

# Eruptive chronology of Tungurahua volcano (Ecuador) revisited based on new K-Ar ages and geomorphological reconstructions

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1	Eruptive chronology of Tungurahua volcano (Ecuador) revisited based on new K-Ar
2	ages and geomorphological reconstructions
3	
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14	
15	ABSTRACT
16	This study focuses on the evolution through time of Tungurahua volcano (Ecuador), and
17	provides new information regarding its history. Eighteen new K-Ar ages constrain its
18	construction and the activity of its three successive edifices. We show that the volcano is
19	much younger than expected. Indeed, the older edifice activity only began around $293 \pm 10$
20	ka, and ended at $79 \pm 3$ ka. After ~50 ka of quiescence, the second edifice started growing at
21	$29 \pm 2$ ka after a major sector collapse, and itself collapsed at ~3 ka. Since then, the third
22	edifice filled the amphitheatre and is still active. Together with numerical reconstructions of
23	the morphology of the three edifices flanks before erosion, these new ages allow us to

 $0.9 \pm 0.2 \text{ km}^3/\text{ka}$  for the two older edifices to  $2.5 \pm 1.0 \text{ km}^3/\text{ka}$  for the youngest, as well as an

quantify the magmatic productivity rates during their construction, from  $0.6 \pm 0.3$  and

erosion rate of  $0.2 \pm 0.1$  km<sup>3</sup>/ka, occurring since the end of Tungurahua I construction. Major 26 27 and trace element contents of lavas from the three edifices display rather similar trends. Combined with our new ages, the magmatic signature through time does not seem to have 28 been significantly affected either by the sector collapses experienced by the volcano, or by 29 changes of the deep magmatic source. Finally, our results show that the K-Ar dating method 30 by the unspiked Cassignol-Gillot technique performed on groundmass can be successfully 31 applied to lava flows older than the Holocene, while the uncertainties related to younger units 32 can prevent an accurate age determination. Particularly, this method can be applied to 33 Quaternary volcanoes from the Ecuadorian arc, with many of them remaining without 34 35 knowledge of the timing of their past activity.

- 36
- 37 Keywords:
- 38 Ecuador
- 39 Tungurahua volcano
- 40 K-Ar dating
- 41 Geomorphology
- 42 Geochemistry
- 43

## 44 **1. Introduction**

The Ecuadorian arc presents a remarkably dense volcanism, composed of about 85 Quaternary volcanic edifices (Hall et al., 2008; Bernard and Andrade, 2011). Twenty-five of them are potentially active or presently erupting, such as Sangay, Cotopaxi, Reventador and Tungurahua volcanoes (Fig. 1; Bernard and Andrade, 2011). Tungurahua volcano (5023 m a.s.l.; Lat. 01°28'S; Long. 78°27'W) is one of the most active volcanoes in the Andean Northern Volcanic Zone with at least one eruption per century since the 13<sup>th</sup> century (Le Pennec et al., 2008, 2016). It is characterized by a strombolian to subplinian activity, and

experienced at least two major sector collapses during the last 30 ka (Hall et al., 1999; Le 52 Pennec et al., 2013). Since 1999, the ongoing eruption has seriously threatened surrounding 53 villages and infrastructures (Samaniego et al., 2008; Le Pennec et al., 2012). The recent 54 55 activity is well studied and carefully monitored (e.g., Molina et al., 2005; Arellano et al., 2008; Kumagai et al., 2011; Hall et al., 2013; Bernard et al., 2014; Hidalgo et al., 2015), but 56 the timing of its pre-Holocene history remains poorly documented. Reconstructing the past 57 58 eruptive history of Tungurahua volcano is essential to better understand its growth and evolution. This study combines stratigraphic analyses, new K-Ar ages and geomorphometric 59 reconstructions to better constrain the construction and destruction stages of Tungurahua 60 61 volcano through time, and to quantify its magmatic output rates, as well as the erosion rate occurring during quiescence periods. In addition, geochemical analyses allow us to study the 62 long-term evolution of the lavas composition. We show in particular that the initial activity of 63 64 Tungurahua volcano is much younger than previously thought, and that its construction is characterized by an increase of the eruptive rate since the last 3 ka BP. 65

