositions in atomic wt. %														
Si	12.3	12.0	14.4	12.2	0.14	1.12	0.32	0.50	0.06	< L.D.	< L.D.	0.04	< L.D.	0.82
Ti	0.94	0.74	0.74	0.63	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Al	1.10	0.82	2.31	0.85	< L.D.	0.20	0.06	0.16	< L.D.	< L.D.	< L.D.	< L.D.	0.0007	0.06
Fe	7.17	5.69	4.98	5.61	0.06	0.23	0.07	0.05	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.20
Mn	0.15	0.10	0.08	0.10	0.00	0.01	0.00	0.00	< L.D.	< L.D.	< L.D.	< L.D.	0.005	0.01
Mg	18.8	17.4	13.5	17.7	0.15	0.93	0.26	0.38	0.04	< L.D.	< L.D.	0.12	9.1	9.32
Ca	7.88	7.11	7.74	8.38	7.17	9.66	10.1	12.7	0.37	< L.D.	< L.D.	0.54	52.1	20.9
Na	3.59	5.21	4.59	4.16	22.7	18.0	19.8	17.9	38.3	39.4	38.7	36.3	28.4	0.06
K	1.02	1.78	3.09	1.62	10.6	11.0	9.27	8.51	0.27	0.15	0.15	0.25	9.4	0.04
P	0.32	0.17	0.21	0.18	< L.D.	0.06	0.07	0.10	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
O	35.1	33.3	34.9	33.7	13.2	14.6	13.5	14.1	na	na	na	na	na	15.6
S	0.29	0.30	0.57	0.25	1.33	4.47	2.90	3.63	0.21	0.04	0.06	0.11	0.02	1.70
Cl	1.05	6.59	4.52	4.79	30.8	16.9	20.4	8.76	57.8	58.3	58.3	56.6	nd	0.35
Total ^[3]	98.5	99.6	100.5	100.2	86.3	94.3	96.0	91.7	97.5	98.0	97.3	94.0	99.0	83.6
K ₂ O/Na ₂ O	0.3	0.3	0.6	0.3	0.4	0.5	0.4	0.4	0.006	0.003	0.003	0.006	na	0.6
C.I. ^[4]	1.0	1.1	1.6	1.1	na	na	na	na	na	na	na	na	na	na

Notes:

[1] For salt analyses, LOI was not measured and [Cl], [CO₂], and [S] were measured instead; [CO₂] and [S] are considered qualitative given the salt matrix.

[2] Total oxide wt.% is the sum of major elements, using FeOtotal. When LOI was determined (e.g. kimberlite samples), total oxide wt.% is calculated using LOI and $LOI \approx [Cl] + [CO_2] + [H_2O] + [S]$. When LOI was not measured (e.g. salt-bearing samples), total oxide wt.% is calculated using $[CO_2] + [H_2O]$ and is < 100% because [Cl] and [S] are not taken into account.

[3] Total atomic wt.% is the sum of major elements in atomic wt.%, plus [CO₂] + [H₂O]. Because it includes [S] and [Cl], it is usually $\approx 100\%$. Total atomic wt.% <100% indicate that either [CO₂], [H₂O], [Cl] or [S] was missing from the analysis.

[4] The contamination index of kimberlite samples is calculated such that $C.I. = (SiO_2 + Al_2O_3 + Na_2O)/(MgO + 2*K_2O)$, according to Kjarsgaard et al. (2009) and references therein. Although this index is not relevant for quantifying the contamination by surficial lithology (e.g. sediments), it gives an indication of the possible incorporation of continental granitic crust. Typically, C.I. values < 1 are considered uncontaminated.

[5] Concentrations in the brine solution are normalised to 100 atomic wt.% in order to allow for a direct comparison with rock samples. The measured total atomic wt.% was 12.51 wt.%, including both major and trace elements.

< L.D. is lower than detection limit; nd is not determined; na is not applicable.

Table 3: Trace element compositions of salty kimberlites and chloride-carbonate nodules from the Udachnaya-East pipe, as well as hydrothermal veins from the same pipe and salt-bearing samples from the sedimentary cover.

