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Abstract:	We report tephrochronological and geochemical data on early Holocene activity from Plosky volcanic massif in the Kliuchevskoi volcanic group, Kamchatka Peninsula. Explosive activity of this volcano lasted for ~1.5 kyr, produced a series of widely dispersed tephra layers, and was followed by profuse low-viscosity lava flows. This eruptive episode started a major reorganization of the volcanic structures in the western part of the Kliuchevskoi volcanic group. An explosive eruption from Plosky (M~6), previously unstudied, produced tephra (coded PL2) of a volume of 10-12 km3 (11-13 Gt), being one of the largest Holocene explosive eruptions in Kamchatka. Characteristic diagnostic features of the PL2 tephra are predominantly vitric spongeshaped fragments with rare phenocrysts and microlites of plagioclase, olivine and pyroxenes, medium- to high-K basaltic andesitic bulk composition, high-K, high-Al and high-P trachyandesitic glass composition with SiO2 = 57.5-59.5 wt%, K2O = 2.3-2.7 wt%, Al2O3=15.8-16.5 wt%, and P2O5= 0.5-0.7 wt%. Other diagnostic features include a typical subduction-related pattern of incompatible elements, high concentrations of all REE (>10x mantle values), moderate enrichment in LREE (La/Yb~5.3), and non-fractionated mantle-like pattern of LILE. Geochemical fingerprinting of the PL2 tephra with the help of EMP and LA-ICP-MS analyses allowed us to map its occurrence in terrestrial sections across Kamchatka and to identify this layer in Bering Sea sediment cores at a distance of >600 km from the source. New high-precision 14C dates suggest that the PL2 eruption occurred

~10,200 cal BP, which makes it a valuable isochrone for early Holocene climate fluctuations and permits direct links between terrestrial and marine paleoenvironmental records. The terrestrial and marine 14C dates related to the PL2 tephra have allowed us to estimate an early Holocene reservoir age for the western Bering Sea at 1410±64 14C yrs. Another important tephra from the Early Holocene eruptive episode of Plosky volcano, coded PL1, was dated at 11,650 cal BP. This marker is the oldest geochemically characterized and dated tephra marker layer in Kamchatka to date, and is an important local marker for the Younger Dryas - early Holocene transition. One more tephra from Plosky, coded PL3, can be used as a marker northeast of the source at a distance of ~110 km. *Manuscript Click here to download Manuscript: Ponomareva et al IntJEarthSci revised.doc Click here to view linked References

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20

21 Abstract

22 We report tephrochronological and geochemical data on early Holocene activity from 23 Plosky volcanic massif in the Kliuchevskoi volcanic group, Kamchatka Peninsula. Explosive 24 activity of this volcano lasted for ~1.5 kyr, produced a series of widely dispersed tephra layers, 25 and was followed by profuse low-viscosity lava flows. This eruptive episode started a major reorganization of the volcanic structures in the western part of the Kliuchevskoi volcanic group. 26 27 An explosive eruption from Plosky (M~6), previously unstudied, produced tephra (coded PL2) of a volume of 10-12 km³ (11-13 Gt), being one of the largest Holocene explosive eruptions in 28 Kamchatka. Characteristic diagnostic features of the PL2 tephra are predominantly vitric sponge-29 30 shaped fragments with rare phenocrysts and microlites of plagioclase, olivine and pyroxenes, 31 medium- to high-K basaltic andesitic bulk composition, high-K, high-Al and high-P trachyandesitic glass composition with $SiO_2 = 57.5-59.5$ wt%, $K_2O = 2.3-2.7$ wt%, $Al_2O_3 = 15.8-59.5$ 32 33 16.5 wt%, and $P_2O_5 = 0.5 - 0.7$ wt%. Other diagnostic features include a typical subduction-related 34 pattern of incompatible elements, high concentrations of all REE (>10x mantle values), moderate 35 enrichment in LREE (La/Yb~5.3), and non-fractionated mantle-like pattern of LILE.

36 Geochemical fingerprinting of the PL2 tephra with the help of EMP and LA-ICP-MS 37 analyses allowed us to map its occurrence in terrestrial sections across Kamchatka and to 38 identify this layer in Bering Sea sediment cores at a distance of >600 km from the source. New high-precision 14 C dates suggest that the PL2 eruption occurred ~10,200 cal BP, which makes it 39 40 a valuable isochrone for early Holocene climate fluctuations and permits direct links between terrestrial and marine paleoenvironmental records. The terrestrial and marine ¹⁴C dates related to 41 the PL2 tephra have allowed us to estimate an early Holocene reservoir age for the western 42 Bering Sea at 1410±64 ¹⁴C yrs. Another important tephra from the Early Holocene eruptive 43 episode of Plosky volcano, coded PL1, was dated at 11,650 cal BP. This marker is the oldest 44 geochemically characterized and dated tephra marker layer in Kamchatka to date, and is an 45 46 important local marker for the Younger Dryas - early Holocene transition. One more tephra from 47 Plosky, coded PL3, can be used as a marker northeast of the source at a distance of ~110 km.

48

49 Introduction

50 Many arc volcanoes are highly explosive and produce voluminous eruptions which may 51 affect climate patterns due to wide dispersal of their tephra and associated aerosols. Existing 52 records of past eruptions, however, are far from being complete, which hampers our 53 understanding of climate-volcano interplay. More than that, volumes of many island arc tephras 54 are likely underestimated because most of the tephras are carried offshore so special terrestrial-55 marine tephra correlations are necessary to assess total eruptive volumes and calculate magma 56 output from explosive eruptions. Also, tephra layers from large eruptions cover broad areas and 57 may serve as isochrones providing direct links between terrestrial and submarine depositional 58 successions. Research on the chronology and geochemical makeup of past eruptions as well as 59 on their eruptive volumes and magnitudes contributes substantially to a better understanding of 60 global paleovolcanic patterns and provides a tephrochronological framework for further 61 volcanological and paleoenvironmental studies.

62 The Kamchatka Peninsula (Fig. 1) hosts a highly active volcanic arc where most of the larger explosive eruptions produced pumice, characterized by andesitic-rhyolitic bulk 63 64 compositions (Braitseva et al. 1997b) and by rhyolitic glass (Kyle et al. 2011). Decades of tephrochronological studies in Kamchatka have permitted documentation of 40 large Holocene 65 explosive eruptions, with tephra volumes ranging from 170 to 0.5 km³ (Braitseva et al. 1997a,b; 66 1998; Ponomareva et al. 2007a). Tephra of these eruptions is widely used for dating and 67 68 correlating various terrestrial deposits and landforms (e.g. Pinegina and Bourgeois 2001; Bourgeois et al. 2006; Braitseva et al. 1983, 1995, 1998; Kozhurin et al. 2006; Ponomareva 69 70 1990). Two particular periods of high-volume explosive eruptions with bulk tephra volumes of 10-170 km³ were identified and dated at ~8600-6800 and 1750-1250 cal BP (Braitseva et al. 71 72 1995; Ponomareva et al. 2007a).

73 Early Holocene (12-10 cal ka BP) explosive volcanism in Kamchatka is less well known 74 because of poorer preservation of related deposits. The general belief is that this time was 75 characterized by dominantly moderate, mafic, cone-building eruptions with very few if any large 76 explosive events (e.g. Braitseva et al. 1995). A better understanding of volcanic activity and 77 improved estimates of volcanic flux for early Holocene time may also offer a clue to the 78 relationships between volcanism and glacial unloading (e.g., Jull and McKenzie 1996). 79 Moreover, well documented tephra markers for this period may serve as sensitive isochrones 80 necessary in the study of rapid climate fluctuations recorded in various terrestrial and marine 81 sediments.

In this paper we document an early Holocene activity of Plosky volcanic massif (Kliuchevskoi volcanic group, Kamchatka) which produced a series of widely dispersed tephra 84 layers, and was followed by profuse lava flows. We provide mineralogical and geochemical data 85 on proximal Plosky tephras (both bulk tephra and individual glass shards) that permits fingerprinting of individual tephra layers and correlation of three of them over the affected area. 86 87 We reconstruct the parameters of a major Plosky eruption (coded PL2), and show that PL2 was 88 one of the largest Holocene explosive events in the NW Pacific. Geochemically fingerprinted 89 and dated Plosky tephra layers may serve as valuable isochrones for paleoclimate research. 90 Correlation of PL2 tephra between terrestrial and marine sediments allows us to provide the firstever estimate of ¹⁴C reservoir age for the western Bering Sea. 91

92 Location and geological context

93 Plosky volcanic massif is a huge, complex edifice which occupies the northwestern sector 94 of a highly productive volcanic cluster (Kliuchevskoi volcanic group), located close to the 95 Kamchatka-Aleutian Arc junction (Figs. 1 and 2). Plosky along with the Tolbachik volcanoes (Fig. 1) are positioned at the rear of the arc, ~ 180 km above the subduction zone (Gorbatov et al. 96 97 1997). Surprisingly little is known about Plosky activity considering its key geodynamic position, enormous volume, and some juvenile volcanic features on its slopes. The whole edifice 98 99 is built on top of the mid-Pleistocene lava plateau underlying Kliuchevskoi volcanic group 100 (Melekestsev et al. 1974). Based on its morphology and the stratigraphic relationship of its lavas 101 with Last Glacial Maximum deposits, Plosky is believed to consist of a 90x50 km² late 102 Pleistocene shield volcano and two superimposed late Pleistocene stratovolcanoes -- Ushkovsky 103 (or Plosky Dalny, elev. 3943 m) and Krestovsky (or Plosky Blizhny, elev. 4108 m). Ushkovsky 104 is crowned with two nested calderas which according to Melekestsev et al. (1974) resulted from 105 magma drainage caused by lava venting lower on the slopes.

106 Summit calderas host a glacier which descends down several valleys and partly obscures 107 proximal deposits and flank vents (Fig. 1). Two ice-clad cinder cones with large craters are 108 located in the younger caldera (Flerov and Ovsyannikov 1991; Shiraiwa et al. 2001). An arcuate 109 rift-like zone punctuated by cinder cones crosses the volcanic massif and goes down its SW and 110 NE flanks (Fig. 1; Melekestsev et al. 1974). The zone started to form in late Pleistocene time and 111 continued its activity into the early Holocene. In the northeastern sector of the summit area, near 112 the larger caldera rim, Holocene lavas from this zone and from the intracaldera vents overlie a 113 40-m-thick cindery tephra (Flerov and Ovsyannikov 1991). Two large Holocene lava flows on 114 the northeastern (Lavovy Shish lava field) and southwestern slopes of the volcanic massif were 115 the most recent from this zone (Fig. 1).

The younger ~4 km-wide caldera at the summit of Ushkovsky formed roughly 8600 ¹⁴C
 years BP as a result of eruptions of lava flows and cinder cones of the Lavovy Shish group

(Braitseva et al. 1995). The same events likely triggered the collapse of Krestovsky volcano; its summit likely collapsed as a toreva block, now forming Mt. Sredny (Fig. 2) (Melekestsev 2005), but few data supporting these suggestions have been published. Two early Holocene tephras were attributed to Plosky and used as local markers by Ponomareva et al. (2007b) but no detailed data reported. The magnitude of Plosky explosive eruptions has not been previously estimated, and thus the volcano has not been listed as a source volcano for large Holocene eruptions (Braitseva et al. 1997b; Ponomareva et al. 2007a; Siebert and Simkin 2002-).