66

#### 67 2. Geological context

68 The Andean volcanic arc originates from the subduction of the oceanic Nazca plate 69 beneath the continental South American plate. The arc comprises four distinct zones, including the Northern Volcanic Zone (NVZ), which lies in Ecuador and Colombia. To the 70 west of the NVZ, an oceanic plateau, the Carnegie ridge, subducts below Ecuador (Fig. 1a). It 71 has been proposed that the subduction of this ridge may impact the thermal gradient at depth 72 73 and the deep magmatic sources (e.g., Samaniego et al., 2002; Bourdon et al., 2003; Hidalgo et 74 al., 2012; Ancellin et al., 2017), which could explain the high density of volcanoes observed in Ecuador (Martin et al., 2014). Tungurahua volcano is located in the southern part of the 75 76 Ecuadorian volcanic arc, on the Eastern Cordillera (Fig. 1b). Constructed upon the

Palaeozoic-Mesozoic metamorphic basement (Aspden and Litherland, 1992), this andesitic 77 stratovolcano is surrounded by the Puela (S), Chambo (W) and Pastaza (N) rivers (Fig. 2). 78 The upper part of the edifice presents steep flanks with  $40^{\circ}$  slopes, while ~20-25° slope 79 plateaux incised by deep valleys constitute its lower part, with a progressive change in 80 steepness. The morphology of the eastern flank shows features of glacial erosion (u-shaped 81 valleys; Clapperton, 1990; Heine, 2000), as well as deep fluvial incisions due to the tropical 82 precipitation regime. It contrasts with the western flank which is smoothed by the recent 83 volcanic deposits. The internal structure and plumbing system of Tungurahua volcano are not 84 well known. Nevertheless, petrological, melt inclusions, seismic tomography and 85 interferometric studies suggest the presence of a subvertical upper conduit located above a 86 shallow magmatic reservoir, supplied by mafic magmas from a deeper reservoir, located 87 around 5 and 8.5 km below the summit, respectively (Molina et al., 2005; Samaniego et al., 88 89 2011; Kumagai et al., 2011; Champenois et al., 2014; Myers et al., 2014).

Previous works showed that Tungurahua volcano was built in three construction stages, 90 91 namely Tungurahua I, II and III, and experienced two major sector collapse events (Hall et al., 92 1999; Le Pennec et al., 2013, 2016). Inclined plateaux of the northern, eastern and southern flanks essentially belong to Tungurahua I activity, which started during the Pleistocene, based 93 on two available whole-rock K-Ar ages of  $770 \pm 5$  and  $350 \pm 4$  ka (Barberi et al., 1988). The 94 western part of Tungurahua I was destroyed by a first sector collapse, <sup>14</sup>C dated at 95  $33.1 \pm 0.2$  ka BP (Le Pennec et al., 2013), which might have been triggered by a silicic 96 cryptodome intrusion (Le Pennec et al., 2006). The resulting amphitheatre volume was 97 estimated at 10 km<sup>3</sup> (Bustillos, 2008), but the collapse scar location is not accurately 98 identified in the present-day edifice morphology. Tungurahua II lavas and deposits then filled 99 the amphitheatre, before being destroyed in turn by a new western sector collapse <sup>14</sup>C dated at 100  $2955 \pm 90$  BP (Hall et al., 1999) and  $2960 \pm 30$  BP (Le Pennec et al., 2013). It was triggered 101