Sample:	salty kimberlites				Chloride-carbonate nodules				Hydrothermal salt veins			Sedimentary cover		
	UV04-24	UV11-70	UV12-119	UV12-120	UV11-180	UV11-201	UV11-203	UV11-203 picked carbonate	UV14-111 grey halite	UV14-111 colorless clear halite	UV14-111 clear blue halite	UV09-720 brine precipitate	UV14-brine regional brine [1]	UV09-305 host sediment
Note:														
Trace element compositions in ppm														
As	1.9	< L.D.	< L.D.	< L.D.	< L.D.	3.4	3.1	3.2	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Ba	966	896	1233	907	28	144	39	112	13	< L.D.	< L.D.	6.4	15	1162
Be	0.51	0.94	4.7	0.90	< L.D.	1.5	1.5	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Bi	< L.D.	< L.D.	< L.D.	< L.D.	1.0	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Cd	0.24	0.14	0.15	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Ce	204	121	133	126	1.6	1.2	1.2	1.1	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	3.5
Co	80	73	62	75	< L.D.	3.5	1.5	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.61	0.85
Cr	1679	970	1131	924	35	28	29	15	90	76	86	76	< L.D.	4.7
Cs	0.40	0.28	1.8	0.38	0.60	0.93	1.2	0.84	< L.D.	< L.D.	< L.D.	< L.D.	2.6	< L.D.
Cu	74	55	61	46	24	10	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	7.6	< L.D.
Dy	3.3	1.8	1.8	1.8	0.061	0.38	0.12	0.11	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.24
Er	1.1	0.60	0.60	0.59	< L.D.	0.25	0.059	0.053	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.13
Eu	2.6	1.5	1.6	1.5	0.035	0.062	0.040	0.033	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.090
Ga	6.9	4.1	7.9	4.1	< L.D.	1.1	< L.D.	0.86	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Gd	6.6	3.6	3.9	3.7	0.086	0.24	0.13	0.11	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.28
Ge	0.9	0.76	0.75	0.77	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Hf	3.6	2.0	2.3	1.9	< L.D.	0.11	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.033
Ho	0.4	0.25	0.26	0.25	0.008	0.087	0.025	0.021	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.051
In	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
La	109	69	75	72	1.6	1.5	1.7	1.8	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	1.8
Lu	0.088	0.051	0.050	0.051	< L.D.	0.035	0.0070	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.018
Mo	1.3	2.8	3.0	1.6	10	24	25	20	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Nb	174	110	112	105	0.68	0.41	0.30	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.20
Nd	73	41	46	43	0.51	0.42	0.37	0.34	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	1.7
Ni	1091	1120	851	1152	< L.D.	16	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	12	5.6
Pb	4.4	5.4	4.3	5.7	208	21	21	3.4	9.9	6.3	8.0	5.1	1.1	2.4
Pr	22	12	14	13	0.15	0.12	0.10	0.091	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.44
Rb	26	53	125	55	123	159	144	110	7.0	6.0	6.5	6.3	100	0.94
Sb	16	8.6	10	9.1	0.95	2.2	3.1	0.62	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Sc	< L.D.	< L.D.	0.22	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Sm	10	5.5	6.0	5.7	0.09	0.12	0.089	0.077	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.34
Sn	1.4	0.81	1.0	0.76	< L.D.	1.2	1.1	1.0	< L.D.	< L.D.	8.8	< L.D.	< L.D.	< L.D.
Sr	835	738	771	847	1313	1635	1766	2506	102	< L.D.	< L.D.	76	9863	51560
Ta	13	8.1	7.6	7.1	0.073	0.037	0.021	0.024	< L.D.	0.081	0.29	< L.D.	< L.D.	0.010
Tb	0.75	0.42	0.44	0.42	< L.D.	0.050	0.018	0.014	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.038
Th	15	8.4	9.4	8.9	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.079
Tm	0.11	0.066	0.066	0.064	< L.D.	0.036	0.0080	0.0060	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.017
U	2.3	2.1	2.3	2.1	< L.D.	0.079	0.087	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.020	0.56
V	97	94	126	89	37	72	64	74	29	28	28	25	< L.D.	1.7
W	0.83	1.5	1.9	1.7	7.0	22	17	18	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.
Y	12	6.8	7.0	6.8	< L.D.	3.2	0.90	0.78	< L.D.	< L.D.	< L.D.	< L.D.	0.045	1.9
Yb	0.64	0.38	0.38	0.36	< L.D.	0.24	0.049	0.041	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	0.12
Zn	81	62	58	63	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	56	14
Zr	156	85	100	83	< L.D.	7.0	2.6	3.0	< L.D.	< L.D.	< L.D.	< L.D.	< L.D.	1.4