125 Plosky activity has been considered to have been mainly effusive with the most recent 126 lavas produced along the rift zone and in the Ushkovsky summit calderas (Flerov and 127 Ovsyannikov 1991). "Active" status has been assigned to Ushkovsky volcano based on weak 128 fumarole activity and presence of thermal spots on its summit (Ovsyannikov et al. 1985). The 129 historic 1890 eruption (Herz 1897) also was likely related to its fumarolic activity (Melekestsev 130 et al. 1991) because no geological evidence of recent explosive activity has been found near its 131 summit (Flerov and Ovsyannikov 1991). Bulk-rock analyses permit identification of two groups 132 of Plosky rocks: medium-K and high-K (Churikova et al. 2001). High-K rocks fill the summit 133 calderas and tend to be associated with the rift-like structure while medium-K lavas belong 134 dominantly to the stratovolcanoes (Flerov and Ovsyannikov 1991).

135 Materials and Methods

136 Samples

137 Tephrostratigraphic studies included measuring and sampling of more than thirty tephra 138 sections at Kliuchevskoi, Plosky and Shiveluch slopes (Figs. 1, 3 and 4) and tracing Plosky 139 tephra layers from site to site while considering changes in thickness and grain size (Fig. 4). 140 Samples from the western Bering Sea floor were collected from cores SO201-2-77KL and 141 SO201-2-81KL (pilot), obtained in 2009 during the R/V SONNE cruise 201 Leg 2 within the 142 framework of the KALMAR project (Dullo et al. 2009). All samples were washed with distilled 143 water. Submarine sample SO201-77-SR1 was sieved to obtain three fractions (>0.1, 0.1-0.05, 144 and <0.05 mm).

145 Geochemistry

Major elements in bulk cinder samples were determined by wet chemistry in the Institute of Volcanology and Seismology (Petropavlovsk-Kamchatsky, Russia). Lava sample from Lavovy Shish lava field was analyzed by XRF in GEOMAR (Kiel). Volcanic glass and minerals were analyzed using a JEOL JXA 8200 electron microprobe equipped with five wavelength dispersive spectrometers including 3 high-sensitivity ones (2 PETH and TAPH) at GEOMAR (Kiel). The analytical conditions for glasses were 15 kV accelerating voltage, 6 nA current and 5 μm 152 electron beam size. The details of the settings and standards used, and of data reduction can be 153 found in Online Resource 1. The INTAV intercomparison of electron-beam microanalysis of 154 glass by tephrochronology laboratories (Kuehn et al. 2011) revealed no systematic error for 155 glasses compositions analyzed at GEOMAR lab (coded as lab #12).

156 Trace elements in glasses were analysed by laser ablation - inductively coupled plasma -157 mass spectrometry (LA-ICP-MS) using a 193nm excimer laser with a large volume ablation cell 158 (Zürich, Switzerland) coupled with a quadrupole-based ICP-MS (Agilent 7500cs) at the Institute 159 of Geosciences, CAU Kiel, Germany. In situ-microsampling was done with 50 µm pit size. The 160 details of the settings used can be found in Online Resource 1.

161

Dating

162 The ages of the two major tephra layers (PL1 and PL2) from Plosky were obtained through AMS ¹⁴C dating on pollen and leaf fragments collected from inside each tephra in a ~7 m deep 163 164 peat section (JB112) near Krutoberegovo village (Fig. 4). AMS radiocarbon analysis was 165 performed by Beta Analytic. Quoted errors represent one relative standard deviation statistics 166 (68% probability). Radiocarbon ages were corrected for isotopic fractionation and were 167 calibrated using the IntCal09 curve (Reimer et al. 2009). Calibrated ranges are reported as two standard deviations. For approximate age estimates of other events we use calibrated ¹⁴C ages 168 169 except for the cases where we cite other authors' published dates.

170 **Results**

171

Proximal tephra and lava sequence

172 Cinder lapilli attributed to Plosky based on similarity of their bulk composition to high-K 173 andesitic Plosky lavas were documented in many outcrops on the slopes of Kliuchevskoi volcano 174 (Fig. 1, 3 and 4; Auer et al. 2009). In this area, a 10-12 m thick Holocene tephra sequence is 175 dominated by numerous dark-gray cinders from Kliuchevskoi, interbedded with ~30 light-176 colored tephra layers from other volcanoes (Portnyagin and Ponomareva 2012). Plosky lapilli lie 177 in the lower part of the sequence, well below a regional marker tephra layer (KZ) dated at ~8250 178 cal BP (Braitseva et al. 1997a; Auer et al. 2009) (Fig. 3).

A series of lava flows similar in bulk composition to the described Plosky cinders and 179 180 high-K andesitic Plosky lavas (Churikova et al. 2001) is associated with several vents on the 181 Plosky slopes. Lava flows on the northeastern slope, usually referred to as Lavovy Shish lava 182 field (Fig. 1), directly overlie the Plosky lapilli and likely close this eruptive episode. At high 183 elevations, where lava is not covered by younger deposits, it bears features typical for low-184 viscosity lavas, such as remnants of lava tubes and fragments of undulating or ropy surfaces. The 185 lava is porphyric trachyandesite (Table 1) with plagioclase crystals up to 1 cm long referred to

186 by Piip (1956) as mega-plagiophyric. Closer to Plosky, Lavovy Shish lavas are partly covered by 187 a glacier and, in their terminal part, they are obscured by a younger debris fan from Kliuchevskoi 188 volcano, hence their real extent is not known. The stratigraphic position of the lava flow on the 189 southwestern slope is less clear because the tephra cover is less stable at elevations >1100 m. 190 However, this lava likely formed in early Holocene because it overlies Last Glacial Maximum 191 moraines and is in turn overlain by KHG marker tephra dated at ~7800 cal BP (Braitseva et al. 192 1997a). Because this lava flow is located within the same rift-like zone as the northeastern lava 193 field and is close to the latter in surface morphology, petrography and age, we include it in the 194 same eruptive episode.

195 In all sections on Kliuchevskoi slopes, Plosky cinders form a package ("Plosky package") 196 of two to four lapilli layers interlayered and topped with a few layers of finer grained sand-sized 197 tephra (Figs. 3 and 4). The lower lapilli layers are separated from upper layers by a 6-10-cm-198 thick sandy loam, which signifies a break in Plosky's explosive activity and contains a 1-2 cm-199 thick layer of bright-yellow pumiceous tephra dubbed "lower yellow". In section 300, one of the 200 lower lapilli layers is >2 m thick and probably is related to one of the cinder cones (Fig. 4). This 201 layer pinches out laterally, unlike other two lapilli layers that can be traced over a large area and 202 likely came from the summit crater. Maximum lapilli size is 10 cm from sample 300-16 (Fig. 4).

203 Continuous sampling of a section through the tephra sequence (K7-T1 on Figs. 1, 3 and 4) 204 and new analyses of bulk cinders and their glass allowed us to geochemically characterize 205 dominant Kliuchevskoi cinders (Portnyagin et al. 2009), and to single out nine individual tephra 206 layers compositionally close to known high-K Plosky rocks (Krasheninnikov 2008; Figs. 3 and 207 4). Glass from all these layers, and minerals from three layers, were analyzed with an electron 208 microprobe (EMP). Glass from the thickest lapilli layer (sample K7-T1-12A) was analyzed by 209 LA-ICP-MS. In addition, we used bulk-rock analyses from this section and sections 300, 350 and 210 1206 (Figs. 1 and 4; Table 1) (Auer et al. 2009, and this study).

211 Plosky tephra comprises vesicular dark-gray porphyric cinders with vitric groundmass 212 (Figs. 5 and 6) containing very rare microlites. Many glass particles have a sponge-like texture 213 with highly elongated vesicles. The mineral assemblage is dominated by large, elongated (≤ 1 cm 214 long) plagioclase phenocrysts (An₄₄₋₇₈, $K_2O= 0.2-1.1$ wt%, FeO= 0.42-0.88 wt%) which are 215 typically normally zoned with the exception of sample K7-T1-16A, where plagioclase 216 phenocrysts exhibit a weak reverse zoning. Rare subphenocrysts and microlites include olivine 217 (Fo₇₁₋₇₂) in sample K7-T1-12A, clinopyroxene (Mg#=69-76 mol%, CaO= 17-19.5 wt %, TiO₂= 218 0.51-0.77 wt %, $Al_2O_3 = 1.79-2.85$ wt%, $Na_2O = 0.22-0.41$ wt %), low-Ca pyroxene (Mg#=66-75) 219 mol%, CaO=1.6-2.1 wt %, TiO₂= 0.25-0.46 wt %, Al₂O₃= 0.77-1.94 wt%, Na₂O=0.01-0.10 wt 220 %), and Ti-magnetite (TiO₂=8-19 wt%, Al₂O₃=2.2-5 wt%) (Online Resource 2). Rare F-Cl 221 apatite grains have been found in sample K7-T1-14A.

222 All tephra consist of fresh magmatic particles, with only a minor amount of recrystallized 223 rock fragments. SiO₂ content in bulk cinder lapilli varies from 56 to 58.5% (Fig. 7). Glass from 224 all the cinders forms a trend in the trachyandesitic-trachydacitic field with SiO₂ ranging from 58 225 to 64.5 wt% (Fig. 7; Online Resource 3). Classification diagrams show that Plosky cinders have 226 intermediate compositions between medium-K basaltic-andesites, and high-K basaltic 227 trachyandesites - trachyandesites (Fig. 7, Table 1), and are different from Kliuchevskoi medium-228 K basalts - basaltic andesites of normal alkalinity (Fig. 7). On the SiO₂ - FeO/MgO diagram most 229 Plosky bulk rock and glass compositions fall into the tholeiitic and medium-Fe fields (Fig. 7).

230 The majority of Plosky glasses have $SiO_2 = 59-61$ wt%, $K_2O = 2.5-3.5$ wt%, MgO = 2-2.7 231 wt% (Fig. 7, Table 2). One lapilli tephra (K7-T1-12A), which forms the thickest layer in the K7-232 T1 section (Figs. 3 and 4), clearly stands apart and has the most mafic glass in the package with $SiO_2 = 58-59.2$ wt%, $K_2O = 2.3-2.5$ wt%, MgO = 2.8-3 wt% (Figs. 8 and 9). Glasses from two 233 234 tephras (K7-T1-11A and K7-T1-11A-3; Figs. 3 and 4) have the most fractionated silicic, high-K, 235 and low-Mg glass compositions (Fig. 8). Temporal variations of glass compositions are irregular 236 except for those for chlorine whose concentrations in glass correlate significantly ($r^2=0.55$) with 237 stratigraphic position of samples (Fig. 8, Table 2). The concentrations of Cl do not correlate with 238 any other element in Plosky glasses and increase progressively from about 0.03±0.01 wt% (±1 239 s.d.) in the oldest samples to about 0.05 ± 0.01 wt% in the youngest ones. This characteristic may 240 be used to discriminate Plosky glasses of different ages.