by a new viscous intrusion or magma mixing occurring in the chamber (Hall et al., 1999; Le 102 Pennec et al., 2006, 2013). The avalanche deposits associated with this second event cover 103 between 23 and 80 km<sup>2</sup>, for a collapse volume estimated between 2.8 and 6 km<sup>3</sup> (Bustillos, 104 2008 and Hall et al., 1999 respectively). However, the area and the volume obtained by Hall 105 et al. (1999) are necessarily higher because they mapped as a single sector collapse the 106 deposits of the two sector collapses of Tungurahua, and the one experienced by Huisla 107 volcano (Fig. 2; Bustillos, 2008). The southern location of the scar boundary is well delimited 108 109 in the morphology, whereas the northern part was first proposed along the Pondoa plateau (Hall et al., 1999), and recently shifted to the west based on geomorphological and 110 seismological studies (Molina et al., 2005; Le Pennec et al., 2006; Fig. 2). Due to this collapse 111 and continuous erosion, remnants of Tungurahua II mainly crop out on the eastern summit 112 area and in the southwestern valleys (i.e. the Tiacos lava sequences of Hall et al., 1999). 113 114 Products from the younger and still active Tungurahua III cone have then filled the amphitheatre left by the second sector collapse (Hall et al., 1999; Le Pennec et al., 2006, 115 116 2013). Lavas and pyroclastic flow deposits, as well as tephra fall and epiclastic layers displaying basaltic andesite to dacitic composition make up the present western flank. Eight 117 pre-Columbian eruptive periods were identified, and five major eruptions occurred during 118 historical times: AD 1640-1641, 1773-1776, 1886-1888, 1916-1918 and 1999-present, with 119 therefore a recurrence rate of about one pyroclastic flow-forming event per century (Hall et 120 al., 1999; Le Pennec et al., 2008, 2016). 121

Given that Tungurahua III activity has already been well described and <sup>14</sup>C dated (Hall et al., 1999; Le Pennec et al., 2006, 2008, 2013, 2016), in this study we focus on the two older edifices, Tungurahua I and II.

125

#### 126 **3. Materials and methods**

Twenty-four fresh hand-size samples of lava flows were collected during several field 128 trips from 2013 to 2016 (Fig. 3a). Geographical coordinates of the samples are provided in 129 130 Table 1 and the associated KMZ file is available in Appendix C. In order to constrain the onset of the volcano activity, seven samples were taken from the basal flows, close to the 131 contact with the metamorphic basement (PS-102, PS-106, PS-110, 16EQ15, 16EQ12, PS-118 132 133 and 16EQ26). Sample 16EQ12 was collected from a breccia containing monogenic blocks. Seven lavas were sampled in the uppermost part of Pondoa, Runtún, Ulba and Patacocha 134 plateaux (Fig. 2). Because of their position in the stratigraphic sequence of these plateaux, we 135 136 infer that they were emplaced late in Tungurahua I history (PS-116, PS-99, 16EQ16, 16EQ17, 16EQ25, TUNG 3, TUNG4). Seven lavas of Tungurahua II were sampled along Ulba valley 137 (PS-111, 16EQ19), in Las Juntas and Juive Grande areas (PS-107, PS-109), and near 138 Palitahua waterfalls (Fig. 2; PS-117, PS-119, 16EQ13). Two recent lavas were also sampled 139 to compare our dating method with published <sup>14</sup>C ages: a dacitic flow near Cusúa (16EQ36), 140 which belongs to the beginning of Tungurahua III activity (Hall et al., 1999), and the Baños 141 lava flow (16EQ37). In addition, a massive lava flow erupted from an unknown source and 142 exposed between the Pastaza valley and Vizcaya village was also sampled (16EQ20). The aim 143 144 was to determine whether it could be contemporaneous with Tungurahua volcano activity.

145

146 *3.2. K-Ar dating* 

The potassium-argon (K-Ar) dating method was applied here by using the unspiked Cassignol-Gillot technique (Cassignol and Gillot, 1982), which was developed for Quaternary volcanics with low radiogenic argon ( $^{40}$ Ar<sup>\*</sup>) contents (Gillot et al., 2006). It has been shown to be especially suitable for dating young subduction lavas with low K and high Ca contents, as is the case for instance in South America and in the Lesser Antilles (e.g., Samper et al., 2009; Germa et al., 2011). The technique relies on the detection of a very small difference between the isotopic  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio extracted from the sample and the atmospheric ratio. The radiogenic argon content, which derived from the radioactive decay of  ${}^{40}$ K, together with the potassium content of the sample and the  ${}^{40}$ K decay constant (Steiger and Jäger, 1977), allow determining the age of the lava sample.

