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1 REVISION 1

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3	Smoking gun for thallium geochemistry in volcanic arcs:
4	nataljamalikite, TII, a new thallium mineral from an active fumarole
5	at Avacha Volcano, Kamchatka Peninsula, Russia
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25 Abstract

This paper describes the new mineral nataljamalikite, the orthorhombic form of thallium iodide (TII), from high temperature fumaroles from the Avacha volcano, Kamchatka Peninsula, Russia. We also present some chemical analyses showing extreme enrichment of Tl in the volcanic gases at the Avacha volcano, and a review of thallium geochemistry that highlights the fascinating processes that led to the formation of nataljamalikite.

31 Nataljamalikite occurs as pseudo-cubic nanocrystals ($\leq 0.5 \,\mu$ m) within vacuoles in an As-32 (Te)-rich amorphous sulfur matrix, and rarely as irregularly shaped aggregates up to $\sim 50 \,\mu\text{m}$ in 33 diameter within the amorphous sulfur matrix. Associated minerals include an unidentified Tl-As-S 34 mineral, barite, and rare inclusions of a Re-Cu-bearing phase. The mean empirical composition based on 4 EDS analyses is Tl_{1.00}(I_{0.95}Br_{0.03}Cl_{0.02}), corresponding to the ideal formula TII. 35 36 Nataljamalikite crystallizes in the orthorhombic system, space group *Cmcm*, which is consistent 37 with the low temperature (<175 °C) synthetic TII polymorph. EBSD data reveal that some grains 38 retain the cubic symmetry (Pm-3m) of the high temperature polymorph, though most analyzed 39 grains display the orthorhombic symmetry. Single crystal X-ray studies of material extracted by the 40 Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) technique, and carried out on the 41 MX2 macromolecular beamline of the Australian Synchrotron, determined the following cell dimensions: a = 4.5670(9) Å, b = 12.803(3) Å, c = 5.202(1) Å, V = 304.2(1) Å³ and Z = 4. The six 42 strongest calculated X-ray reflections and their relative intensities are: 3.31 Å (100), 2.674 Å (73), 43 3.20 Å (43), 2.601 Å (28), 2.019 Å (21) and 2.284 Å (19). The combination of EBSD analysis 44 45 (providing an efficient test of the crystallinity and crystal symmetry of a population of µm-sized grains) and synchrotron single crystal X-ray micro-diffraction (beam size ~7.5 µm) on micro-46 47 aggregates extracted using FIB-SEM opens the way to the characterization of challenging specimen 48 - in this case, the sulfur matrix is highly beam sensitive, and the nataljamalikite grains could not be isolated using optical microscopy. 49

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50 The high temperature (>600 $^{\circ}$ C) sulfidic (~1.2 wt% S) vapors at Avacha are extremely 51 enriched in thallium; with 34 ppm, they contain an order of magnitude more Tl than the richest 52 volcanic gases analyzed to date, and ~100 times more Tl than most metal-rich fumarolitic fluids 53 associated with volcanic arcs. The formation of nataliamalikite illustrates the complex processes 54 that control thallium geochemistry in magmatic arc systems. Thallium minerals have now been 55 reported in andesitic (Avacha), basaltic (Tolbachik, Kamchatka), as well as rhyolitic (Vulcano, 56 Eolian Islands, Italy) volcanoes. Ultimately, these thallium minerals result from the transfer of 57 thallium from subducted sediments to volcanic gases in arc volcanoes. We suggest that the 58 extremely thallium-enriched vapors from which nataljamalikite formed result from complex and 59 transient interactions between Tl-rich sulfosalt melts and magmatic vapors, a process that may be 60 important in controlling metal distribution in boiling epithermal systems.

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Keywords: Nataljamalikite; new mineral; thallium; fumaroles; vapor transport; Avacha Volcano,
Kamchatka Peninsula, Russia.

64

65 Introduction

66 Thallium (Tl) is a toxic heavy metal that has an upper crustal abundance of 550 ppb, comparable to 67 that of Mo (600 ppb) and Bi (230 ppb) (Hu and Gao, 2008). Yet, minerals containing Tl as an essential element are scarce, mainly because Tl(I) can behave both as a chalcophile element, 68 69 substituting for example for Pb(II), or as lithophile element, in which case it substitutes for K(I). As 70 a result, exceptional processes are required to form Tl minerals (Christy 2015). In this paper we 71 describe a new locality with Tl-dominant mineralogy, including the new mineral nataljamalikite, 72 TII. Nataljamalikite forms in high temperature fumaroles at the Avacha andesitic stratovolcano, 73 Kamchatka Peninsula, Russia. This represents the third occurrence of Tl minerals associated with 74 fumarolitic activity in arc volcanoes. The aim of this paper is to provide a formal description of

nataljamalikite as a new mineral, as well as an overview of the processes that give rise to high local
concentrations of Tl, leading to the formation of exotic Tl-minerals.

77 Nataljamalikite, a new mineral

78 Occurrence

Nataljamalikite occurs at the Avacha volcano, on the Kamchatka Peninsula, Far Eastern
Russia (53°15′18″ N, 158°49′48″E), in association with active high temperature (to 620–640 °C)
fumarolic vents (Figure 1). The Avacha (or Avachinsky) volcano lies 25 km NE of Petropavlovsk–
Kamchatka, the largest city on the Peninsula.

83 The Kamchatka Peninsula is one of the longest-lived volcanically active areas on the planet, 84 with activity dating back to the Late Triassic (Bindeman et al., 2002; Pedoja et al., 2006; Waltham, 85 2001). Holocene volcanic products comprise basalts, basaltic andesites, andesites, basaltic 86 trachyandesites, trachyandesites, trachyte/trachydacites, dacites and rhyolites (Viccaro et al., 2012). 87 The Avacha volcano is one of the most active volcanoes on the Kamchatka Peninsula, and began 88 erupting in the middle to late Pleistocene era. The Avacha volcano is of the Somma-Vesuvius type, 89 with a base \sim 4 km in diameter. The active cone is located in a horseshoe-shaped caldera (\sim 2300 m 90 altitude), which formed 30-40,000 years ago in a major landslide, which covered an area of 500 km² south of the volcano (Levin et al., 2004; Taran et al., 1997; Waltham, 2001). The active 91 92 cone began rising approximately 5000 years ago and currently sits on the SE border of the Somma 93 caldera, resulting in an asymmetrical appearance with respect to the center of the caldera 94 (Koulakova et al., 2014). The Young Cone is 2741 m in altitude, with a summit crater ~350 m wide. 95 Magmatism at the volcano displays a range of products, typically classified as basalts, 96 basaltic andesites and andesites. The most recent large eruption (VEI=4) occurred in 1945, when 97 about 0.25 km³ of magma was ejected. The volcano has since had small eruptions in 1991 and 2001 98 (Ivanov et al., 1996; Melekestsev et al., 1994b; McGimsev et al. 2004; Viccaro et al. 2012), shaping 99 the modern morphology and fumarolitic activity (Figure 1a). The products of the 1991 effusive

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100 activity generally have basaltic andesite compositions. Lava filled the ~175 m deep 1945 crater 101 before overflowing on the southern and south-eastern flanks of the young cone (Figure 1a). The minor 2001 eruption started on October 5th by a small steam and ash explosion in the summit area 102 (McGimsey et al. 2004). On October 17th, a helicopter observed a new fracture, cutting ESE-WNW 103 104 across the 1991 lava flow that had filled a pre-existing summit crater, and extending another 100-105 150 m down the flank of the cone. Significant fumarolic activity and sulfur deposition was noted at 106 the intersections of the fracture and the edifice (McGimsey et al. 2004). This fumarolic activity is 107 ongoing to this day (Figure 1a). Nataljamalikite occurs in deposits associated with high temperature 108 fumarolic vents along the 2001 fracture (Figures 1a,b), as a minor component in a bright orange, X-109 ray amorphous, As-rich (~20 mole% As) S-rich coating on lava and scoria around the vents.