241 Compared to glasses from Kliuchevskoi cinders (Fig. 9), Plosky glasses tend to have more 242 silicic, exclusively trachyandesitic compositions. In the field of andesitic compositions, Plosky 243 glasses have lower FeO and TiO₂ and higher Al₂O₃, K₂O and P₂O₅ compared to the most evolved 244 Kliuchevskoi glasses. Concentrations of phosphorous provide particularly useful criteria for 245 reliable discrimination of Plosky and Kliuchevskoi glasses. All Plosky glasses have 246 concentrations of P₂O₅ >0.5 wt%, whereas those from Kliuchevskoi have P₂O₅ <0.5 wt%.

247 Trace element data obtained for Plosky cinder K7-T1-12A include bulk rock analysis (high 248 precision XRF on pressed tablets, Auer et al. 2009) and LA-ICP-MS data on single glass shards 249 (Table 3, this study). The data are compared with each other and with published compositions of 250 lavas from Plosky and Kliuchevskoi volcanoes in Fig. 10. The compositions of bulk rock and 251 glass for Plosky lapilli sample K7-T1-12A are similar. Approximately 10 rel. % lower 252 concentrations of incompatible elements in bulk rock analyses (Rb, Ba, Nb, La, Pb, Zr, Y) 253 indicate the presence of Sr-rich plagioclase phenocrysts (~10%) in the bulk rock. Both bulk 254 tephra and glasses show a typical pattern for evolved Kamchatka magma formed in subductionrelated environments (e.g., Gill 1981). The compositions are enriched in all REE ($\geq 10x$ mantle values), moderately enriched in light REE (LREE) over heavy REE (La/Yb ~ 5.3), strongly enriched in Pb, U and large-ion lithophile elements (LILE) (Ba, Rb, Cs), and depleted in Nb and Ta relative to LREE (e.g. Pb_N/Ce_N=4.3, Ba_N/La_N=3.2, Nb_N/La_N=0.27 in glasses, where N refers to mantle-normalized values). The pattern of LILE (Cs, Rb, Ba) and U is unfractionated while the ratios of these elements are similar to those in primitive mantle (i.e. Ba_N/Rb_N ~ 1, Rb_N/U_N ~ 1, etc., Fig. 10).

262 The pattern of trace elements in the tephra is subparallel to those of high-K basaltic and 263 basaltic andesitic Plosky lavas, which suggests a possible genetic link between these magmas by 264 fractional crystallization from a common parental magma. Lower Sr and Ti concentrations and a 265 more pronounced negative Eu anomaly in the andesitic glass, compared to the high-K Plosky 266 lavas, implies that the fractional crystallization involved plagioclase (a major host for Sr and Eu) 267 and Fe-Ti oxides (hosts for Ti) along with Fe-Mg silicates (olivine and pyroxenes) in good 268 agreement with the petrographic observations. Middle-K lavas from Plosky and Kliuchevskoi 269 volcano have distinctively lower concentrations of most incompatible elements and exhibit a 270 characteristic Ba enrichment relative to similarly incompatible trace elements (e.g., $Ba_N/Rb_N \sim 2$ 271 in Kliuchevskoi and middle-K Plosky lavas). This observation indicates that the high-K and 272 middle-K series of Plosky volcanic massif originated from different parental magmas.

Overall, the geochemical characteristics of Plosky tephra make it quite a rare type of Holocene volcanic composition in Kamchatka, resembling to a certain extent only the most evolved lavas of Gorely volcano (Duggen et al. 2007). This specific composition facilitates identification of this tephra in distal localities.

277

Distal tephra sections

278 *Terrestrial sections.* The Plosky tephra package was directly traced from section to section 279 northeast of the source, to the southern and eastern slopes of Shiveluch volcano, and farther east 280 towards Ust'-Kamchatsk and Krutoberegovo villages over the distance of ~150 km (Figs. 4 and 281 11b). In all these distal sections it consists of three layers of black or brownish-black cinders, 282 from bottom to top -- fine tephra overlain by medium-to-coarse tephra overlain by very fine 283 tephra (Fig. 12). Because of their dark color, Plosky tephra layers are visible among light-284 colored, pumiceous Shiveluch tephras and are good markers for Shiveluch sections. The 285 direction from Plosky volcano towards Shiveluch sites goes close to K7-T1 section (Fig. 11b), 286 where we have geochemically characterized the Plosky tephra package in detail. Therefore all 287 three Plosky tephra found at Shiveluch and farther east must be present in section K7-T1.

Appearance of glass shards from the cindery tephra layers found on Shiveluch slopes (Figs. 5 and 6) is similar to that from Plosky tephras. Microprobe analyses of glass from selected 290 samples (Fig. 4) allow us to correlate these three tephra layers to the layers found in section K7-291 T1 (Fig. 13, Online Resource 3). The lower layer correlates to the lower lapilli tephra K7-T1-292 16A and the middle layer to the most mafic lapilli tephra K7-T1-12A. Glasses from the upper 293 very fine tephra are close to those in K7-11A-2 fine tephra in section K7-T1. At similar SiO₂ 294 content, glasses from this upper tephra have slightly lower TiO₂, FeO and MnO content 295 compared to samples of similar age in the Plosky package in K7-T1 section (K7-10A, K7-11A-1; 296 Tables 2 and 4). To confirm the correlation of the most mafic Plosky tephra (K7-T1-12A) with 297 the distant terrestrial samples, trace elements were obtained by LA-ICP-MS for this (most mafic) tephra from the sites K7-T1 (Kliuchevskoi slope), 1264b (Shiveluch) and YK-2008-01 (Ust'-298 299 Kamchatsk area) (Figs. 4 and 14). The concentrations of trace elements in all three samples are 300 indistinguishable within 15 rel. % and confirm the origin of these tephra layers from the same 301 eruption.

302 Given the wide spatial dispersal of the three Plosky tephras, we assigned them simpler 303 identification codes: PL1 for the lower layer, PL2 for the (most mafic) middle tephra layer, and 304 PL3 to the upper fine-grained tephra (Figs. 4 and 13). Thickness measurements of tephra layers 305 as well as direct field tracing of the layers and study of their glass compositions have allowed us 306 to compile isopach maps for PL1 and PL2 (Fig. 11). The number of observations was not enough 307 to constrain reliable isopachs for PL3. PL1 was dispersed NNE from the source (Figs. 4 and 308 11b). Because this tephra is less distinct geochemically it is difficult to identify it in sections 309 where PL2 tephra is not present and thus where stratigraphy is less clear. The dispersal axis for 310 PL2 goes towards the Kamchatka River mouth (Fig. 11) while the northern margin runs roughly 311 north of Shiveluch volcano. The northern limit of PL2 is constrained by its absence at the Uka 312 site (Fig. 11a; Dirksen et al. in press), the southern margin lies south of Bezymianny volcano 313 (Fig. 1), and its easternmost limit is constrained by absence of a visible PL2 layer in a peat 314 profile on Bering Island (Fig. 11a) (Kirianov et al. 1990; Kyle et al. 2011). The most distal 315 terrestrial site where the two larger tephra falls (PL1 and PL2) were described and analyzed is 316 Krutoberegovo village, site JB112 (this study, Fig. 11b; Online Resource 3).

317 Prior studies have assigned distal tephra layers to Plosky based on stratigraphy and bulk 318 chemical analyses only, and some of those correlations can now be revised or refined. For 319 example, Braitseva et al. (1995) assigned to Plosky (PL2 in this paper) one of the cinder layers 320 sampled at the bottom of the Kliuchi section (sample 1206'-1, Figs. 1 and 4). However, our 321 microprobe data suggest that its glass has a more evolved composition than PL2 (Fig. 13b; 322 Online Resource 3) and may either correlate to some other tephra from the K7-T1 site or may 323 have originated from a flank cinder cone. West of the volcano, we measured and analyzed the 324 early Holocene Plosky package in an archaeological excavation at Ushki-V (Figs. 1 and 4) 325 (Dikov 2003; Goebel et al. 2003). Here, all tephra layers are less than 2 cm thick, suggesting that 326 this site lies off the dispersive axes for the two major Plosky tephras (PL1 and PL2, Fig. 11). The 327 stratigraphic context as well as a relatively evolved composition of glass from these layers, with 328 slightly elevated Cl content (Table 4), allow us to assign these tephras to eruptions younger than 329 PL2 (e.g., section K7-T1). At Ushki (west of Plosky) as well as in tephra sections located south 330 and southeast of the volcano (Fig. 1) there is no evidence of any other Holocene Plosky tephra 331 packages or layers besides the early Holocene package, which suggests that the above-described 332 eruptive episode comprising PL1 and PL2 large tephras represents the only significant episode of 333 explosive activity from Plosky volcanic massif during the Holocene.

334 Western Bering Sea cores. Dark-gray, fine to very fine tephra was sampled in cores 335 SO201-2-77KL (core depth 116-117 cm) and SO201-2-81KL (pilot) (10-13 and 14-17 cm) (Fig. 336 11a; Dullo et al. 2009). This tephra, coded SR1 during the on-board description, came from 337 semi-liquid sediments enriched in diatoms and carbonate detritus (small, thin-shelled forams and 338 their fragments; coccoliths), which suggests they were deposited during the late glacial - early 339 Holocene warming period (12.4-8.3 cal ka BP according to Gorbarenko et al. 1996, 2002). In 340 core SO201-2-77KL, strongly bioturbated sediments rich in up to 3 cm-thick tephra lenses are 341 present between 113 and 122 cm. Average thickness of the tephra layer was estimated at 2-3 cm. 342 Microprobe analyses of this tephra show that most of the glass shards in fractions >0.1 and 0.1-343 0.05 mm match mafic PL2 tephra (Table 4, Figs. 14 and 15). Trace element concentrations in 344 these glasses are indistinguishable within 15 rel. % from those in terrestrial PL2 samples and 345 thus confirm the correlation initially based on major element composition of the glasses (Fig. 346 14). BSE images of these glass shards also support their relation to Plosky tephras (Fig. 5). In the 347 samples from the pilot core SO201-2-81KL, PL2-like glasses are less abundant but present at 348 both 10-13 and 14-17 cm levels (Online Resource 3), being more abundant in the lower level 349 (Fig. 15). In the finer fractions of the same samples (<0.1 mm in SO201-2-81KL and <0.05 mm 350 in SO201-2-77KL) we found several populations of more silicic glasses (Fig. 15, Online 351 Resource 3) which, with a few exceptions, are different from Plosky glasses.