157

#### 158 *3.2.1. Sample preparation*

The groundmass is the last phase to crystallize when lavas cool. It is thus enriched in 159 incompatible elements, including potassium, and in equilibrium with the atmosphere. Hence 160 the initial argon isotopic ratios in the groundmass are atmospheric, and it is devoid of 161 radiogenic argon ( ${}^{40}Ar^*$ ). On the other hand, phenocrysts can carry inherited  ${}^{40}Ar^*$ , that might 162 bias ages significantly (e.g., Harford et al., 2002; Samper et al., 2008). We therefore carried 163 out our measurements on the groundmass following a careful mineralogical separation. 164 Observation of thin sections (available on Appendix A) helped us to attest of the samples 165 166 freshness, and to determine the size fraction. The selected samples were crushed and sieved at 80-125 µm, 80-160 µm, or 125-250 µm, then ultrasonically washed with a 10% nitric acid 167 solution and deionized water. Heavy liquids, mainly bromoform, were used to isolate the 168 groundmass by removing heavy mafic minerals, and light weathered fractions, if present. 169 Finally, the separation was refined with a magnetic separator, which removed non-magnetic 170 plagioclases remaining within the magnetic groundmass, as their respective ranges of density 171 overlap. The obtained fractions of groundmass, which amount to only a few percent of the 172 initial sample, have a narrow density range, with a typical value of 2.71. Their homogeneity 173 174 was checked under a binocular magnifier, and both potassium and argon measurements were carried out at the Laboratoire GEOPS of Université Paris-Sud (Orsay, France). 175

176

#### 177 *3.2.2. Potassium and argon measurements*

Potassium was measured with an Agilent 240 Series AA flame absorption spectrometer, after dissolving samples with an acid attack. Results were corrected with reference values of MDO-G (K = 3.510%; Gillot et al., 1992) and BCR-2 (K = 1.481%; Raczek et al., 2001) standards.

Argon was measured using a mass spectrometer similar to the one described by Gillot and Cornette (1986). Very stable conditions reached during the measurements rendered the use of the <sup>38</sup>Ar spike, needed for the conventional K-Ar technique, unnecessary. Gases extracted by fusing the sample were purified with high temperature Ti foam and SAES getters. An air pipette containing a known amount of <sup>40</sup>Ar atoms was used to calibrate the mass spectrometer. Another air pipette, with the same <sup>40</sup>Ar signal as the sample to be dated, allows an accurate atmospheric correction to be performed.

The accuracy of this correction and of the  ${}^{40}$ Ar calibration are routinely checked by analyses of international standards samples measurements, such as ISH-G (1301-1302 AD; Gillot et al., 1992) and HD-B1 (24.21 ± 0.32 Ma; Hess and Lippolt, 1994).

## 192 The total relative age uncertainty ( $\sigma_{tot}$ ) is calculated using the following formula:

193 
$$\sigma_{tot} = \sqrt{\sigma_K^2 + \sigma_{40}^2_{Ar_{cal}} + \sigma_{40}^2_{Ar^*}}$$

194 The relative uncertainties of the potassium content ( $\sigma_K$ ) and the <sup>40</sup>Ar calibration ( $\sigma_{40_{Ar_{cal}}}$ ) are 195 both evaluated at 1%. The uncertainty of radiogenic argon ( $\sigma_{40_{Ar^*}}$ ) depends on the radiogenic 196 content of the sample. For young samples, this uncertainty is larger because of their high 197 atmospheric and low radiogenic argon contents. The <sup>40</sup>Ar\* detection limit of our 198 measurements is presently at 0.1% (Quidelleur et al., 2001).