Notes:

[1] Concentrations in the brine solution are normalised to 100 atomic wt.% in order to allow for a direct comparison with rock samples. The measured total atomic wt.% was 12.51 wt.%, including both major and trace elements. Measured contents before normalisation were 13 ppm for Rb and 1233 ppm of Sr.
< L.D. is lower than detection limit.

Table 4: Rb-Sr concentrations and isotopic compositions of salt-rich nodules and other samples from the Udachnaya-East kimberlite pipe and area.

Sample	Rock type	Method	Fraction	[Rb] (ppm)	± 2σ	[Sr] (ppm)	± 2σ	⁸⁷ Rb/ ⁸⁶ Sr	± 2σ	⁸⁷ Sr/ ⁸⁶ Sr	± 2σ	⁸⁷ Sr/ ⁸⁶ Sr _{365Ma} [4]	± 2σ
UV11-201	carbonate	[1]	whole-rock	206.64	1.10	1745.32	0.91	0.34	0.01	0.70739	0.00044	0.70564	0.00045
UV11-203	carbonate	[1]	whole-rock	206.12	1.16	1872.78	0.15	0.32	0.01	0.70695	0.00007	0.70532	0.00008
UV04-24	salty kimberlite	[2]	whole-rock	26.45	3.97	751.24	2.15	0.10	0.15	0.70435	0.00203	0.70383	0.00217
UV11-70	salty kimberlite	[2]	whole-rock	53.18	2.66	721.72	1.01	0.21	0.05	0.70611	0.00099	0.70502	0.00103
UV12-119	salty kimberlite	[2]	whole-rock	125.40	6.27	738.52	0.33	0.49	0.05	0.70739	0.00032	0.70488	0.00041
UV12-120	salty kimberlite	[2]	whole-rock	54.54	2.73	754.49	8.46	0.21	0.05	0.70606	0.00798	0.70499	0.00799
UV09-305	host sediment	[1]	leachate [3]	0.65	0.004	1878	0.47	0.001	0.01	0.70881	0.00018	0.70880	0.00018
brine	regional brine	na	solution	10.23	0.03	949.74	0.06	0.03	0.003	0.70893	0.00007	0.70877	0.00007

Notes:

[1] In this first method, we used acetic acid for the second leaching following water, and separated Rb and Sr using AG50-X8 cation resin.

[2] In this second method, we used HCl for the second leaching following water, and separated Rb and Sr using Sr-spec resin. For Sr-rich samples, columns with Sr-spec resin failed to separate Rb and Sr effectively enough to prevent some interference of ⁸⁷Sr on ⁸⁷Rb. The [Rb] and associated uncertainties for those samples correspond to SARM analyses.

[3] Due to the precipitation of fluorides when preparing the silicate residue of this sample, we only analysed its acetic acid leachate (71 wt.% of the whole-rock, Table 1).

[4] ⁸⁷Sr/⁸⁶Sr ratios at the time of kimberlite eruption (365Ma) are calculated using the measured ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr ratios in the Rb-Sr decay equation:

$$^{87}\text{Sr}/^{86}\text{Sr} = [^{87}\text{Sr}/^{86}\text{Sr}]_{@365\text{Ma}} + ^{87}\text{Rb}/^{86}\text{Sr} * (e^{\lambda t} - 1) \text{ where } \lambda^{87}\text{Rb} = 1.3972 \times 10^{-11} \text{ per year is the decay constant of } ^{87}\text{Rb} \text{ and } t = 365 \times 10^6 \text{ years is the time since eruption.}$$

na: not applicable

Table 5: Sm-Nd concentrations and isotopic compositions of nodules and other samples from the Udachnaya-East kimberlite pipe and area.