352 Heavy minerals in the above-described samples were low- and high-Ca pyroxenes, Ti-353 magnetite and amphibole, some of which closely resemble minerals in the proximal Plosky 354 samples and thus support the correlation of SR1 with PL2 (Online Resource 2). However, some 355 of the minerals [low-Ti and low-Al low-Ca (CaO=0.9-1.2 wt%, TiO₂=0.14-0.20 wt%, 356 Al₂O₃=0.4-1.2 wt%) and high-Ca (CaO=20.4-21.4 wt%, TiO₂=0.25-0.40 wt%, Al₂O₃=0.9-1.8 357 wt%) pyroxenes and particularly amphibole] are lacking in Plosky tephras and may be related to 358 the silicic population of glasses from the SR1 layer. The presence of different tephras in the same 359 layers in the marine cores may have resulted from low background accumulation rate,

bioturbation and contamination during the coring. In all these cases, ¹⁴C dates for the Holocene tephra layers obtained in such cores are not likely to be as accurate as those from the detailed terrestrial sections.

- In sum, based on tephra stratigraphy as well as on the appearance and composition of glass from terrestrial and marine samples, we correlate K7-T1-12A (PL2) tephra from the Kliuchevskoi slope to coarse tephra found on the slope of Shiveluch and in the Ust'-Kamchatsk area, and farther east to tephra SR1 from Bering Sea cores. Both cores lie on the extended terrestrial axis for this tephra (Fig. 11a), which provides further support for the correlation.
- 368

Volumes of PL2 and PL1 tephra and eruption magnitudes

369 The finding of a 2-3 cm thick PL2 tephra layer at a distance of >600 km from the source 370 dramatically changes the estimates of its volume calculated from terrestrial deposits only. Legros 371 (2000) proposed a method of estimating the minimum volume of a tephra deposit based on a 372 single isopach. Using his formula Vmin = 3.69 TA (where T is thickness, and A is area within 373 any isopach) with the terrestrial isopachs 50 and 10 cm we obtain Vmin = 0.34 and 0.82 km³, 374 respectively (Table 5). However, including the data from marine cores (2-3 cm PL2 tephra thickness at site SO201-2-77KL) we obtain minimum volume estimates about an order of 375 magnitude larger - 4.87-7.3 km³. Calculations based on the method of Bonadonna and Costa 376 (2012) provide an even larger estimate for PL2 volume of 10.4-12.3 km³ for the 2-3 cm laver 377 378 thickness in the core SO201-2-77KL (Table 5).

379 More precise estimates of tephra volume are not possible at this stage as only one distal 380 point with measured thickness is available. We realize that this thickness could differ from the 381 original one because of bioturbation or other processes. At the same time, we note that although 382 PL2 tephra is not expressed as a distinct layer in the neighboring core SO201-2-81KL, it is 383 mixed into the sediments in a thick interval between 10 and 17 cm with a peak at 14-17 cm, so 384 its original thickness could be similar to that in core SO201-2-77KL. Both cores lie at the 385 extension of the terrestrial tephra fall axis (Fig. 11a). In addition, the dominantly large grain size 386 (>0.1 mm) of PL2 (SR1) ash in the inspected cores suggests that the real area of dispersal of 387 finer ash could be far larger, so even the larger calculated values of PL2 volume may be quite conservative. These values allow us to estimate the magnitude of PL2 eruption at 6.0-6.1 (based 388 389 on calculations proposed by Pyle 1995, 2000; at a measured cinder density of 1.1 g/cm³, and 390 erupted mass of 11.44-13.53 Gt). Minimum volume of the lava flows following the PL2 tephra eruption is estimated at $\sim 2 \text{ km}^3$ assuming an average thickness of 10 m (Fig. 1). 391

The older PL1 tephra yields smaller bulk volume (0.4 km³) and (Pyle method) eruption magnitude (4.6) compared to PL2. These estimates, however, are based on terrestrial measurements only and may significantly increase if distal PL1 tephra were found offshore. 395 Other Plosky tephras including PL3 are less thick and extensive, hence smaller in volume to PL1 and PL2 and likely not exceeding 0.1 km^3 .

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397

Age estimates for Plosky tephras

398 Radiocarbon dating of organic matter associated with tephra material offers the best age 399 estimates for Holocene tephra in Kamchatka. For PL1 and PL2 Plosky tephras, we base our age estimates on ¹⁴C measurements obtained at distal terrestrial site JB112 (Figs. 4 and 11b) because 400 401 no datable materials are available in proximal sections. The age of PL1 was obtained on a pollen 402 aliquot from inside the tephra (at 683-682 cm depth). The obtained date of 10,080±40 BP (Beta-403 320735) provides the most probable 2-sigma calendar interval for this eruption of 11,397-11,825 404 cal BP with the median probability at ~11,650 cal BP. The sample for dating PL2 is a 405 combination of pollen and leaf fragments from *Isoetes spp.* collected from the lower part of the 406 PL2 cinder layer at a depth of 669.5-669 cm. These leaves and pollen were buried by 6-cm thick 407 PL2 tephra hence the dated material should provide the best age estimate for the tephra. The 408 obtained date of 9040±50 BP (Beta-305867) provides the most probable 2-sigma calendar 409 interval for the PL2 eruption of 10,146-10,287 cal BP with the median probability at ~10,200 cal 410 BP (Stuiver and Reimer 1986; Stuiver and Reimer 1993; Reimer et al. 2009). This date fits well 411 in the stratigraphic succession on Shiveluch and elsewhere (Fig. 4; Pevzner et al. 2012). The 412 uppermost marker tephra in Plosky package (PL3 at Figs. 4 and 12) is likely only ~120 yr 413 younger than PL2 based on the average accumulation rate for the K7-T1 sequence of ~1 mm/yr 414 (Portnyagin and Ponomareva 2012) and a thickness of sandy loam between these Plosky layers 415 of 12 cm.

416 Braitseva et al. (1995) reported two dates for the main Plosky tephra (PL2) obtained from bulk paleosol samples: 8610±60 ¹⁴C yrs from below the tephra in Kliuchi town (site 1206, 417 sample 1206'-1), and 8620 ± 100^{14} C yrs from above the coarse tephra in Kamaki, site 58 (Figs. 1, 418 419 4 and 11). However, as discussed above, Kliuchi sample 1206'-1, collected above the dated 420 paleosol, does not match the PL2 tephra geochemically (Fig.13b; Online Resource 3) and may 421 represent some other tephra from the Plosky package. Therefore, the date of 8610 ± 60^{-14} C yrs is not valid for (below) PL2. The dates of 8620±100 yrs in site 58 (Braitseva et al. 1995) and 422 8670±80 ¹⁴C yrs from a proximal section at Shiveluch slope (Ponomareva et al. 2007b) were 423 424 obtained above PL2 tephra and do not contradict the newly obtained date.

425 Discussion

426 PL2 eruption

The PL2 eruption produced 10-12 km³ of tephra-fall deposits dispersed over an area of 427 428 $>70,000 \text{ km}^2$. Virtually no very fine ash (<0.05 mm) has been reported either in proximal or 429 distal PL2 tephra. A low proportion of very fine ash is typical for mafic tephra and may be 430 explained in part by lack of pyroclastic flows in these eruptions and thus low rate of secondary comminution of pyroclasts (Rose and Durant 2009). Indeed, the PL2 eruption did not produce 431 432 ignimbrites so co-ignimbrite ash did not contribute to the distal fall deposits. Far larger dispersal 433 area and volume of PL2 tephra than expected from its terrestrial deposits (Table 5) might prompt 434 that even for relatively mafic tephra with only a small if any amount of very fine ash, a large 435 proportion of the deposit can be missed if the volume calculations rely only on proximal 436 deposits.

437 The PL2 eruption appears to be one of the largest Holocene explosive events known in 438 Kamchatka, exceeding in tephra volume the largest reported eruptions from highly explosive 439 and esitic volcanoes Shiveluch (SH₂, 2.5 km³) and Avachinsky (IAv2, >8-10 km³) and approaching volumes of caldera-forming eruptions at Ksudach (KS₂+KS₃, 9-11 km³) and 440 441 Karymsky (13-16 km³) (Braitseva et al. 1997a, 1998; Ponomareva et al. 2007b). This re-442 evaluation of eruptive volume further suggests that the smaller, 4 km-wide Holocene summit 443 caldera at Ushkovsky volcano likely formed as a result of the catastrophic PL2 eruption rather 444 than as a result of lava effusion as previously thought (Melekestsev et al. 1974; Braitseva et al. 445 1995).

446 Early Holocene time (12-10 cal ka BP) in Kamchatka was not previously regarded as a 447 period of large explosive eruptions but rather as a time of dominantly mafic eruptions with only 448 moderate explosive activity (Braitseva et al. 1995, 1997b; Melekestsev et al. 1974; Ponomareva 449 et al. 2007a). Our data, however, suggest that the onset of the described explosive activity from 450 Plosky is close in time to recently dated onset of neighboring Shiveluch vigorous explosive 451 activity (Pevzner et al. 2012). Our on-going detailed studies of early Holocene tephra in the area 452 should allow us to reconsider explosive activity of this period and also permit better understanding of the temporal patterns in eruptive activity over the entire volcanic arc. 453

454

Plosky eruptive activity in early Holocene time

The compact stratigraphic position of Plosky tephra in all studied sections suggests a single early Holocene episode of activity from the volcano. It started about 11,650 cal BP with a M~4.6 explosive eruption (PL1) and probably formation of some cinder cones in the northeastern part of the rift zone, followed by ~1000 yrs of weak activity recorded by several thin tephra layers enclosed in sandy loam (Fig. 4). About 10,200 cal BP there was a violent explosive eruption (PL2) with (Pyle method) M6.0-6.1, followed by a few weak eruptions including PL3. All explosive eruptions were magmatic with no obvious phreatic component. Explosive activity was followed by profuse low-viscosity lava flows with a total volume of $>2 \text{ km}^3$. The whole eruptive episode lasted for ~1500 years and is the only known Holocene activity from Plosky volcanic massif.

465 A rift-like structure, superimposed on the Plosky massif (Fig. 1), consists of NNE-trending 466 rifts with a right-lateral strike-slip component probably accommodating high extension rates and 467 high magma supply in this part of the Central Kamchatka depression, related to oceanward 468 stretching of the arc crust (Kozhurin 2009). The structure resembles rifts on Mauna Loa, Mauna 469 Kea, Etna, and other shield volcanoes albeit on a smaller scale. In Kamchatka, the closest 470 analogues are: a zone of cinder cones, which crosses Plosky Tolbachik volcano (Fig. 1); the 471 fissure feeding the most recent lava flows from Gorely volcano (Selyangin and Ponomareva, 472 1999); and probably a rift structure which crosses Krasheninnikov volcano and caldera 473 (Ponomareva 1990). All these volcanoes host summit calderas or unusually large nested craters. 474 Another common feature of all these volcanoes is a tholeiitic evolution trend in magmas erupted 475 along the rift zones (Volynets 1994).