110 Name and type material

111 The mineral is named for Natalja Alexandrovna Malik (Н.А. Малик) (born 24.03.1981). Dr. 112 Malik graduated at the Kaliningrad State University (specialization geoecology). Since 2004, she 113 has been a researcher at the Institute of Volcanology and Seismology of the Far Eastern Branch of 114 The Russian Academy of Sciences in Petropavlovsk-Kamchatsky, Russia. Her main interests 115 revolve around the study of fumarolic activity, volcanic gases, explosive eruptions, tephra, and ash 116 leachates. She has published 12 publications in peer-reviewed journals (e.g. Moiseenko and Malik, 117 2014; Zelenski et al., 2014). One holotype specimen is deposited in the collections of the Museum 118 Victoria, Melbourne, Australia, catalogue number M53602. The mineral and name have both been 119 approved by the IMA Commission on New Minerals and Mineral Names (IMA2016-022).

120 Physical and optical properties

121 Nataljamalikite occurs most widely as pseudo-cubic nanocrystals ($\leq 0.5 \,\mu$ m) within 122 vacuoles in an As–rich, X-ray amorphous, sulfur–rich matrix (Figure 2a). A few crystals were 123 observed on mascagnite [(NH₄)₂SO₄] balls (Figure 3). Rarely, larger, irregularly shaped aggregates 124 up to ~50 µm in diameter occur in vacuoles or within the S–rich matrix (Figure 2b). In some of

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these aggregates, nataljamalikite appears to be intergrown at μ m scale with an unidentified Tl–As–S mineral. Other associated minerals include barite and rare inclusions of a Re–Cu–bearing phase (1-3 µm in size). The silica associated with the S–(As)–rich crusts contains rare inclusions (~1 µm) of native (Te,Se).

129 Color (macroscopic), streak, luster, hardness, cleavage, fracture and parting could not be 130 observed due to the size of the mineral grains, their scarcity within the samples, and their 131 occurrence in a dark orange, translucent matrix of amorphous arsenian sulfur. The synthetic 132 analogue is yellow, but is photosensitive and blackens readily upon exposure to light. In reflected 133 light, the color is medium grey; internal reflections could not be observed, again because the small 134 grains are embedded in yellow to dark orange arsenian sulfur. Density could not be measured 135 because there is insufficient material available. Density calculated based on the ideal TII formula and the unit cell from the single crystal X-ray data (see below) is 7.23 g \cdot cm⁻³. 136

137 Chemical composition

Analysis of the material is challenging, as a result of the combination of (i) the small size of single crystals; (ii) the composite nature of the larger aggregates; and (iii) the extreme beam sensitivity of both the mineral and the surrounding matrix. We present four analyses (Table 1) from different grains obtained using standard-free analysis on a Tescan Lyra FIB–SEM equipped with an Oxford Instruments Aztec Synergy system X-Max 150 mm² EDS detector. Operating conditions were: no tilt, accelerating voltage 10 kV and beam current 0.5 nA. The empirical formula based on 2 *apfu* is $Tl_{1,00}(I_{0.95}Br_{0.03}Cl_{0.02})$. The theoretical composition has 61.69 wt% Tl and 38.31 wt% I.

145 <u>Room temperature electron backscatter diffraction (EBSD)</u>

There are two well-established polymorphs of TII (Table 2). According to the phase diagram of Brightwell et al. (1983), at ambient pressure the low-temperature orthorhombic modification is stable at <175 °C, and the cubic form with caesium chloride structure is stable at T >175 °C. Note

149 that the cubic form is also thermodynamically stable at high pressure (e.g., above \sim 3 kbar at 20 °C;

150 Samara et al., 1967).

151 We used EBSD (Figure 4) to distinguish between the cubic and orthorhombic forms in the 152 type specimen, in order to verify that the orthorhombic form identified by the single crystal x-ray 153 diffraction study is indeed the polymorph present in the sample at ambient conditions. This is 154 important since the crystal structure was determined at 100 K on a micro-crystal extracted via 155 FIBing. The EBSD measurements were carried out on two different samples at the Monash 156 University Centre of Electron Microscopy, Australia (A); and at the Tescan Russia demonstration 157 laboratory, St. Petersburg, Russia (B). Both samples unambiguously contained the orthorhombic 158 modification (Table 3). While EBSD data could be collected on two grains with the orthorhombic 159 structure at Monash, Tescan Labs identified two grains with a cubic crystal structure alongside two 160 grains with the orthorhombic crystal structure. Table 3 shows the goodness of fit parameters for the 161 four crystals on which good data could be obtained, demonstrating an orthorhombic crystal 162 structure.

163 The following instruments and analytical conditions were used in Melbourne (A) and Moscow (B). (A) Quanta 3DFEG equipped with a 10 mm² SDD EDAX Pegasus detector and a TSL 164 165 Hikari EBSD system. Analytical conditions for EDS mapping were 10 kV accelerating voltage, 166 8 nA beam current. Conditions for EBSD were 20 keV accelerating voltage and 16 nA beam current. Grains were polished using a 5 keV, 2.3 nA Ga⁺ ion beam at a 6° glancing angle to improve 167 168 surface crystallinity and obtain good quality EBSPs. (B) Tescan Lyra 3 GM with Ga ion gun equipped with an Oxford Instruments Aztec Synergy system with X-Max 150 mm² EDS detector 169 170 and a NordlysMax EBSD camera. Analytical conditions for EDS mapping were no tilt, acceleration 171 voltage of 10 kV, and a beam current of 0.5 nA. A protective and conductive Pt layer (ca. thickness 172 100 nm) was applied before milling and polishing for EBSD analysis. FIB milling was done at a tilt 173 -7° to ion gun, at 30 kV for milling and 5 kV for polishing. The EBSD patterns were collected with 174 a tilt of 77° at 20 kV and 0.5 to 1 nA currents.