All potassium and argon measurements were performed at least twice in order to checktheir reproducibility within uncertainty. Final ages and uncertainties were calculated by

averaging each analysis, weighted by their  ${}^{40}$ Ar\* content. However, for the youngest samples where  ${}^{40}$ Ar\* content is lower than 0.1%, ages were calculated using an unweighted average. Ages obtained here are given at the 1  $\sigma$  confidence level (Table 1).

204

205 *3.3. Geochemical analyses* 

Major and trace element whole-rock contents of all samples were measured at the 206 207 Laboratoire Géosciences Océan of the Université de Bretagne Occidentale (Brest, France). Agate-crushed powders of the twenty-four samples were analysed by ICP-AES (Inductively 208 Coupled Plasma - Atomic Emission Spectrometry), following the analytical procedure 209 210 detailed in Cotten et al. (1995). Relative uncertainties are  $\leq 2\%$  for major elements and  $\leq 5\%$ for trace elements. Major elements data were recalculated to a total of 100% on a water free-211 basis and together with trace elements are provided in Table 2. Our geochemical database was 212 completed by seventy-two unpublished major and trace elements analyses of samples from 213 the three edifices and blocks from the sector collapse deposits (Hall et al., 1999; Bustillos, 214 215 2008), which are presented in Appendix B.

216

## 217 3.4. Numerical reconstructions of past morphology

Numerical reconstructions of palaeotopographies were used to model the morphology of the volcano during its main phases of construction, erosion and collapse. They provided information regarding evolution of the magmatic productivity through time, and the erosion rates, which are influenced by precipitation and glacial-interglacial alternating periods. The present topographic data are extracted from a 30-m SRTM Digital Elevation Model (DEM). The reconstruction method used here was developed in Lahitte et al. (2012) and improved in Germa et al. (2015). It is summarized below.

Past Tungurahua topographic models are constrained from points selected from the 225 present-day topography, as belonging to non-eroded surfaces. In general, they are from crests, 226 upper parts of plateaux, planeze surfaces or recent deposits (Fig. 4a and b). ShapeVolc, a 227 228 specifically developed method, is used for modelling the different palaeotopographies based on these points (Lahitte et al., 2012). This method first finds a global model, by defining the 229 best summit location and the parameters of the function that define a revolution surface, 230 which best fit the selected points following a least-squares method adjustment. Thereby, 231 Tungurahua I reconstruction displays a conical shape with linear flank profiles and an 232 elliptical base, while Tungurahua II and III have an exponential shape with a concave profile 233 (Fig. 4c). The software then adjusts the first-order modelling by modifying locally the 234 parameters of the global function, in order to take into account local elevation variations, i.e. 235 the irregularity of the surface of each stage of construction (Lavigne et al., 2013; Germa et al., 236 2015). These second-order surfaces correspond to our final construction models. The 237 evolution of Tungurahua I altitude after its erosion is calculated by lowering each elevation of 238 239 the model as a linear function of time, between the model elevation and the present 240 topography. Moreover, as the geometry of the depressions of the collapses is not precisely known, we modelled them by an interpolation between points currently located on the edge of 241 the scars and two profiles forming the possible bottom surface represented by the 242 discontinuous curves in Fig. 4a, located so as to respect the collapse volumes estimates, 243 respectively of ~10 and ~2.8 km<sup>3</sup>, based on the deposits located in the Río Chambo valley 244 (Hall et al., 1999; Bustillos, 2008). 245

Finally, the reconstruction of pre-Tungurahua topography is obtained by selecting DEM points which belong to the metamorphic basement outcropping around the volcano, in order to extrapolate them under the present volcano surface. This palaeosurface is modelled applying a Local Polynomial Interpolation method with a resolution of 100 m, using ArcGis software. The model is therefore smooth, since we cannot constrain the exact morphology ofthe basement 300 ka ago, which is currently overlaid by Tungurahua products.