476 As we showed above, high-K and medium-K rock series of Plosky volcanic massif 477 originated from different parental magmas. The early Holocene activity from Plosky which 478 produced high-K rocks was related to a superimposed rift structure where magma partly 479 exploited pathways that earlier had fed medium-K chamber of Ushkovsky stratovolcano. In the 480 same way, high-K basalts from Plosky Tolbachik Holocene eruptions were produced by a 481 regional rift zone rather than by the stratovolcano itself (Ermakov and Vazheevskaya 1973; 482 Braitseva et al. 1983). At Tolbachik (Fig. 1), the same pathways in the rift zone were also used 483 by a very different type of magma -- medium-K high-Mg basalt - which first appeared 1600 cal 484 BP and later erupted repetitively along with the dominating high-K subalkaline basalts 485 (Braitseva et al. 1983). Magma erupted during the early Holocene Plosky activity is not the same 486 as that of Tolbachik high-K basalts, but they both are probably related to basalts -basaltic 487 andesites of the shield volcano preceding Ushkovsky and Krestovsky stratovolcanoes, and 488 plateau lavas comprising the Kliuchevskoi group basement (Churikova et al. 2001; Portnyagin et 489 al. 2007). To date, all these high-K basalts-basaltic and esites are the oldest and the most 490 voluminous magmatic component for the Kliuchevskoi group rocks, which has been persisting 491 throughout its activity starting from at least mid-Pleistocene time (Melekestsev et al. 1974; 492 Calkins 2004).

Activity of the Plosky rift zone last surged in the early Holocene and then waned soon after 10,200 cal BP, close to the time when the Tolbachik zone started to form (Braitseva et al. 1983), i.e., the Plosky rift was replaced by the new Tolbachik one. This was a major reorganization of volcanic structures in the western part of the Kliuchevskoi volcanic group, probably related to 497 some changes in the parameters of oceanward stretching of the crust driven by dynamics of the498 dangling Pacific slab (Park et al. 2002; Kozhurin 2009).

499

Marker tephra layers from Plosky

500 Plosky tephra (PL2 especially) are exceptional because andesitic tephra are frequently 501 considered to be less important for regional tephrochronology compared to more silicic ones. In 502 general, andestic tephra have relatively small tephra volumes and dispersal areas and are not well 503 preserved (Cronin et al. 1996; Platz 2007). They also are considered difficult for geochemical 504 fingerprinting because of large heterogeneity in glass (which reflects mixing of different magmas 505 prior to the eruption) (Shane et al. 2005; Donoghue et al. 2006) and because of high crystallinity 506 that hampers reliable glass analyses (Platz et al. 2007). On the contrary, PL2 basaltic andesite-507 andesitic tephra has large volume and dispersal area, is dominantly vitric, and is characterized by 508 quite homogeneous glass composition. Whereas cindery tephras are rarely used as markers 509 because they look alike in the field and cannot be easily traced from one section to another, 510 distinctive petrographic features and geochemical composition of PL cindery tephras permit their 511 identification and thus use as markers.

512 Distinctive petrographic and geochemical features of the PL2 tephra useful for its 513 identification and correlation include: 1) predominantly vitric sponge-shaped fragments with 514 very rare phenocrysts and microlites of plagioclase, olivine and pyroxenes; 2) medium- to high-515 K basaltic andesitic bulk composition; 3) high-K, high-Al and high-P trachyandesitic glass 516 composition (SiO₂ =57.5-59.5 wt%, $K_2O = 2.3-2.7$ wt%, $AL_2O_3 = 15.8-16.5$ wt%, $P_2O_5 = 0.5-0.7$ 517 wt%); and 4) typical subduction-related pattern of incompatible elements, high concentrations of 518 all REE (>10x mantle values), moderate enrichment in LREE (La/Yb~5.3), and non-fractionated 519 pattern of Cs, Rb, Ba and U (i.e., mantle normalized Ba/Rb, Ba/U etc. are close to 1).

520 PL1 tephra is compositionally similar to some younger Plosky tephras produced by weaker 521 eruptions (including PL3), so it has a less distinct geochemical signature than PL2. However, it 522 is a good marker for Shiveluch and Kliuchevskoi slopes as well as for the area east of Shiveluch 523 (Fig. 11), where both PL2 and PL1 are present (Fig. 4 and other sections). Compared to PL2, 524 PL1 glass has a more silicic composition (SiO₂ = 59.6-61.5 wt%) and higher K₂O content (2.9-525 3.4 wt%). PL1 is an important marker for the late glacial – Holocene transition and is thus far the 526 oldest dated and geochemically characterized marker tephra layer in Kamchatka. PL3 tephra is a 527 good marker in the sections at the south slope of Shiveluch volcano where it has disctinct 528 stratigraphic position (Fig. 12) and is finer grained than PL1 or PL2 tephras.

529 On land, Plosky tephra layers are good markers for dating and synchronizing records of 530 early Holocene volcanism (eruptive activity; petrological and geochemical variations in erupted 531 products), tectonic (faulting events), environmental changes (pollen, macrofossils) and human

532 occupation currently emerging for this area (e.g., Ponomareva et al. 2007b; Dirksen et al. in 533 press; Pinegina et al. 2012; Hulse et al. 2011). The whole Plosky tephra package may serve as a 534 composite marker in some studies. For example, in Ushki archaeological site the whole Plosky 535 package falls between levels 5 and 6 of human occupation (Dikov 2003) (Fig. 4). Level 6 was dated to ~13,200-11,200 cal BP (Goebel et al. 2003) and level 5 to ~8790±150 ¹⁴C yr BP (9536-536 10,204 cal BP) by Dikov (2003) and \sim 7640±80 ¹⁴C yr BP (8317-8596 cal BP) by Goebel et al. 537 538 (2003). Based on our stratigraphy, we would favor the latter age estimate for the level 5 because 539 it lies distinctly higher in the section than the Plosky package and thus should be younger than 540 10,000 cal BP.

541 Terrestrial-marine correlation of individual tephra layers provides an excellent tool for 542 direct comparisons between terrestrial and marine paleoclimate records (e.g. Davies et al. 2008; 543 Lowe 2011). Major Plosky tephra PL2 was found in Bering Sea cores at a distance of >600 km 544 from the source. This is the second Holocene Kamchatka tephra with a known source identified 545 in marine cores; the other is the KO tephra associated with the Kurile Lake caldera (Gorbarenko 546 et al. 2002). PL2 is the only Holocene tephra thus far identified in marine cores on the east side 547 of the peninsula. The PL2 tephra layer serves as an isochrone for sediment sequences over an area of >70,000 km² and is a tie-point for comparing and dating terrestrial and marine 548 549 paleoclimate records near the early Holocene Pre-Boreal - Boreal transition. A high-quality new 550 ¹⁴C date from a terrestrial excavation restricts its most probable age to a short interval of 10,146-551 10,287 cal BP and provides a great age constraint for early Holocene marine deposits in the 552 southwestern Bering Sea.

553

Reservoir age for the western Bering Sea in early Holocene time

554 Our finding of PL2 tephra both in the terrestrial and marine sediments allows us to estimate 555 for the first time a reservoir age for the western Bering Sea. Carbonate samples from the ocean 556 surface have an apparent radiocarbon age ~400 years older on average than contemporaneous 557 terrestrial samples (Stuiver and Braziunas 1993). This offset or *reservoir age* is known as R(t) 558 and is built into the marine calibration curve (currently Marine09). The regional value of R(t) is 559 time dependent while ΔR , the deviation from the average ocean surface age, is constant to a first 560 approximation (Stuiver and Braziunas 1993). To calibrate marine radiocarbon ages the regional 561 deviation needs to be estimated and the ages corrected or calibrated with the marine calibration 562 curve. It is also possible to calibrate by subtracting R(t) from the sample radiocarbon age and use 563 the atmospheric calibration curve (currently IntCal09), but because the ocean attenuates the 564 atmospheric signal this is not the generally accepted procedure. The virtually instantaneous 565 deposition of tephra over onshore and offshore areas permits comparison of stratigraphically related on-land and marine ¹⁴C dates and calculations of reservoir age (R(t)) and of deviation 566

from the average ocean surface age (ΔR) (e.g. Ascough et al. 2004; Eiriksson et al. 2004; Thornalley et al. 2011). In locations where both marine and terrestrial samples are deposited, R(t) can be calculated from the difference in radiocarbon age between the marine and terrestrial sample.

Estimates of the reservoir age for the western Bering Sea are lacking so, in order to calibrate marine radiocarbon ages, researchers have to use $\Delta R = 698\pm50^{-14}$ C yrs obtained ~2000 km southwest, at Sakhalin Island in the Okhotsk Sea (Kuzmin et al., 2007) or a value from two known age shells of *Mytilus edulis* from ~1550 km northeast at Port Clarence, Alaska which yield a mean ΔR and standard deviation of 497 ± 83 ¹⁴C yrs (McNeely et al 2006).

576 We presume that the deposition of PL2 tephra on land and on the seafloor represented in 577 core SO201-2-77KL was virtually instantaneous despite several caveats. Stratigraphic position of 578 a tephra layer in marine sediments may be distorted due to various factors. Tephra particles may 579 sink through soft organic-rich sediments and occur lower in a core than its original stratigraphic 580 position as described for the lake deposits (e.g. Beierle and Bond, 2002). Tephra also can be 581 deposited from icebergs with some delay and thus occur higher in the section (Brendryen et al. 582 2010). In case of PL2 tephra in the core SO201-2-77KL, however, none of these complications 583 seems likely because the PL2 ash (though bioturbated) forms quite a distinct layer (Dullo et al., 584 2009), the axis of the distal ash coincides with that for the terrestrial PL2 tephra (Fig 11a), and 585 the glaciers did not reach the coast in early Holocene so iceberg formation at this time is unlikely 586 (Melekestev et al., 1974).

587 Dates for PL2 tephra obtained on both terrestrial and marine materials allow us to make a 588 tentative estimate reservoir ages for the western Bering Sea in the early Holocene. Max et al. (2012) published an AMS ¹⁴C age of 10450±40 BP (OS-85658) on the planktonic foraminifera 589 590 sampled in the core SO201-2-77KL at a depth of 115-116 cm immediately above the PL2 tephra. 591 Using the terrestrial radiocarbon date of 9040±50 BP discussed above and this marine date we 592 calculate $R(t) = 1410\pm64$ and $\Delta R = 1064\pm55$ for this time period using the Marine09 and 593 IntCal09 curves following the method of Stuiver and Braziunas (1993). Because the dated 594 for a for a had to have been deposited slightly later than the PL2 tephra these numbers provide 595 just a minimum estimate. The calculated R(t) and ΔR values for the western Bering Sea are 596 much larger than expected from the modern estimates detailed above, however they are close to estimates for the last glacial period R(t) of ~2000 14 C yrs from the southwest Pacific (Sikes et al. 597 598 2000). We treat our calculated values as tentative because they are based on one pair of samples 599 only and the relative position of PL2 tephra and the dated foraminifera could have been 600 influenced by bioturbation of the sediments (or mixing during coring).