175 Microsampling

The size of the nataljamalikite aggregates (mostly $<30 \ \mu\text{m}$; Figs. 2,3) and the fact that they are nearly invisible under optical microscopy necessitated an appropriate method to obtain material for crystal structure determination. A 20 x 10 x 2 μm^3 fragment consisting of a fine mixture of nataljamalikite and amorphous arsenian sulfur was cut from a polished section using a focused Ga⁺ ion beam SEM (FIB–SEM), following the method of Ciobanu et al. (2014). The extracted foil (Fig. 2c) was transferred onto a nylon micro-loop for single crystal data collection.

182 Single crystal X-ray study at 100 K

The single-crystal study was carried out at the macromolecular beam line MX2 of the Australian Synchrotron (Table 4). The beam diameter was reduced to 7.5 μ m using a collimator. The location of the measurement spot on the 20 x 10 x 2 μ m³ FIB cut was selected on the basis of EDS spectra; the chosen point shows mainly Tl with little As contamination (the EDS detector has a thick window and is not sensitive to S and I). Data were collected using an ADSC Quantum 315r 2D detector and monochromatic radiation with a wavelength of 0.71086 Å. The crystal was maintained at 100 K in an open-flow nitrogen cryostream.

190 A φ scan was employed with frame widths of 1° and a counting time per frame of 1 s. The 191 intensity data sets were processed using XDSauto and SADABS. Both atoms were found using 192 SHELXS-97 (Sheldrick, 2008), and then refined anisotropically using SHELXL-97 (Sheldrick, 193 2008). The final model converged to $R_1 = 4.01\%$ for 268 reflections with $F_0 > 2\sigma(F)$.

The measured crystal is orthorhombic, space group *Cmcm* with the unit cell parameters: a = 4.5670(9) Å, b = 12.803(3) Å, c = 5.202(1) Å, V = 304.2(1) Å³ and Z = 4 (Table 4). Table 5 shows the calculated powder XRD pattern based on the results of the structure refinement of the natural phase, compared with existing data on the synthetic equivalent from the PDF database.

198 Crystal structure

199 The crystal structure of nataljamalikite has only two atoms in the asymmetrical unit 200 (Table 6; Figure 5). Both atoms occupy a 4c special position $(0, y, \frac{1}{4})$. The structure is considered to 201 be a distorted version of rock salt, where every anion is surrounded by eight cations and has cubic 202 coordination geometry. Thallium and I atoms have similar coordination environments. The full Tl 203 (and I) coordination can be described as 1+4+2, where Tl atoms are coordinated by 4 iodide at 204 \sim 3.4819(18) Å in a slightly out-of-plane square planar configuration, with one additional iodide ion 205 at 3.3067(15) Å in an axial position. The opposite axial position is occupied by the Tl(I) lone 206 electron pair (Brugger et al., 2016), and two more distant iodine atoms (3.846 Å) located on the 207 same side as the Tl lone pair are weakly but significantly bonded. The Tl-Tl distance is 208 3.7603(12) Å. Slight corrugation of the Tl-I layers lying || (040) causes the shortest interlayer 209 distances I...I to be 4.340 Å, while Tl...Tl distances are rather short at 3.760 Å, implying that there are attractive dipole-dipole interactions between lone pairs across the interlayer. This structure is 210 211 also formed by NaCl and NaBr at very high pressures (~30 GPa), with short dipole...dipole 212 interactions between the large, polarizable anions (Léger et al., 1998). Isopuntal compounds such as 213 CrB can have much stronger bonding interactions between like atoms across the "interlayer" (zigzag B-B chains with B-B = 1.74 Å (Kiessling 1949). 214

215 Relation to other species

216 Nataljamalikite is chemically related to lafossaite Tl(Cl,Br) (*Pm*-3m; a = 3.8756(3) Å, V = 58.213(8) Å³ and Z = 1) from Vulcano, Italy (Roberts et al., 2006). Both minerals form from 217 218 high temperature fumaroles on active volcanoes. The limited incorporation of I in lafossaite and of 219 Cl in nataljamalikiite (Table 1) reflects the large difference in size between the anions, with the 220 crystal structure of nataljamalikite favoring the large iodide ion. Note that a thallium chloride phase 221 was identified on the basis of qualitative EDS analyses as equant inclusions $1-12 \,\mu\text{m}$ in diameter 222 within polycrystalline diamonds from the Udachnaya kimberlite pipe (Yakutia, Russia), together 223 with Cr spinel, native iron, native chromium, native copper, and native tantalum (Gorshkov et al.,

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224	1998). The other known thallium halide minerals are steropesite, Tl_3BiCl_6 (<i>Cc</i> ; $a = 26.686(5)$ Å,
225	$b = 15.127(3)$ Å, $c = 13.014(3)$ Å, $\beta = 108.11(2)^{\circ}$ and $V = 4993(2)$ Å ³ ; Demartin et al., 2009), and
226	hephaistosite, TlPb ₂ Cl ₅ (<i>P</i> 2 ₁ /c; $a = 8.9477(6)$ Å, $b = 7.9218(7)$ Å, $c = 12.4955(5)$ Å, $\beta = 90.092(4)^{\circ}$
227	and $V = 885.70(7) \text{ Å}^3$; Campostrini et al. 2008) both from the high temperature fumaroles from
228	Vulcano, Italy; and chrysothallite, $K_6Cu_6Tl^{III}Cl_{17}(OH)_4 \cdot H_2O$ (<i>I4/mmm</i> , <i>a</i> = 11.3689(7) Å,
229	c = 26.207(2) Å, $V = 3387.3(4)$ Å ³) from the Second scoria cone of the Northern Breakthrough of
230	the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia; the latter mineral
231	contains Tl(III) rather than Tl(I), and results from interactions involving high-temperature sublimate
232	minerals, fumarolic gas and atmospheric water vapor at temperatures ≤ 150 °C (Pekov et al. 2015).

233 Thallium concentrations in fumarolitic vapors

234 Thallium is a volatile element in high temperature magmatic hydrothermal systems (Henley and 235 Berger, 2013). Table 7 shows the measured Tl concentrations reported from a number of 236 geothermal waters and fumarolitic vapors, compared to the other volatile metals Cd and Pb, as well 237 as to Rb (Rb(I) has the same ionic radius as Tl(I), i.e. 1.61 vs 1.59 Å in 8-fold coordination; 238 Shannon 1976). Many localities show measurable Tl concentrations <20 ppb; concentrations above 239 100 ppb are rare, and were reported from single samples from Kudryavy Volcano (Kuril Islands; 240 140 ppb) and Mutnovsky volcano (Kamchatka; 110 ppb). Recently, the vapors emitted from the 241 2012–2013 Tolbachik eruption were shown to contain an order of magnitude more Tl (1,470-242 1,700 ppb) than geothermal waters and fumarole fluids by two independent studies (Zelenski et al., 243 2014; Chaplygin et al. 2016). There is no correlation amongst the Tl and Rb concentrations reported 244 in Table 7, but high Pb and Cd contents generally correspond to high Tl contents.