252

## 253 *3.5. Magmatic productivity and erosion rates*

The volume (V), either constructed (Vc) or eroded (Ve), corresponds to the integration 254 of the difference between the upper and the lower surface, over the area of the edifice 255 considered. In this fashion, the eroded volume is the difference between the modelled surface 256 and the present topography ( $\Delta z$ ). The deposits volume for each edifice corresponds to the 257 258 difference between the surface elevation modelled at the end of their constructions and the one which preceded the edifice construction. Erosion that occurred during the Tungurahua I 259 and II construction lowered the apparent volume of emitted magma. To take into account this 260 261 erosion, we added to the raw volume the eroded volume estimated by considering that the erosion rate calculated for the last 80 ka was rather constant though time. The volume 262 uncertainty ( $\sigma_V$ ) is calculated using the following formula: 263

264 
$$\sigma_V = V \cdot \frac{\sigma_z}{\Delta z}$$

where the uncertainty of the elevation ( $\sigma_z$ ) is defined as  $\sigma_z = \sqrt{\sigma_i surf^2 + \sigma_f surf^2}$ , where the uncertainties of the initial ( $\sigma_i surf$ ) and the final ( $\sigma_f surf$ ) surface elevation are estimated to 200 m for the interpolated surface before Tungurahua construction, 50 m for our surface models, and null for the present elevation. These uncertainties are obtained from the standard deviation of the elevation dispersion of the points selected to construct the palaeotopographies around the surface model, and calculated from the error map of the kriging interpolation method for the pre-Tungurahua surface (Ricci et al., 2015a).

Together with our new K-Ar ages, these volumes, divided by the period of activity or quiescence ( $\Delta$ T), allow us to calculate the apparent magmatic productivity (*MPR*) and erosion (*ER*) rates of Tungurahua volcano, with  $MPR = \frac{Vc}{\Delta T}$ , and  $ER = \frac{Ve}{\Delta T}$ . As the parameters involved in these ratios are independent, the uncertainty of the  $\frac{\sigma_R}{R}$  ratio is then defined as the square root of the quadratic sum of the relative uncertainties of both stage duration ( $\sigma_T$ ) and volume ( $\sigma_V$ ). Consequently, the uncertainty of the magmatic productivity or erosion rate ( $\sigma_R$ ) is calculated using the following formula:

279 
$$\sigma_R = R \cdot \sqrt{\left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_T}{\Delta T}\right)^2}$$
 where *R* is the considered rate.

The uncertainty on the duration is estimated from K-Ar ages uncertainty, which 280 281 constrains the timing of each edifices construction and erosion. Consequently, because of the relatively good age precision,  $\sigma_R$  is mainly dominated by the volume uncertainty. Moreover, 282 this technique of calculation based on numerical reconstructions is more accurate than 283 traditional methods, which generally use approximate volumes. We also present the minimum 284 and maximum values of emission rates, considering the upper and lower values of both 285 volume and time period. However, we chose to only use the previous calculation method for 286 discussion and comparisons, since it provides a more realistic result and takes into account the 287 Gaussian distribution of the data. Results of the volumes, magmatic productivity and erosion 288 rates calculations are provided in Table 3. 289

290

#### 291 **4. Results**

#### 292 *4.1. Petrography of the samples*

There is no clear mineralogy difference between the lava flows from the three edifices. Most of the Tungurahua lava flow samples have porphyric textures with a variable amount of plagioclase, orthopyroxene, clinopyroxene and olivine phenocrysts, except samples of Vizcaya lava flow (16EQ20) and the lower Runtún plateau (PS-110 and PS-106), which present a vitreous texture with scarce crystals (Appendix A). Sample PS-119, from the southern flank, also present some amphibole crystals, but none of our lava flow sample contains biotite crystals. The groundmass contains plagioclase, pyroxene and Fe-Ti oxide microcrysts separated by volcanic glass, and mainly represents about 50-70% of the rock volume. Moreover, some samples present color variations of their groundmass, such as 16EQ15 and 16EQ17 from the Ulba plateau, 16EQ19 and PS-111 from the bottom of Ulba Valley, PS-99 from the Runtún upper part, as well as PS-117 and PS-118 from the southern flank (Fig. 3). These variations correspond to more or less differentiated magmas and display that magma mixing processes occurred.