601 **Conclusions: lessons from this study**

602 Obviously, the mapping of tephra distribution from eruptions in island arcs and from other 603 volcanoes where winds carry eruptive products offshore is a challenge without offshore 604 sampling. Moreoever, because of the "soupy" nature of Holocene sediments in many marine 605 cores, identification of tephra and assessing of its original stratigraphic position requires careful 606 sampling and analysis. In the case of the early Holocene Plosky PL2 tephra studied herein, the 607 discovery of tephra offshore was fortuitous because marine cores were taken (for other reasons) 608 along the axis of ash dispersal, which was in fact not well known when the cores were taken. The 609 discovery of the PL2 tephra offshore dramatically increases its volume calculations, and this 610 must be the case for many other tephras; we urge those taking marine cores to pay particular 611 attention to the possibility of tephra presence—even if not well preserved in a layer, tephra 612 presence can be an important component to mapping the tephra and calculating eruptive volume, 613 which in turn affects both scientific and hazard evaluations of volcanic activity. Moreoever, the 614 correlation of a <50 ka old tephra in both terrestrial and marine settings provides the important possibility of paired ¹⁴C dates and thus for calculations of local marine reservoir ages. 615

616 Our tephrochronological studies, including geochemical fingerprinting, in the highly 617 productive Kliuchevskoi volcanic group have allowed us to document an early Holocene 618 eruptive episode of medium- to high-K basaltic andesites – andesites from Ushkovsky volcano 619 (Plosky volcanic massif), consisting of a suite of explosive eruptions followed by profuse lava 620 flows. This eruptive episode was followed by a major reorganization of volcanic structures in the 621 western part of the Kliuchevskoi volcanic group, probably related to some changes in the 622 parameters of oceanward stretching of the crust. The more mafic composition of the PL2 tephra and yet its high volume and broad distribution is of particular interest. The PL2 eruption 623 produced 10-12 km³ of tephra-fall deposits dispersed over an area of >70,000 km². Virtually no 624 625 very fine ash (<0.05 mm) has been reported either in proximal or distal PL2 tephra. A low 626 proportion of very fine ash is typical for mafic tephra and may be explained in part by lack of 627 pyroclastic comminution; indeed, the PL2 eruption did not produce ignimbrites. The lesson from 628 this case is that even for relatively mafic tephra with little very fine ash, the total eruptive 629 volume can be significantly underestimated if relying only on proximal deposits.

Our findings suggest that PL2 was one of the larger Holocene explosive eruptions in Kamchatka, yieldng a tephra volume of 10-12 km³ and magnitude of ~6. PL2 tephra was ¹⁴Cdated at ~10,200 cal BP, making it a valuable marker for the study of early Holocene climate fluctuations, e.g., the Pre-Boreal - Boreal transition. This correlation permits direct links between terrestrial and marine paleoenvironmental records. We have also documented a second early Holocene (late Glacial), voluminous tephra from the Plosky massif (PL1) in terrestrial sections and dated it at ~11,650 cal BP. The measured age of PL1 and possibility to identify it 637 geochemically, particularly when it occurs together with PL2, makes it an important local marker 638 for Younger Dryas - early Holocene transition. PL1 is thus far the oldest dated and 639 geochemically characterized marker tephra layer in Kamchatka. One more tephra from Plosky, 640 coded PL3, is ~120 years younger than PL2. Compositionally it is close to PL1 tephra and can be 641 used as a marker northeast of the source at a distance of ~110 km, in the sections where PL1 and 642 PL2 are also present.

643

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- 868

869 **Figure captions**

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872 collapse craters on Krestovsky and Ostry Tolbachik. Plosky massif comprises Ushkovsky

Fig. 1. Top: Digital elevation map showing Kliuchevskoi volcanic group with active volcanoes

labeled. Note nested summit calderas on Ushkovsky and Plosky Tolbachik and sector

and Krestovsky volcanoes; its Holocene vents are shown with red circles and their lava flows

are shown in purple. Locations of tephra sections with measured early Holocene Plosky

875 package are shown with black filled circles, and locations of the sections where Plosky

tephras have been analyzed with yellow filled circles. Numbers of sections with analyzed

877 Plosky tephra are given next to each circle. Dashed black lines show approximate directions

878 of the arcuate rift-like structures that cross Ushkovsky and Plosky Tobachik volcanoes

879 (according to Melekestsev et al. 1974). Glaciers are shown in light blue. Bottom: Position of
880 the Plosky volcanic massif relative to the Aleutian-Kamchatka arc junction. Other volcanoes
881 mentioned in the text are Gorely and Krasheninnikov (Krsh at the figure).

882 Fig. 2. Panorama photos of the Kliuchevskoi volcanic group including the Plosky volcanic

883 massif, the latter made up by Ushkovsky (Plosky Dalny) and Krestovsky (Plosky Blizhny)

volcanoes. Upper photo: view southward from the slope of Shiveluch volcano; lower photo:

view eastward from along the Kamchatka River valley (see Fig. 1 for orientation). Photos byPhilip Kyle.

Fig.3. Left: Photo of section K7-T1 (Fig. 1) through a ~12 m thick Holocene tephra sequence on
the slope of Kliuchevskoi volcano. Right: photo detail with the Plosky tephra package. The
sequence is dominated by dark-gray cinders from Kliuchevskoi volcano interbedded with

890 ~30 light-colored tephra layers from other volcanoes (Portnyagin and Ponomareva 2012).

891 Plosky package lies close to the bottom of the Holocene tephra sequence and in this area

includes 2-4 cinder lapilli layers and a few tephra layers of fine to very fine sand size. The

lowermost lapilli layer is separated from the upper layers by a sandy loam with intercalated

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894 yellow pumiceous tephra ("lower yellow"). Analyzed Plosky samples are shown with 895 arrows; full sample ID consists of section ID (K7-T1) followed with the sample number. 896 Regional marker tephra layers: KHG (Khangar volcano, ~7800 cal BP, Bazanova and 897 Pevzner, 2001), and KZ (Kizimen volcano, ~8250 cal BP, Braitseva et al., 1997b). 898 Fig. 4. Graphic measured sections at selected terrestrial sites (inset) from the Khangar marker 899 tephra (KHG) down through the early Holocene Plosky tephra package; only details of 900 Plosky and major marker tephra are shown. Sediments interlayered with Plosky layers are 901 represented by sandy loams, peat and other tephra, the latter dominantly from Kliuchevskoi 902 and Shiveluch; proximity to these volcanoes can dramatically alter the total-package 903 thickness. Where the sections are graphically compressed, true thickness is shown in meters, 904 within ovals. Analyzed samples' IDs are provided right to each column (black font for bulk 905 tephra, blue – for glass analyses), full sample ID is given except for K7-T1 where "K7-T1" is 906 the official prefix for each of these samples. Radiocarbon dates (left side of column) are from 907 Goebel et al. (2003), Braitseva et al. (1988, 1995), Ponomareva et al. (2007b), Pevzner et al. 908 (2012), and this study. Regional marker tephra layers: KHG (Khangar volcano, ~7800 cal 909 BP, Bazanova and Pevzner, 2001), and KZ (Kizimen volcano, ~8250 cal BP, Braitseva et 910 al., 1997b). Archaeological levels 5 and 6 in Ushki from Dikov (2003). 911 Fig. 5. Backscattered electron images of analyzed PL2 tephra collected in different sites from 912 proximal (top) to distal marine (bottom). Labeled mineral phases: Ol - olivine, Pl -913 plagioclase Terrestrial samples: K7-T1-12A (23 km from source), 1264b-4 (78 km), JB112-914 669-670 (140 km). Marine sample SO201-2-77KL-116-117 is 635 km from the source. 915 Sample numbers correspond to those in Figs. 3 & 4, Tables 2, 3 and 4, and Online Resources 916 2 and 3. 917 Fig. 6. Backscattered electron images of analyzed PL1 tephra collected from the same terrestrial 918 localities as shown in Figure 5. Sample numbers correspond to those in Figs. 3 & 4, Tables 2,

919 3 and 4, and Online Resources 2 and 3.

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920 Fig. 7. Classification diagrams for proximal Plosky (glass and bulk) and Kliuchevskoi (bulk)

921 cinders. In the TAS diagram (top) fields are according to Le Bas et al. (1986): B – basalt, BA

922 – basaltic andesite, A – andesite, D – dacite, TB – trachybasalt, BTA – basaltic

923 trachyandesite, TA - trachyandesite, TD – trachydacite. In the SiO₂ vs K₂O diagram (middle),

924 the fields of low-, medium- and high-K rocks are according to Gill (1981). In the $SiO_2 vs$

925 FeO/MgO diagram (bottom) tholeiitic and calc-alkalic series after Miyashiro (1974), and

low-, medium- and high-Fe series after Arculus (2003). FeO in bulk samples refers to total

927 Fe expressed as FeO.

928 Fig. 8. Graph of temporal variations in composition of glasses from individual Plosky tephra

929 layers, in stratigraphic order from excavation K7-T1 (Fig. 3 and 4). Small symbols denote

930 individual glass-shard analyses; large circles are sample averages. The three major Plosky

tephras discussed in this paper are indicated by gray bars.

932 Fig. 9. Graphs of major element composition of glasses from proximal Plosky tephra deposits.

933 Glasses from Kliuchevskoi tephra older than 7700 cal BP are shown for comparison

934 (Krasheninnikov, 2008; M. Portnyagin and V. Ponomareva, unpublished data).

Fig. 10. Plot of trace element composition of proximal Plosky tephra PL2 (sample K7-T1-12A)

normalized to primitive mantle (McDonough and Sun, 1995). Bulk analyses (closed circles)

937 are from Auer et al. (2009); average LA-ICP-MS glass analyses (open circles) are from this

study. The composition of high-K and middle-K Ushkovsky lavas and Kliuchevskoi lavas

939 after Churikova et al. (2001).

940 Fig. 11. Maps of dispersal of Plosky tephras. **a** – approximate position of a 2.5 cm isopach for

941 PL2 tephra. Sites at Uka and on Bering Island are peat sections where no Plosky tephra has

been found. **b** – enlarged inset from 11a showing isopach lines for PL2 (magenta) and PL1

943 (dark-purple); thickness in cm. Other symbols as in Fig. 1.