Fumarole gases from the Avacha volcano were sampled by placing 20 mm diameter quartz tubes in the fumaroles. The tube was connected by a hose made of silicone rubber to two bubblers cooled using a snow-water mixture and connected in series (Fig. 1b). The line was connected to an electric pump, operated at a rate of 1 liter/min (see Fig. 3 in Zelenski et al., 2014). The condensates

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were analyzed by ICP-MS and ICP-AES for trace elements. The chemical analyses of the vaporsfrom the Avacha volcano are shown in Table 8.

The low temperature, crystalline-sulfur-depositing fluids (≤ 100 °C) are unusually enriched in Tl (up to 782 ppb). They are also rich in Cd (up to 8,230 ppb), compared to exhalations from other volcanoes (Table 7; up to 660 ppb). This unusual enrichment is magnified in the high temperature vapor (600 °C) condensate, which contains an astonishing 34 ppm Tl, as well as 240 ppm Cd. Iodine was not measured, but the bromine concentration reaches 5 ppm. Other metals (or metalloids) that are highly enriched in this vapor include As, Rb, Ag, In, Sn, Sb, Cs, Mo and Bi (Table 8).

258 Discussion

The formation of nataljamalikite and other Tl minerals associated with the degassing of arc volcanoes reflects the extreme fractionation of Tl during magmatic–hydrothermal processes. Thallium minerals have now been described from rhyolitic (Vulcano, Italy; Campostrini et al. 2008; Cheynet et al., 2000; Demartin et al., 2009; Roberts et al., 2006), andesitic (Avacha; this study) and

263 (alkali) basaltic (Tolbachik, Kamchatka, Russia; Pekov et al. 2015; Siidra et al., 2014a,b,c; Zelenski

et al., 2014) volcanoes. In this discussion we first succinctly review the main processes that cause

265 Tl fractionation and enrichment to levels where minerals containing Tl as an essential element form,

and then discuss the origin of nataljamalikite in light of this information.

267 <u>Processes of thallium enrichment and mineralization – a review</u>

268 Christy (2015) found that 40 out of 70 considered chemical elements displayed a good positive 269 correlation between the crustal abundance of the element and the number of mineral species in 270 which that element is an essential constituent. One of the elements that shows the most dramatic 271 deviation from this trend is Rb, which is hidden in substitution for K, and hence is an essential 272 constituent in only a handful of minerals. Given the similarity of charge and radii between the Tl(I) 273 and Rb(I) ions (1.59 vs. 1.61 Å; Shannon 1976), one may expect a poor diversity of Tl minerals;

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274 nevertheless, Tl is one of the 40 elements that follow the main trend defined by Christy (2015). 275 However, thallium chemistry is more complex than that of Rb (multiple oxidation states; 276 stereochemically active lone pair for the most common oxidation state, Tl(I); chalcophile and 277 lithophile characters), and extreme enrichment of Tl occurs in many environments (Fig. 6) as a 278 result of a number of different processes, making Tl geochemistry rather unique (Hettmann et al., 279 2014), and leading to concentrations of Tl at levels sufficient for it to become an essential 280 component in minerals. Thus, Tl is an example of an element where factors that encourage 281 geochemical dispersal and a low number of species are compensated by factors that would normally 282 generate a superabundance of species (Christy, 2015), leading to the apparent "normal trend" 283 behavior that is observed. To date >65 minerals with Tl as an essential component have been 284 described, compared to just 3 Rb minerals, despite the low crustal abundance of Tl (550 ppb) 285 compared to Rb (90 ppm).

286 The key processes involved in enriching Tl are (see also Fig. 6):

(1) Magma Incompatibility. The solar system abundance of Tl is 142 ppb (Anders and Grevese, 287 288 1989), yet mantle abundance is only \sim 3 ppb. This strong mantle depletion is primarily due to the 289 volatile nature of TI; volatile elements are depleted in the Earth and other rocky planets due to the 290 high temperature and violent processes active during planetary growth (e.g., O'Neill and Palme, 291 2008). However, Tl behaves as a highly incompatible element in silicate magmatic systems (Shaw, 292 1952), and so a component of the mantle depletion reflects its partitioning into the crust. Thallium 293 concentrations increase via magmatic differentiation, reaching 100's of ppb in the continental crust. 294 Extreme Tl enrichment via magmatic differentiation occurs in some highly evolved magmatic 295 systems, most notably peralkaline magmatism (e.g., Lovozero and Khibina massifs, Kola Peninsula, 296 Russia; Ilimaussaq, Greenland), where late magmatic activity results in widespread formation of Tl-297 rich sulfide assemblages (Hettmann et al., 2014; Pekov and Agakhanov, 2009).

(2) Hydrothermal transport and deposition. Thallium exhibits both lithophile and chalcophile
behaviors; as a chalcophile element, it forms numerous hydrothermal sulfide and sulfosalt minerals.

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300 Thallium is transported as chloride complexes (Bebie et al., 1998) and possibly bisulfide complexes 301 (Xiong, 2007) in hydrothermal fluids (Brugger et al., 2016), and large Tl concentrations are 302 associated with hydrothermal, sulfide-rich deposits. Thallium is recovered primarily as a by-product 303 of Zn smelting (thallium sits within the sphalerite structure; Xiong, 2007), but only a few 304 hydrothermal Zn deposits contain Tl-bearing minerals (e.g., Wiesloch, Germany; Seeliger, 1963). 305 Spectacular Tl enrichment associated with a complex mineralogy are found in some As-rich 306 volcanogenic hydrothermal deposits (e.g., Allchar, Macedonia; Amthauer et al., 2012; Jankovic and 307 Jelenkovic, 1994; Volkova et al. 2006) and in Carlin-type gold deposits in Nevada, USA (Large et 308 al., 2011; Muntean et al., 2011). Scale deposits in boreholes and hot spring deposits from active 309 geothermal fields provide a modern analog for such hydrothermal Tl enrichment, as they contain up 310 to 1000 ppm Tl (Weissberg, 1996). Note that these enrichments do not require highly enriched 311 fluids; for example the Champagne Pool sediments in New Zealand contain >300 ppm Tl (Weissberg, 1996), but the waters carry only 27 ppt Tl (Pope et al. 2004). At Vulcano, Italy, 312 313 fumarolitic fluids carry 14-82 ppb Tl (Table 7; Cheynet et al. 2000), but altered rocks around the 314 fumaroles carry more than three orders of magnitude more Tl (up to 280 ppm Tl; Boyce et al. 2007; 315 Fulignati and Sbrana 1998). This highlights the importance of deposition mechanisms in controlling 316 Tl enrichment (e.g., evaporation; coprecipitation or sorption – see also process (3)).