Sample	Rock type	Fraction	[Sm] (ppm)	± 2σ	[Nd] (ppm)	± 2σ	¹⁴⁷ Sm/ ¹⁴⁴ Nd	± 2σ	¹⁴³ Nd/ ¹⁴⁷ Sm	± 2σ	εNd _{365Ma} [2]	± 2σ
UV11-201	chloride-carbonate nodule	whole-rock	0.071	0.00001	0.374	0.0001	0.114	0.0003	0.512707	0.00015	5.21	2.86
UV11-203	chloride-carbonate nodule	whole-rock	0.063	0.00001	0.357	0.0002	0.107	0.0005	0.512525	0.00024	2.01	4.70
UV04-24	salty kimberlite	whole-rock	9.085	0.008	66.653	0.087	0.082	0.002	0.512600	0.00001	4.61	0.19
UV11-70	salty kimberlite	whole-rock	5.461	0.007	41.253	0.047	0.080	0.002	0.512570	0.00001	4.13	0.21
UV12-119	salty kimberlite	whole-rock	5.444	0.004	41.367	0.073	0.079	0.002	0.512514	0.00001	3.05	0.22
UV12-120	salty kimberlite	whole-rock	4.704	0.006	34.886	0.037	0.081	0.002	0.512569	0.00001	4.03	0.19
UV09-305	host sediment	leachate [1]	0.407	0.00007	2.186	0.001	0.112	0.0004	0.512206	0.00019	-4.50	3.64

Notes:

[1] Due to the precipitation of fluorides when preparing the silicate residue of this sample, we only analysed its acetic acid leachate (71 wt.% of the whole-rock, Table 1).

[2] ¹⁴³Nd/¹⁴⁴Nd ratios at the time of kimberlite eruption (365Ma) are calculated using the measured ¹⁴³Nd/¹⁴⁴Nd and ¹⁴⁷Sm/¹⁴⁴Nd ratios in the Sm-Nd decay equation:

$$[^{143}\text{Nd}/^{144}\text{Nd}] = [^{143}\text{Nd}/^{144}\text{Nd}]_{@365\text{Ma}} + [^{147}\text{Sm}/^{144}\text{Nd}] \times (e^{\lambda t} - 1)$$

where $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12}$ per year is the decay constant of ¹⁴⁷Sm and $t = 365 \times 10^6$ years is the time since eruption.

Nd isotopic compositions are then expressed in epsilon, as: $\epsilon_{\text{Nd}} = (([^{143}\text{Nd}/^{144}\text{Nd}]_{\text{sample}} / [^{143}\text{Nd}/^{144}\text{Nd}]_{\text{CHUR}}) - 1) \times 10000$

where $[^{143}\text{Nd}/^{144}\text{Nd}]_{\text{CHUR}} = 0.512170$ at 365 Ma, calculated from the current CHUR values of 0.512638 and a ¹⁴⁷Sm/¹⁴⁴Nd ratio of the CHUR of 0.1967.

Table 6: S concentrations and isotopic compositions (as sulfide and sulfate) of nodules and other samples from the Udachnaya-East kimberlite and area

Sample	Rock type	$\delta^{34}\text{S}_{\text{sulfide}}$ (‰ vs V-CDT)	[S] _{sulfide} (ppm)	$\delta^{34}\text{S}_{\text{sulfate}}$ (‰ vs V-CDT)	[S] _{sulfate} (ppm)	$\delta^{34}\text{S}_{\text{bulk}}$ (‰ vs V-CDT)	[S] _{bulk} (ppm)
UV11-201	chloride-carbonate	-1.24	386	11.86	38270	11.73	38656
UV11-203	chloride-carbonate	-2.72	169	11.47	25048	11.38	25217
UV04-24	salty kimberlite	-0.40	230	12.04	2724	11.07	2954
UV11-70	salty kimberlite	-2.82	159	11.25	2459	10.40	2618
UV12-119	salty kimberlite	nd	nd	11.40	2348	nd	> 2348
UV12-120	salty kimberlite	-2.40	178	11.51	1625	10.14	1803
UV09-305	host sediment	nd	nd	33.73	17000	33.73	17000
UV14-brine	brine	nd	nd	33.45	31	33.45	31

Note:

nd = not determined