944 Fig. 12. Photos of Plosky tephra package interlayered with Shiveluch tephra, a and b: at the

southeastern slope of Shiveluch volcano, Kabeku River, site 1264b, 78 km NE from the

- 946 source (Fig. 11b), and **c**, farther east, site K11-17, 107 km ENE from the source (located on
- 947 Fig. 11b).
- 948 Fig. 13. Graphic plots of composition of tephra glasses from different distal terrestrial sections
- 949 correlated with proximal Plosky tephras. Sites are located on Figure 11.
- 950 Fig. 14. Plot of trace element composition of volcanic glass from PL2 tephra sampled in
- terrestrial and marine sections, normalized to primitive mantle (McDonough and Sun, 1995).
- 952 Sample sites are located on Figure 11.
- 953 Fig. 15. Graphic plot of glass compositions from the SR1 layer in marine sediment cores from
- 954 Shirshov Ridge in the Bering Sea (Fig. 11a), compared with proximal Plosky PL2 and other
- 955 Plosky glasses. Core 81KL is a pilot core.
- 956 Tables
- 957 Table 1. Major element composition of Plosky tephra and lava
- 958 Table 2. Average electron probe analyses of volcanic glass from proximal Plosky tephras
- **Table 3.** Major and trace element concentrations in single tephra glass shards and referenceglasses obtained by LA-ICP-MS
- 961 Table 4. Average electron probe analyses of volcanic glass from distal Plosky tephras
- 962 **Table 5.** Volume estimates for Plosky tephra
- 963

964 **Online Resources**

- 965 Online Resource 1. Details of the EMP and LA-ICP-MS settings and data processing
- 966 Online Resource 2. Composition of minerals from proximal Plosky tephra and distal Plosky
- 967 tephra contaminated with exotic tephra
- 968 Online Resource 3. Electron probe data on volcanic glass from Plosky tephra

Sample#	Site location	Tephra code	SiO ₂	TiO ₂	Al_2O_3	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Total
300-19	Kliuchevskoi volcano		56.05	1.35	17.59	3.20	4.99	0.19	2.65	7.38	3.80	2.23	0.58	100.00
300-18	_ " _		56.53	1.33	17.63	2.02	5.35	0.15	3.30	7.61	3.62	1.96	0.50	100.00
300-18	"		56.00	1 32	17 30	3 51	1 28	0.17	3.04	7.07	3 71	2 14	0.56	100.00
duplicate			30.90	1.32	17.50	5.51	4.20	0.17	5.04	7.07	5.71	2.14	0.50	100.00
300-16	_ " _	PL2	56.47	1.34	17.34	2.88	4.87	0.18	2.81	7.25	3.91	2.32	0.65	100.00
300-14	_ " _		58.40	0.95	17.13	3.60	4.18	0.16	2.00	6.94	3.41	2.72	0.50	100.00
300-13	_ " _		58.54	0.98	17.49	3.67	4.03	0.16	2.05	6.24	3.55	2.71	0.59	100.00
300-11	_ " _	PL1	58.34	1.03	17.47	3.64	3.84	0.15	2.35	6.71	3.59	2.69	0.20	100.00
350-3	_ " _		56.42	0.99	20.51	3.00	4.54	0.17	2.51	6.24	3.31	1.78	0.53	100.00
350-2	_ " _		56.43	1.08	19.35	4.04	4.34	0.19	2.55	6.54	3.04	1.92	0.52	100.00
350-1	_ " _	PL1	56.64	1.07	18.96	3.51	4.69	0.17	2.40	6.74	3.24	2.01	0.56	100.00
1206´-1	Kliuchi town		56.81	1.24	19.91	2.99	4.03	0.10	2.29	7.10	3.59	1.94	0.00	100.00
K8-39 (lava)	Kliuchevskoi volcano	Lavovy Shish	57.48	1.01	20.08		5.46*	0.09	1.63	7.54	4.01	2.15	0.56	100.00

Table 1. Major element composition of Plosky tephra and lava

Note: All analyses except for the last one were performed by wet chemistry method in the Institute of Volcanology, Petropavlovsk-Kamchatsky, Russia. Sample K8-39 was analyzed by XRF in GEOMAR (Kiel). *-total Fe as FeO.

Sample#	K7-T1-1	0A	K7-T1-1	1A-1	K7-T1-1	11A	K7-T1-1	1A-2	K7-T1-1	1A-3	K7-T1-	12A	K7-T1-	13A	K7-T1-1	4A	K7-T1-	16A
Eruption ID							PL3	1			PL2						PL1	
Grain size	e Fine to very fine ash		Fine to very fine ash		Fine to very fine ash		Fine to very fine ash		Fine to very fine Lapilli		Fine to very fine ash		Fine as	sh	Lapil	li		
Age (cal BP)	<1020	0	<1020	00	<1020	00	<1020	00	<1020	00	1020	0	10200-1	1650	10200-11	650	1165	0
N anls.	14		7		11		10		6		13		10		12		17	
	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.
SiO ₂	59.80	0.47	59.95	0.59	62.27	0.83	60.37	0.51	63.17	1.08	58.58	0.33	61.23	0.47	60.44	0.42	60.47	0.56
TiO ₂	1.60	0.06	1.64	0.07	1.69	0.09	1.53	0.04	1.48	0.03	1.42	0.04	1.41	0.10	1.51	0.04	1.48	0.03
Al_2O_3	15.23	0.32	14.93	0.47	14.30	0.44	15.49	0.12	14.97	0.36	16.14	0.13	15.35	0.53	15.19	0.20	15.31	0.12
FeO	7.65	0.30	7.63	0.57	7.12	0.58	7.13	0.51	6.24	0.43	7.66	0.27	6.70	0.55	7.41	0.25	7.47	0.25
MnO	0.16	0.05	0.16	0.04	0.12	0.04	0.09	0.04	0.11	0.04	0.14	0.03	0.14	0.04	0.14	0.04	0.13	0.04
MgO	2.57	0.14	2.50	0.11	1.71	0.27	2.50	0.14	1.61	0.34	2.86	0.06	2.31	0.14	2.29	0.09	2.31	0.15
CaO	5.42	0.25	5.32	0.31	4.17	0.37	5.07	0.28	3.78	0.38	5.96	0.12	4.81	0.15	5.13	0.17	5.20	0.25
Na ₂ O	3.94	0.16	3.85	0.09	4.02	0.17	4.10	0.25	4.33	0.13	4.13	0.14	4.12	0.26	3.90	0.10	3.65	0.10
K ₂ O	2.84	0.16	3.15	0.24	3.73	0.28	2.94	0.18	3.54	0.31	2.43	0.06	3.18	0.18	3.21	0.07	3.21	0.13
P_2O_5	0.68	0.05	0.76	0.08	0.75	0.09	0.69	0.04	0.67	0.08	0.58	0.04	0.65	0.08	0.72	0.05	0.69	0.06
Cl	0.06	0.01	0.05	0.01	0.06	0.01	0.05	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.03	0.01	0.03	0.01
F	0.04	0.04	0.04	0.06	0.05	0.05	0.02	0.03	0.05	0.05	0.04	0.05	0.06	0.04	0.02	0.03	0.02	0.03
SO ₃	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.02
Total	100		100		100		100		100		100		100		100		100	

Table 2. Average electron probe analyses of volcanic glass from proximal Plosky tephras

Note: All samples are from K7-T1 section located 23 km northeast of Plosky Volcano (Fig. 3). All analyses are normalized on unhydrous basis. Analyses of individual glass shards are presented in Supplementary table 1.

Sample		K7-T1-1	12A	YK-2008	8-01-9	1264t	p-4	SO201-7	7-SR1	NIST612		BCR-2G			KL-2G	
Eruption / Layer ID		PL2		PL	2	PL2	2	PL2 / S	SR1							
Elements	Units	MEAN (n=5)	STDEV	MEAN (n=5)	STDEV	MEAN (n=4)	STDEV	MEAN (n=4)	STDEV	REF	REF	MEAN (n=5)	STDEV	REF	MEAN (n=6)	STDEV
SiO ₂	wt%	62.3	1.1	63.8	1.9	66.2	0.8	58.9	1.1	71.9	54.4	58.3	1.6	50.3	53.5	2.3
CaO	wt%	5.95	0.00	5.98	0.13	6.24	0.03	5.61	0.00	11.9	7.06	0.0	0.0	10.9	0.0	0.0
Li	ppm	27.1	0.7	28.0	0.8	28.8	1.0	26.5	0.8	42	9	10.5	0.3	5.1	6.8	0.3
Sc	ppm	23.5	0.2	24.3	0.8	24.5	0.7	22.2	0.2	41	33	34.9	0.4	31.8	32.9	0.1
Ti	ppm	8118	114	8363	429	8350	197	7655	94	38	13620	12689	210	15360	14348	231
V	ppm	252	5	258	10	259	10	241	4	39	425	434	4	309	328	5
Cu	ppm	179	4	172	36	202	14	180	2	37	21	16.3	0.3	87.9	76.9	2.4
Zn	ppm	104	7	107	4	132	16	104	7	38	125	146	4	110	108	5
Ga	ppm	21.8	0.8	23.9	1.9	25.2	1.7	21.6	1.2	36	23	23.4	0.2	20	22.5	1.0
As	ppm	6.69	0.41	7.27	0.91	7.32	0.33	6.43	0.33	37		1.18	0.05		0.26	0.14
Rb	ppm	79.2	2.5	81.1	1.9	84.0	4.7	77.5	2.1	31.4	47	51.3	0.7	8.7	9.6	0.4
Sr	ppm	297	7	302	7	321	5	286	4	78.4	342	326	4	356	348	10
Y	ppm	47.9	0.7	49.1	1.2	51.0	1.7	45.2	0.6	38	35	32.2	0.7	25.4	23.8	0.6
Zr	ppm	331	7	358	21	359	12	313	5	38	184	175	3	152	147	6
Nb	ppm	6.97	0.21	7.46	0.35	7.53	0.16	6.64	0.08	40	12.5	12.4	0.2	15.0	15.1	0.6
Mo	ppm	3.70	0.13	3.81	0.13	3.99	0.29	3.54	0.08	38		278	3		4.0	0.4
Sb	ppm	0.96	0.04	1.03	0.06	1.10	0.03	0.94	0.08	38		0.34	0.03		0.14	0.02
Cs	ppm	2.85	0.06	2.96	0.10	2.97	0.15	2.71	0.05	42		1.25	0.05		0.14	0.01
Ba	ppm	833	19	833	19	857	23	784	16	39.7	683	681	12	123	125	5
La	ppm	25.6	0.8	26.1	0.9	26.4	1.0	24.1	0.7	35.8	24.7	24.2	0.5	13.1	13.0	0.5
Ce	ppm	63.2	1.8	63.3	1.9	64.4	2.3	59.6	1.7	38.7	53.3	51.6	0.4	32.4	32.6	1.3
Pr	ppm	8.84	0.33	8.91	0.33	8.97	0.48	8.23	0.12	37.2	6.70	6.33	0.08	4.60	4.42	0.18
Nd	ppm	41.2	1.4	41.5	1.4	42.4	2.8	38.3	0.9	35.9	28.9	28.0	0.4	21.6	21.5	0.9
Sm	ppm	9.79	0.42	9.83	0.32	10.23	0.63	9.03	0.21	38.1	6.59	6.44	0.11	5.54	5.59	0.21
Eu	ppm	2.20	0.08	2.25	0.05	2.30	0.04	2.05	0.06	35	1.97	1.84	0.01	1.92	1.86	0.07
Gd	ppm	9.15	0.32	9.42	0.33	9.64	0.36	8.54	0.30	36.7	6.71	6.19	0.20	5.92	5.51	0.27
Tb	ppm	1.39	0.03	1.39	0.04	1.44	0.12	1.29	0.03	36	1.02	0.93	0.01	0.89	0.82	0.03
Dy	ppm	8.93	0.18	9.10	0.25	9.20	0.59	8.34	0.22	36	6.44	6.11	0.18	5.22	5.04	0.19
Но	ppm	1.79	0.05	1.80	0.04	1.84	0.14	1.64	0.05	38	1.27	1.22	0.02	0.96	0.93	0.03
Er	ppm	5.05	0.07	5.11	0.18	5.19	0.32	4.72	0.10	38	3.70	3.47	0.05	2.54	2.40	0.09
Tm	ppm	0.72	0.02	0.74	0.03	0.77	0.06	0.68	0.02	38	0.51	0.50	0.02	0.33	0.32	0.02
Yb	ppm	4.80	0.13	4.86	0.16	5.06	0.29	4.49	0.07	39.2	3.39	3.25	0.08	2.10	1.97	0.12
Lu	ppm	0.70	0.02	0.70	0.02	0.74	0.05	0.66	0.01	36.9	0.50	0.48	0.01	0.29	0.26	0.01
Hf	ppm	7.82	0.33	8.21	0.54	8.33	0.69	7.36	0.12	35	4.84	4.48	0.05	3.93	3.64	0.13
Та	ppm	0.46	0.02	0.48	0.03	0.48	0.03	0.43	0.00	40	0.78	0.77	0.02	0.96	0.91	0.05
W	ppm	0.64	0.05	0.63	0.03	0.65	0.03	0.58	0.03	40		0.55	0.03		0.48	0.04
Pb	ppm	11.67	0.77	12.82	0.88	13.80	1.56	10.94	0.57	38.57	11.0	11.6	0.41	2.07	2.14	0.16
Th	ppm	3.65	0.18	3.77	0.19	3.82	0.19	3.36	0.13	37.79	5.90	5.74	0.14	1.02	0.96	0.04
U	ppm	2.40	0.11	2.44	0.06	2.44	0.08	2.25	0.06	37.38	1.69	1.70	0.04	0.55	0.56	0.04