317 (3) Sorption and oxidation. Nielsen et al. (2006b) used chemical and isotopic mass balance 318 calculations to estimate the hydrothermal flux of Tl from oceanic crust into oceans at $\sim 0.72 \times 10^{13}$ kg/yr from high temperature fluids, and $(0.2-5.4) \times 10^{17}$ kg/yr from low temperature 319 320 fluid seepage at ridge flanks. Much of this Tl is retained in oceanic sediments (34 ppm Tl in ridge 321 sediments), with extreme enrichments (150 ppm on average) in ferromanganese nodules (Fig. 6). 322 Thallium(I) is the only oxidation state relevant for magmatic and hydrothermal processes, but 323 Peacock and Moon (2012) showed that Tl(I) species are oxidized to insoluble Tl(III) following 324 sorption onto hexagonal birnessite. The magnitude of this process and the association with a strong 325 isotopic fractionation compared to magmatic and hydrothermal processes make thallium a

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diagnostic element for deep marine sediments, to such an extent that addition of minor amounts of
 Mn-rich crusts into the mantle can explain the pronounced thallium-isotope variations recorded in
 ocean-island basalts (Nielsen et al., 2006a,b).

329 (4) Low melting point assemblages. Partial melting of sulfide ores can generate melts that are 330 highly enriched in low melting point chalcophile (LMPC) elements and precious metals such as Tl, 331 As, Sb, Bi, Te, Pb, Ag and Au (Frost et al., 2002; Tomkins et al., 2007); upon cooling these melts 332 can crystallize a number of unusual sulfosalt minerals, including many Tl minerals (Frost et al., 2002; Tomkins and Mavrogenes, 2002). LMPC melts can also precipitate directly from 333 334 hydrothermal fluids via reaction mechanisms such as fluid-rock interaction (Tooth et al., 2008, 2011). An important part of the melting and fractional cooling process is that a series of steps 335 336 results in progressive enrichment of the elements with greatest tendency to stay in the lowest 337 temperature sulfosalt melts, of which Tl may have the most pronounced proclivity: melts persist to 338 <275 °C along the Tl₂S-As₂S₃ joint, for example (Tomkins et al. 2004). Well-studied examples of 339 partial melting leading to extreme local enrichment in Tl include sediment-hosted base metal 340 deposits such as the Lengenbach Pb-Zn-As-Tl-Ba deposit, Switzerland (Hofmann and Knill, 341 1996); Jas Roux, French Alps (Johan and Mantienne, 2000); and the Monte Arsiccio mine (Alpi 342 Apuane, Tuscany, Italy) (Biagioni et al., 2013); as well as the shear-hosted Hemlo gold deposit, 343 Canada (Harris, 1989; Tomkins et al., 2004).

344 (5) Volatile. As mentioned above, it is well known that Tl and Cd are volatile, being discharged in 345 high temperatures magmatic vapors (Henley and Berger, 2013). This behavior was confirmed 346 experimentally by Johnson and Canil (2011). Baker et al. (2009) estimated the Tl flux from subaerial volcanoes at $(6.9 \pm 4.7) \times 10^5$ kg/yr. The composition of the fumaroles from Avacha 347 348 (34 ppm Tl), and of the magmatic vapors (>1000 °C) from the 2012-13 Tolbachik eruption 349 (~1500 ppm Tl) highlight the fact that vapor partitioning itself can lead to the formation of highly 350 enriched fluids, which may become supersaturated with Tl via cooling, fluid mixing, or fluid-rock 351 interaction.

352 Formation of nataljamalikite

Nataljamalikite is defined as the orthorhombic form of TII. Given the melting point of TII (442 °C) and arsenic sulfides (<321 °C), and the high temperature deposition in the fumarolic environment (~600 °C), it is possible that droplets of Tl-, As- and halogen-rich liquid were first condensed from vapor (Mavrogenes et al., 2010), before crystallization of the cubic polymorph of nataljamalikite (Figure 2a) and associated minerals upon cooling. On the other hand, the rare occurrence of nataljamalikite on mascagnite (Fig. 3) suggests that, at least for this sample, the condensation temperature was less than 400 °C and perhaps even as low as 250 °C.

360 The observation of the pseudo-cubic morphology of most nataljamalikite crystals supports initial crystallization of the high-temperature cubic polymorph, the present predominant 361 362 orthorhombic structure resulting from phase transformation after cooling below 175 °C. Under 363 laboratory conditions, the high temperature, cubic polymorph usually transforms rapidly into the 364 orthorhombic form upon cooling. However, Brightwell et al. (1983) found that the quenching properties of pure cubic TII are dependent upon the crystal's thermal history: "attempts to quench in 365 366 the high temperature form of TII by rapid cooling to -196 °C failed, but it was found that after repeated runs in the differential scanning calorimeter, TlI showed a sharp transition at 175 °C; 367 368 after thermal soaking at 200 °C, in order to eliminate completely the low temperature form, the reverse transition did not occur during cooling, at a rate of 8 K min⁻¹, to room temperature. The 369 370 high temperature red form then took several weeks to undergo a complete transition to the vellow 371 form at room temperature". The coexistence of the orthorhombic and cubic modifications of TII can 372 be explained three-ways: (i) the addition of minor amounts of elements such as Br and Ag have 373 been shown to extend the stability of the cubic form (Brightwell et al., 1983); (ii) the cubic form can 374 also be synthesized at low temperature (<15 °C) via vapor deposition on amorphous surfaces 375 (Blackman and Khan, 1960); (iii) slow transformation of the cubic to orthorhombic forms after the 376 samples were collected.

Nataljamalikite

377 As illustrated in Figure 2a, many vacuoles in the amorphous S-rich matrix contain nano-378 crystals of nataljamalikite. This is suggestive of direct condensation of the nataljamalikite precursor 379 phase from the vapor. A simple mass balance calculation suggests that the size and distribution of 380 the nataliamalikite nanocrystals are consistent with the measured Tl concentrations in the vapor 381 (34 ppm): a 10 nm nataljamalikite crystal can form from the vapor contained within a 6 µm radius 382 bubble. The observed radii of the vapor bubbles are mostly between 4 and 5 μ m, and many contain 383 10–50 nm nataljamalikite crystals. The larger crystals (exceptionally up to nearly one μ m in size) 384 most likely reflect the difficulty of nucleating nataljamalikite – i.e. a nataljamalikite crystal will not 385 nucleate in every vacuole.

386 Origin of the Tl-rich fumarolitic fluids

387 The enrichment of Tl to 10-100 ppb levels in gases resulting from the shallow degassing of 388 magmas has been recognized for a long time (e.g., Fulignati and Sbrana 1998; Table 7). However, 389 the 2012-13 basaltic Tolbachik eruption provided the first evidence for extreme Tl enrichment in 390 Cl-rich magmatic vapors (to ~1.5-2.0 ppm; Chaplygin et al. 2016; Zelenski et al. 2014; Table 7). 391 Avacha represents a new example of extreme Tl enrichment in gasses from degassing magmas. 392 Even the low temperatures funarolitic fluids display record Tl contents (to 782 ppb), with the 393 condensates from high temperature fumaroles containing 34 ppm Tl. At least some of the 394 nataljamalikite crystals clearly formed directly from the vapor during cooling (Fig. 2a). Deeper 395 within the fumarolic system, repeated periods of greater and lesser vapor flux would promote 396 refinement of element distribution. The more volatile elements like Tl and As would be 397 concentrated at higher levels in the system; hence, deposition of LMPC assemblages (As-Se-Te-Tl-398 Bi-(Pb)) at shallow depth is likely. The precious metals (Ag, Au, Re) would be concentrated at the 399 first appearance of liquid sulfosalts (Tooth et al. 2011). We suggest that interaction between the 400 liquid sulfosalts (containing wt% levels of Tl) and magmatic vapors can explain the extremely high 401 Tl concentrations in the high-T fumaroles at Avacha.