306

#### 307 *4.2. K*-*Ar* dating

308 K-Ar ages obtained in this study are presented in Table 1 and Fig. 3 and 5. Six samples were not considered because they were either altered (16EQ12) or too contaminated by 309 310 atmospheric argon (16EQ13, 16EQ19, 16EQ36, TUNG3) to yield a meaningful age. 311 Moreover, as the base and the top of Ulba sequence are well constrained by samples 16EQ15 and 16EQ17 respectively, dating sample 16EQ16 was not necessary, since it is an 312 intermediate lava located between the other two samples. Eighteen samples were successfully 313 dated, with the K content of the groundmass ranging between 1.122% and 3.253%, and the 314 maximum radiogenic argon content reaching 13.78%. These new data allow us to refine the 315 316 timing of activity of Tungurahua volcano. The oldest edifice is well constrained by eleven ages, and was built between  $293 \pm 10$  and  $79 \pm 3$  ka. Our ages obtained for the lavas from 317 Ulba, Pondoa and Runtún plateaux range between  $92 \pm 1$  and  $79 \pm 3$  ka, and suggest a gap of 318 319 activity between 76 ka and the ~33 ka first sector collapse event (Fig. 5; Le Pennec et al., 320 2013). The construction of Tungurahua II started at least  $29 \pm 2$  ka (PS-117), therefore 321 quickly after the first sector collapse. Similarly than for Tungurahua I, we have no evidence of 322 activity between 27 and 15 ka. The five youngest ages are below 15 ka, but their relatively 323 large uncertainties prevent us to determine whether they belong to Tungurahua II, or are

younger than 3 ka and are part of Tungurahua III. Only lava from the sample PS-109 clearly belongs to Tungurahua II. We propose that samples PS-107, PS-111 and PS-119 are related to Tungurahua II activity, while the sample of Baños lava flow (17EQ37) was emitted in the early stage of Tungurahua III construction, based on their stratigraphic relationships, further described in the discussion. Finally, the Vizcaya lava flow (16EQ20) dated at  $253 \pm 5$  ka, is coeval with the early construction of Tungurahua I.

330

## 331 *4.3. Whole-rock geochemical analyses*

The major and trace element contents for all samples are presented in Table 2. Loss on ignition (L.O.I) measurements are low, with a maximum value of 1.15%, which attests for samples freshness and their low content in volatiles.

335

#### 336 4.3.1. Major elements

337 Tungurahua lava flows show typical trends of subduction-related volcanic rocks, and 338 are similar to the previous analyses from its different units and the published data from the Eastern Cordillera (Fig. 6). Indeed, most samples fall within basaltic andesite and andesite 339 fields in the K<sub>2</sub>O vs. SiO<sub>2</sub> diagram (Peccerillo and Taylor, 1976; Fig. 6), and two samples are 340 341 dacites (16EQ17 and 16EQ20). Silica content ranges between 53.3 and 67.0 wt.%, and K<sub>2</sub>O content between 1.3 and 3.6 wt.%. Consequently, rocks from Tungurahua belong to the 342 medium-K calc-alkaline series, except for some samples from Tungurahua I, which are more 343 alkaline-rich and belong to the high-K calc-alkaline series. 344

Variation diagrams, shown as a function of Th (as a differentiation index), also show typical trends of subduction zone volcanism (Fig. 7). Th is a highly incompatible element, which is not fractionated during partial melting or fractional crystallization process. The decrease of MgO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and TiO<sub>2</sub> (Fig. 7a, b, c and d) suggests fractional crystallization of plagioclase and Fe-Ti oxide phenocrysts present in the samples, sometimes
along with pyroxene and olivine crystals (Appendix A). Magmas are not evolved enough to
loose K<sub>2</sub>O and Na<sub>2</sub>O through incorporation into crystals, and hence the alkali content
increases as the fractional crystallization proceeds (Fig. 7e and f).