Table 3. Major and trace element concentrations in single tephra glass shards and reference glasses obtained by LA-ICP-MS.

Note: Represented analyses are mean values from 5 to 6 acquisitions on different points for every sample (MEAN). STDEV refers to 1 standard deviation of the mean. The reference compositions (REF) of NIST-612, BCR-2G and KL-2G are recommended from the GeoReM compilation (GeoRem, 2011) except for Ti concentration in NIST-612 which was set to 38 ppm (instead of recommended 44 ppm) to reproduce the concentrations in BCR-2G and KL-2G by using calibration based on NIST-612. The data on referce materials were obtained during the same analytical session with tephra analyses (November, 23, 2011).

Table 4. Average ele	ectron probe ana	inyses of vo	icanic glass from	ii uistai rios	sky tephras					
Sample#	1264b	-1	763-	1	97057	7-8	97051	-19	JB112_68	2-683
Eruption / Layer ID	PL1		PL1		PLI	l	PL1		PL1	
Age (cal BP)	11650	C	1165	0	1165	50	1165	0	11650	0
I AT / I ONG	N 56 5061° F	161 4784°	N 56 5671° F	161 4770°	N 56 6322° F	161 4608°	N 56 6572° F	161 4969°	N 56 2533° F	162 7140°
Section location	Shivelyeh y	rolaana	Shivelyeh	roleene	Shiveluch	voloono	Shiveluch		Lat Komaha	102.71 4 0
		olcallo		voicano		voicalio		volcano		usk area
N anis.	20		20		13		13		18	
	Average	1 s.d.	Average	l s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.
SiO_2	60.40	0.47	60.65	0.45	60.51	0.39	60.29	0.69	60.74	0.44
TiO_2	1.52	0.04	1.50	0.03	1.48	0.03	1.48	0.03	1.50	0.03
A1.O.	15.00	0.15	15 10	0.19	15.00	0.10	15 17	0.02	15.00	0.14
лц ₂ 0 ₃	15.20	0.15	15.10	0.18	15.22	0.12	15.17	0.23	15.20	0.14
FeO	/.4/	0.23	7.42	0.19	/.36	0.32	7.59	0.40	/.18	0.27
MnO	0.14	0.04	0.14	0.05	0.15	0.05	0.14	0.05	0.13	0.05
MgO	2.31	0.10	2.24	0.10	2.30	0.10	2.39	0.14	2.27	0.12
CaO	5.36	0.16	5.22	0.19	5.15	0.15	5.25	0.30	5.18	0.21
Na ₂ O	3.59	0.12	3.67	0.15	3.83	0.08	3.76	0.08	3.70	0.13
K ₂ O	3 1/	0.07	3 77	0.10	3 17	0.00	3 1/	0.13	3 73	0.13
	5.14	0.07	3.22	0.10	5.17	0.09	5.14	0.15	5.25	0.13
P_2O_5	0.73	0.05	0.71	0.06	0.71	0.05	0.70	0.05	0.71	0.04
Cl	0.04	0.01	0.03	0.01	0.03	0.01	0.04	0.01	0.04	0.01
F	0.04	0.03	0.03	0.03	0.06	0.05	0.03	0.03	0.03	0.03
SO_3	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.02
Total	100		100		100		100		100	
	100		100		100		100		SO201-77-SR1	>0.1 116-
Sample#	1761h	-4	VK JUUO	-01-9	IR110 64	54-665	SO201 2 81	14-17 cm	117 av	~ •.1_110- m
Emption / Lover ID	DI 2	-+	DI 2	-01-2)+-005	DL 2 / 0	$\frac{14-1}{0}$	DI 2 / S	D 1
	FL2	n	FL2	, 	FL2		FL2/3		FL2/3	
Age (cal BP)	10200	J	1020	0	1020	1 (2 71 400	1020		10200	
LAT / LONG	N 56.5061° E	161.4784°	N 56.4752° E	162.2904°	N 56.2533° E	162.7140°	N 56.7165° E	170.4962°	N 56.3305° E	170.6997°
Section location	Shiveluch v	olcano	Ust-Kamcha	atsk area	Ust-Kamch	atsk area	Shirshov Ridge,	Bering Sea	Shirshov Ridge,	Bering Sea
N anls.	20		8		20		6		19	
	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.
SiO ₂	58.50	0.31	58.62	0.47	58.64	0.46	58.61	0.25	58.48	0.43
TiO	1 /1	0.02	1 46	0.12	1 41	0.02	1.40	0.01	1.40	0.02
1102	1.41	0.03	1.40	0.12	1.41	0.03	1.40	0.01	1.40	0.03
Al_2O_3	16.07	0.13	16.23	0.12	16.18	0.15	16.09	0.19	16.08	0.15
FeO	7.82	0.22	7.55	0.40	7.67	0.38	7.75	0.24	7.67	0.32
MnO	0.15	0.04	0.12	0.05	0.12	0.04	0.09	0.04	0.14	0.06
MgO	2.86	0.06	2.84	0.16	2.88	0.12	2.94	0.08	2.91	0.09
CaO	6.23	0.11	5.97	0.21	6.10	0.16	6.10	0.13	6.12	0.23
Na _o O	2.04	0.00	4.02	0.14	2 90	0.14	2.02	0.22	4.04	0.10
	3.84	0.08	4.02	0.14	5.89	0.14	5.92	0.55	4.04	0.10
K_2O	2.40	0.04	2.50	0.18	2.41	0.08	2.45	0.06	2.47	0.09
P_2O_5	0.61	0.04	0.60	0.05	0.60	0.04	0.59	0.02	0.59	0.03
Cl	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.04	0.01
F	0.03	0.03	0.00	0.00	0.02	0.03	0.01	0.02	0.02	0.04
SO.	0.02	0.02	0.04	0.00	0.02	0.02	0.02	0.02	0.04	0.02
5 0 ₃	0.04	0.02	0.04	0.02	0.03	0.05	0.02	0.02	0.04	0.03
Total	100		100		100		100		100	
Sample#	K 11 00	10	K0 115	13	K0 115	1/10	K0 115	1 <i>1</i> h	K0 115	15
Sample#	K11-09	-19	K9-03-	-13	K9-03-	·14a	К9-05-	140	К9-03-	15
Eruption / Layer ID	PL3		100		100	00	100	20	1020	
Age (cal BP)	<1020	10	<1020	JU 1 7 0 01500	<102		<102		<1020	
LAT / LONG	N 56.5061° E	161.4800°	N 56.1651° E	159.9460°	N 56.1651° E	159.9460°	N 56.1651° E	159.9460°	N 56.1651° E	159.9460°
Sampling site #	K11-0	19	K9-U	5	K9-U	J5	K9-U	15	K9-U	5
Section location	Shiveluch v	olcano	Kozyrevsk towr	n, Ushki site	Kozyrevsk tow	n, Ushki site	e Kozyrevsk tow	n, Ushki site	Kozyrevsk town	i, Ushki site
N anls.	18		18		14		14		16	
	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.	Average	1 s.d.
SiO ₂	60.67	0.53	63.11	1.85	60.12	0.25	60.70	1.56	61.97	0.74
TiO	1 17	0.00	1 50	0.00	1 = 7	0.05	1 55	0.00	1 27	0.10
	1.4/	0.06	1.30	0.09	1.57	0.05	1.55	0.08	1.37	0.10
AI_2O_3	15.54	0.38	14.58	0.63	15.03	0.19	15.22	0.35	15.68	0.39
FeO	6.99	0.24	6.72	0.49	7.77	0.23	7.33	0.55	6.31	0.24
MnO	0.12	0.05	0.13	0.04	0.14	0.04	0.16	0.04	0.14	0.03
MgO	2.44	0.14	1.58	0.52	2.37	0.10	2.20	0.49	1.93	0.29
CaO	5.12	0.30	3.83	0.77	5.19	0.13	4.80	0.97	4.65	0.36
Na.O	2.05	0.17	1.05	0.1.4	2.02	0.15	2.00	0.10	A 17	0.07
11u ₂ O	3.95	0.17	4.05	0.14	3.83	0.15	3.99	0.12	4.1/	0.07
К ₂ О	2.89	0.23	3.75	0.47	3.11	0.10	3.18	0.63	3.12	0.25
P_2O_5	0.72	0.05	0.64	0.10	0.77	0.05	0.72	0.09	0.54	0.04
Cl	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01
F	0.02	0.01	0.05	0.04	0.02	0.01	0.07	0.01	0.05	0.04
SO	0.02	0.03	0.00	0.04	0.04	0.05	0.07	0.05	0.05	0.07
50 ₃	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.01
Tatal	100		100		100		100		100	

Table 4. Average electron probe analyses of volcanic glass from distal Plosky tephras

Note: All analyses are normalized on unhydrous basis. Analyses of individual glass shards are given in Supplementary table 1 .

Table 5. Volume estim	ates for Plosky	y tephra
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Tephra	Isopach (cm)	Area (km²)	Vmin (km ³), Legros (2000)	Tephra volume (km ³), Bonadonna and Costa (2012)
PL2	50	182.2	0.34	
PL2	10	2222.7	0.82	
PL2	5	7118.4	-	
PL2	3	65927.6	7.3	12.3
PL2	2	65927.6	4.87	10.4
PL1	2	5420.1	0.4	-

Note: Vmin – minimum tephra volume







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Figure Click here to download Figure: Fig_13.eps



Figure Click here to download Figure: Fig_14.eps



Figure Click here to Download Figure: Fig_15.eps



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