402 Implications

The determination of the nataljamalikite structure in this study demonstrates the value of combining FIB–SEM techniques for *in-situ* extraction of small volumes of well-characterized material from the surface of a polished section for single crystal X-ray analysis using synchrotron radiation, in combination with SEM-based EBSD to provide some statistics on the nature of the grains affected by potential polymorphism.

The formation of Tl minerals such as nataljamalikite from active fumaroles provides a vivid illustration of the role of subduction and arc-related volcanism as "Nature's refineries" (Henley and Berger, 2013) (Fig. 6). The mechanisms that result in enrichment of Tl by 4 orders of magnitude from the mantle source (3 ppb) to a magmatic vapor (33 ppm) are complex, involving hydrothermal leaching of Tl(I), concentration via oxidation to immobile Tl(III) on the surface of deep-sea Mn minerals, partial melting of the Tl-rich subducted source, and complex vapor-liquid sulfosalt-fluidsolid equilibria during the fumarolitic stage of the volcanic eruption.

415 The high temperature fumarolitic fluids from Avacha not only contain >400 times more Tl 416 than the Vulcano fumaroles (that also deposit Tl minerals), they are also highly enriched in As, Sb, 417 Cd, Re and Te (Table 8). The processes that led to the formation of nataljamalikite illustrate the 418 ability of low-density vapors to carry significant amounts of metals (e.g. Hurtig and Williams-419 Jones, 2015), and also provide an insight into the processes that can lead to the formation of fluids 420 with extreme metal contents. In this case, we hypothesize that the interaction between vapors and 421 melts was the main factor at work: (1) at a shallow depth (vapor stable) in the geothermal system 422 below the Avacha volcanic edifice, sulfosalt melts rich in As, Se, Te and Tl interact with vapor and 423 enrich it in these elements. A vertically extensive (from summit at 2741 m to -1000 m altitude) 424 geothermal reservoir characterized by mixing of magmatic water and volatiles with surface waters 425 (glacier melting) has been delineated on the basis of seismicity underneath the Avacha volcano 426 (Kiryukhin et al. 2015). (2) Cooling of Tl-rich vapor bubbles near the surface allows direct 427 condensation of TII, either as melt droplets or as the cubic form of TII. These eventually convert to

428 nataljamalikiite on cooling. This is in contrast to the occurrence of Tl minerals at Vulcano, for 429 example, where the fumarolitic fluids do not display extreme enrichment in Tl, and Tl is 430 concentrated via depositional processes to levels conducive to the formation of Tl minerals. The 431 processes that result in extreme enrichment of Tl (and other volatile metals and semi-metals) in 432 vapors are obviously transient and rarely preserved; however, these processes may be important in 433 controlling the distribution of these metals in vapor-dominated epithermal systems.

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- 673 Tables
- 674
- 675
- Table 1. Analytical data (in wt%) for nataljamalikite (n=4), compared to Lafossaite.

Constituent Mean		Range	SD	Lafossaite ^{††}
T1	61.40	61.07-62.01	0.4	81.74(1.49)
Ι	36.00	32.65-37.33	2.2	
Br	0.65*			5.99(0.28)
Cl	0.21*			10.79(0.57)
As^		0.64-1.42		
Al^		0.76, 0.91		
Si^	1.00*			
Total	98.30 [†]	100.0-101.1		

- 677 * Detected in a single point.
- 678 † taking into account only structural elements.
- 679 *†*† from Roberts et al. (2006).
- 680 ^ Contamination from matrix.
- 681 682

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Table 2. Unit cell data for polymorphs of TII.

Orthorhombic, 'yellow form', 'Lt'; Helmholz (1937)	T < 175°C	orthorhombic	Стст	$a = 4.57(2) \text{ Å,} b = 12.92(1) \text{ Å and} c = 5.24(2) \text{ Å;} 309(3) \text{ Å}^3$
Caesium chloride, 'red form'; Samara et al. (1967)	T > 175°C	cubic	Pm-3m	a = 4.2099(3) Å (at 20°C, extrapolated from measurements 150-295°C)
Cubic, 'Ht', Shamovskii and Shushkanov (1968) – <i>in</i> <i>error</i> ?	T > 175°C	cubic	Fm-3m	<i>a</i> = 6.94 Å
Caesium chloride-type, 'red form'; Blackman and Khan, (1960)*	≤15 °C*	cubic	Pm-3m	<i>a</i> = 4.205 Å (15 °C)

684 * vapor deposited on amorphous base.

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Nataljamalikite	Page 28
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- 691
- 692 Table 3. Summary of EBSD Mean Angle Deviation (MAD) for nataljamalikite (orthorhombic,
- 693 CMCM; structure from Helmholz 1937).

Grain# / Instrument	1 / A	2 / A	3 / B	4 / B
MAD [°]	0.9	0.49	0.31	0.58

⁶⁹⁴ Instrument: (A) Quanta 3DFEG equipped with a 10 mm² SDD EDAX Pegasus detector. (B) Tescan

696 Max 150 mm² EDS detector. See text for details.

⁶⁹⁵ Lyra 3 GM with Ga ion gun equipped with an Oxford Instruments Aztec Synergy system with X-

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698 Table 4. Data collection and structure refinement details for nataljamalikite.

Diffractometer	ADSC Quantum 315r detector
Radiation	synchrotron ($\lambda = 0.71086$ Å)
Temperature	100(2) K
Structural Formula	TII
Space group	Стст
Unit cell dimensions	a = 4.5670(9) Å
	b = 12.803(3) Å
	c = 5.202(1) Å
V	304.2(1) Å ³
Ζ	4
Absorption coefficient	62.9 mm ⁻¹
<i>F</i> (000)	536
θ range	3.18 to 29.99°
Index ranges	$-6 \le h \le 6, -17 \le k \le 17, -7 \le l \le 7$
Refls collected / unique	$2869 / 272; R_{\text{int}} = 0.056$
Reflections with $F > 2\sigma(F)$	268
Refinement method	Full-matrix least-squares on F^2
Parameters refined	10
GoF	1.227
Final <i>R</i> indices $[F_o > 2\sigma(F)]$	$R_1 = 0.0401, wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.0410, wR_2 = 0.0894$
Largest diff. peak / hole	+6.37 / -2.42 <i>e</i> /A ³
$\overline{R_{\text{int}}} = \Sigma F_{\text{o}}^2 - F_{\text{o}}^2(\text{mean}) / \Sigma [F_{\text{o}}]$	$\int_{0}^{2} [. \text{GoF} = S = \{ \Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] / (n - p) \}^{1/2} . R_{1} = \Sigma F_{0} - F_{c} / \Sigma F_{0} .$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2 - F_c^2)^2] \}$	$[F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0, b is
394.6636 and <i>P</i> is $[2F_c^2 + M_c^2]$	$ax(F_{o}^{2},0)]/3.$
	Diffractometer Radiation Temperature Structural Formula Space group Unit cell dimensions V Z Absorption coefficient F(000) θ range Index ranges Refls collected / unique Reflections with $F > 2\sigma(F)$ Refinement method Parameters refined GoF Final R indices $[F_0 > 2\sigma(F)]$ R indices (all data) Largest diff. peak / hole $*R_{int} = \Sigma F_0^2 - F_0^2(mean) / \Sigma [F_0]$ $wR_2 = {\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(G_0^2 - F_c^2)^2] / \Sigma[w(G_$

Page 30

726	Table 5. Powder diffraction data for nataljamalikite calculated from the crystal structure, compared
727	to PDF#74-1056.

	Calculated from the crystal structure				PDF#74-1056		
	refinement (CrystalDiffract6).				Cell $a=5.24$ Å: $b=4.57$ Å:		
					<i>c</i> =12.92 Å		
h	k	l	d _{calc} [Å]	I/I _{max}	d _{meas} [Å] I/I _{max}		
0	2	0	6.40	2.3	6.46 2.4		
1	1	0	4.30	10.8	4.31 8.6		
0	2	1	4.04	8.1	4.07 6.6		
1	1	1	3.31	100.0	3.33 100		
0	4	0	3.20	43.0	3.23 44.3		
1	3	0	3.12	0.4	3.13 0.4		
0	4	1	2.726	9.6	2.749 7		
1	3	1	2.674	73.1	2.689 69.5		
0	0	2	2.601	28.1	2.620 26.9		
0	2	2	2.410	0.4	2.427 0.3		
2	0	0	2.284	18.8	2.285 17.3		
1	5	0	2.234	6.9	2.249 5		
1	1	2	2.226	3.9	2.238 3.2		
2	2	0	2.151	0.3	2.153 1.1		
$\tilde{0}$	6	Ő	2.131	1.0	2.105 1.1		
1	5	1	2.151	11.0	2 067 11 9		
1	0	1	2.032	11.1	2 034 20 5		
0	4	2	2 019	21.4	2.031 20.3		
1	3	$\frac{2}{2}$	1 997	0.2	1 992 2		
2	2	1	1 988	0.2 2 4	1.772 2		
$\frac{2}{2}$	4	0	1.859	16.1	1 865 14 9		
$\frac{2}{2}$	4	1	1.055	4.6	1 757 2 9		
$\frac{2}{2}$	0	2	1.751	14.0	1 722 12 6		
2	U	2	1./10	17.2	1 711 1 8		
					1.711 1.0		
1	7	0	1 698	21	1.686 0.5		
1	5	2	1.694	2.1 5 <i>A</i>	1.000 0.5		
0	2	2	1.674	0.7	1663 0.8		
2	$\frac{2}{2}$	2	1.677	0.7	1.605 0.6		
1	27	1	1.61/	12.6	1.618 0.5		
1	1	3	1.014	12.0	1.615 7.7		
0	1 Q	0	1.008	10.0	1.015 7.7		
2	6	0	1.000	2.7	1567 05		
2 0	8	1	1.539	0.7	1.507 $0.51.542$ 2.1		
0	0	1	1.530	4.0	1.545 5.1		
1	4	2	1.525	1.4	1.550 1.1		
1 2	5 1	3 7	1.515	10.7	1.517 14		
2 2	4	∠ 1	1.312	14.9 67	1.301 0.3 1.452 5.7		
5	1 7	1	1.432	0./	1.435 5./		
1	2	2 1	1.422	2.1	1.432 1.3		
5	5	1	1.382	1.3	1.585 0.5		
	2	5	1.3/0	2.5	1.3/9 2.9		
U	8	2	1.363	2.8	1.3/4 3.3		

730

Table 6. Atom coordinates and displacement parameters $(Å^2)$ for nataljamalikite.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}
T1	0.50	0.60605(6)	0.75	0.0200(5)	0.0173(5)	0.0190(5)
Ι	0.50	0.86433(9)	0.75	0.0167(6)	0.0148(6)	0.0172(6)

732 Note: U_{23} , U_{13} , U_{12} set to zero (site symmetry constraint).

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735	Table 7.	Concentrations	of	thallium	and	а	few	geochemically	related	elements	in	selected
736	geotherm	al waters and fur	mar	olic gas co	onden	sat	tes.					

Sample description	Temperature [°C]	Tl [ppb]	Rb [ppb]	Pb [ppb]	Cd [ppb]	Reference
Seawater	2	0.014	120	0.0021	0.067	Li (1991)
East Pacific Rise vent fluids	~350	6.5	n/a	63.8	9	Hannington et
(average)						al. (2016)
Deep Chloride Waters from	195-320	0.4 to 15	n/a	<0.1 to	<0.1 to	Simmons et al.
wells, New Zealand				808	13.3	(2016)
Ohaki hydrothermal pool,	95	0.3	n/a	n/a	n/a	Weissberg
New Zealand						(1969)
Broadlands drill core 2,	294 (max)	7	n/a	n/a	n/a	Weissberg
New Zealand						(1969)
Champagne Pool, New	75	0.027	1170	< 0.1	< 0.029	Pope et al.
Zealand						(2004)
Iceland geothermal aquifers	30 to 298	0.001-15	0.3 to	<0.01 to	< 0.002	Kaasalainen et
			3,770	0.38	to 0.8	al. (2015)
Reykjanes geothermal	285	9.0	3,770	< 0.1	0.38	Kaasalainen et
aquifer, Iceland						al. (2015)
Reykjanes geothermal	279 to 314 (n=6)	8.2-12.1	n/a	124 to	38 to 491	Hannington et
aquifer, Iceland				1,991		al. (2016)
Kudryavy Volcano, Iturup,	1060 to 1070	140	n/a	1,250	230	Churakov et
Kuril Islands						al. (2000)
Kudryavy Volcano, Iturup,	870	65	n/a	580	5500	Taran et al.
Kuril Islands						(1995)
Fumaroles at La Fossa	560	82	n/a	1,000	5	Cheynet et al.
crater, Vulcano (June 1993)	428	14		2,000	12	(2000)
	494	16		3,200	117	
Tolbachik volcano,	1060 to 1070	1,700	1,000	740	660	Zelenski et al.
Kamchatka (2012-3		(400)*	(200)*	(170)*	(100)*	(2014)
eruption)						
Tolbachik volcano,	1030	1470	1,700	940	436	Chaplygin et
Kamchatka (2012-3						al. (2016)
eruption)						
Mutnovsky volcano,	480	110	1	140	32	Zelenski and
Kamchatka	507	98	3	130	25	Bortnikova
	410	31	3	25	7	(2005)†
	450	36	3	40	11	
Kizimen Volcano,	210 to 215	2.9	9.1	14	3.9	Measured for
Kamchatka ^{††}						this study ^{††}
Colima volcano, Mexico	742	24	n/a	451	55	Taran et al.
	828	53		78	740	(2001)
	738	34		480	45	
Kawah Ijen volcano,	Up to >450	22	n/a	60	15.1	Berlo et al.
Indonesia						(2014)

737 *means of 14 samples and standard deviation.

⁷³⁸ † also provide I and Br concentration: 0.35/1.1/1.1/1.7 ppm I; 3.8/3.7/4.0/6.0 ppm Br.

†† The last major eruption of the Kizimen volcano was in 2010-2011, producing >0.5 km³ of
 andesitic lava (Dvigalo et al. 2013). The condensate was collected at 2280 m, 11-12 October 2014;

sampling and analysis conditions similar to those of the Avacha sample. The vapor contains

742 3.30 wt% S, 0.57 wt% Cl, and 3.32 ppm Br.

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Table 8. Chemical analyses of condensates from Avacha fumaroles collected in May 2016. Samples AC-5 and AC-4 are from low temperature gas condensates (T \sim 100 °C) associated with native sulfur deposition, and sample AC-1 was taken from the same fumarole that deposits nataljamalikite;

			.	
747	vapor temperativ	ature was	~600 °C	(Fig. 1b).

		AC-5	AC-4	AC-1
Element	DL, ppb	ppb	ppb	ppb
S	533	9,917,342	9,958,559	11,596,551
Na	184	< DL	1,357	5,687
Mg	122	< DL	425	440
Al	30	171	254	1118
Si	128	5,469	5,111	22,258
Р	463	< DL	< DL	< DL
Κ	94	$< \Pi O$	< 110	4678
Ca	583	2,635	2,393	3,461
Mn	3	< DL	4.1	25.3
Fe	144	< DL	< DL	667
В	16	235	1,859	62,065
As	2	< DL	< DL	2,854
Br	331	< DL	< DL	5,154
Tl	14	211	782	33,836
Se	10	< DL	< DL	149
Sr	2	< DL	< DL	7.6
Ba	3	104	105	1,319
Hg	0.4	1.5	< DL	18.3
Pb	1	28.7	11.7	464
Li	182	< DL	1019	2310
Rb	236	< DL	< DL	14,651
Zr	166	783	848	11,569
Ag	734	1628	869	1,218
Zn	21	28.2	< DL	124
Cd	172	4,000	8,230	240,168
In	117	< DL	< DL	4,002
Sn	818	< DL	< DL	69,662
Sb	212	< DL	< DL	65,114
Te	225	532	420	15,866
Cs	33	< DL	56.0	8,239
Hf	50	< DL	< DL	610
W	138	304	1,065	< DL
Mo	293	628	667	2,795
Re	15	< DL	< DL	576
Pt	34	< DL	< 91	508
Au	41	371	< 100	< DL
Bi	25	144	92.3	5,131
U	28	< DL	< DL	45.5

 $\begin{array}{ll} \hline 748 & \underline{Notes:} \ DL = detection \ limits. \ The \ following \ elements \ were \ below \ DL \ in \ all \ three \ samples: \\ \hline 749 & Sc < 2 \ ppb; \ Ti < 24 \ ppb; \ V < 3 \ ppb; \ Cr < 27 \ ppb; \ Co < 4 \ ppb; \ Ni < 7 \ ppb; \ Cu < 11 \ ppb; \ Ga < 2 \ ppb; \\ \hline 750 & Ge < 2 \ ppb; \ Be < 206 \ ppb; \ Y < 193 \ ppb; \ Nb < 151 \ ppb; \ Ru < 106 \ ppb; \ Rh < 145 \ ppb; \\ \hline 751 & Pd < 156 \ ppb; \ La < 102 \ ppb; \ Ce < 29 \ ppb; \ Pr < 26 \ ppb; \ Nd < 77 \ ppb; \ Sm < 51 \ ppb; \ Eu < 21 \ ppb; \\ \hline 752 & Gd < 19 \ ppb; \ Tb < 10 \ ppb; \ Dy < 19 \ ppb; \ Ho < 8 \ ppb; \ Ho < 8 \ ppb; \ Er < 50 \ ppb; \ Tm < 5 \ ppb; \\ \hline 753 & Yb < 25 \ ppb; \ Lu < 4 \ ppb; \ Ta < 44 \ ppb; \ Os < 23 \ ppb; \ Ir < 13 \ ppb; \ Th < 32 \ ppb. \\ \end{array}$

755 Figure captions

754

155	rigure captions
756 757	Figure 1. The occurrence of nataljamalikite at the Avacha Volcano, Kamchatka, Russia. (a) Aerial
758	view of the somma and associated fumarole field. The 1991 lava flow fills the summit crater and
759	spills over the south-southwest rim. The 2001 fracture, steaming profusely at both ends, cuts across
760	the surface of the 1991 lava flow (McGimsey et al. 2004). (b) Close view of the sample locations.
761	Nataljamalikite was found both in natural sublimates near high-T fumaroles and in quartz tubes
762	places within the hosted fumaroles.
763	
764	Figure 2. SEM images showing the occurrence of nataljamalikite in the natural fumarole deposits at
765	Avacha. (a) High resolution image of an unpolished sample, showing occurrence of pseudo-cubic
766	nanocrystals of nataljamalikite within vacuoles in an As-(Te)-rich sulfur matrix. Secondary electron
767	mode, 10 keV. (b) Rare larger aggregates of nataljamalikite within the arsenian sulfur matrix. Back-
768	scattered electron image, 25 keV. (c) FIB composite nataljamalikite/matrix fragment used for the
769	single crystal analysis, mounted on tungsten needle (ion image).
770	
771	Figure 3. Nataljamalikite grains on mascagnite, (NH ₄) ₂ SO ₄ .
772	
773	Figure 4. Example EBSD patterns. (a) raw pattern, (b) indexed pattern.
774	
775	Figure 5. The crystal structure of nataljamalikite. Thallium(I) in green, and I(-I) in purple. Thallium
776	atoms are coordinated by 4 iodide ions at 3.4819(18) Å in slightly out-of-plane square planar
777	configuration (rendered solid bonds), with one additional iodide ion at 3.3067(15) Å in axial

position (rendered stripped bonds); the opposite axial position being occupied by the thallium(I)

- 1779 lone electron pair, with two weakly bonded iodide ions at 3.846(2) Å around the lone electron pair
- 780 (dashed line).
- 781
- 782 Figure 6. Schematic view of thallium cycling and the geotectonic location of deposits containing Tl-
- 783 minerals. Background images from http://minerva.union.edu/hollochk/kth/illustrations.htmvz.



Northern part of the Eastern Group fumaroles

Nataljamalikiite type locality

Quartz Tube

Bubblers, cooler in water+ice

Pump

(b)





(NH4)2SO4-

TI

(S,As









Solar system: 142 ppb (Anders and Grevesse 1992)