353

#### 354 *4.3.2. Trace elements*

Spider diagrams of trace elements, normalized to the primitive mantle (Sun and McDonough, 1989; Fig. 8a), shows enrichment of Large-Ion Lithophile Elements (LILE; Rb, Ba, and K) and depletion of High-Field Strength Elements (HFSE; Nb, Ti and Y), also typical of subduction magmas. These signatures are also found on the Rare Earth Elements (REE) diagram normalized to chondrites values (Sun and McDonough, 1989; Fig. 8b), with an enrichment in Light REE (LREE; to the left) compared to Heavy REE (HREE, to the right), without a negative Eu anomaly.

Overall, lavas from Tungurahua I have higher REE contents, which can be linked with 362 363 its high-K signature (Fig. 6). In the Sr/Y versus Y diagram (Fig. 9e), most of the rocks plot in the classical calc-alkaline arc lavas field, but some lavas are more depleted in Y and tend 364 toward an "adakitic" signature. However, all samples are too enriched in Yb and too depleted 365 in La to reach the "adakitic" domain in the La/Yb versus Yb diagram (Fig. 9f). Moreover, the 366 Sr/Y ratio decreases as the fractional crystallization proceeds, whereas La/Yb and Th are 367 positively correlated (Fig. 9c and d, respectively). Tungurahua I lavas are rather scattered, 368 particularly for Pondoa basal unit and younger plateau lavas, which differ significantly from 369 the general trend (Fig. 7). Indeed, old lavas of Pondoa, including PS-102, show a high 370 371 enrichment in all incompatible elements and REE, notably Y and Yb (Fig. 8; Fig. 9e and f). Overall, all samples are porphyritic except one from the upper part of Ulba plateau (16EQ17), 372 373 which is almost entirely crystallized and presents a trachytic texture (Appendix A). It is the

most evolved sample of plateau lavas, and presents high enrichment in the most incompatible
elements and REE (Fig. 7; Fig. 8; Fig. 9).

Tungurahua II and III lavas compositions are rather homogeneous, and major and trace 376 377 element contents do not allow us to clearly discriminate between these two different edifices. However, it can be noticed that sample PS-117, which corresponds to the beginning of 378 Tungurahua II activity shortly after the first sector collapse event, is the most depleted in 379 HFSE and HREE, notably in Nb, Y and Yb (Fig. 8; Fig. 9e and f). Moreover, the composition 380 of the "Cusúa dacite" sample (16EQ36) is slightly less differentiated than the one of Hall et 381 al. (1999), with 62.2 wt.% of SiO<sub>2</sub>. Finally, the Vizcaya lava flow (16EQ20) differs 382 significantly from Tungurahua lavas for most major elements (Fig. 6; Fig. 7) and for some 383 trace elements (Fig. 9b). 384

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#### 386 *4.4. Geomorphological reconstructions*

Palaeotopographical reconstructions were used to propose a temporal evolution of
Tungurahua volcano morphology (Fig. 10; Table 3).

The morphology of the metamorphic basement suggests that a north-south crest was present under the present edifice before its construction (Fig. 10a), extending the one currently found south of the volcano. As the volcano grew, Río Chambo and Pastaza palaeovalleys (Fig. 2), which were present initially, were shifted westward and northward.

Overall, the present Tungurahua edifice presents a conic morphology, with a rather circular base and a concave profile. According to our extrapolation of the basement and the present topography, the present volume of this volcano is  $108 \pm 30 \text{ km}^3$  (Table 3), with a basal surface of about 150 km<sup>2</sup>. Given our maximum age of  $293 \pm 10$  ka, the apparent production rate is  $0.4 \pm 0.1 \text{ km}^3/\text{ka}$ .

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In detail, Tungurahua I was a volcano with a rather flat summit, which peaked at a 398 minimum elevation of 4500 m (Fig. 10b), 2 km southeast to the present summit. Based on our 399 numerical reconstructions, the volume of Tungurahua I at the end of its construction was 400  $56 \pm 33 \text{ km}^3$ . Considering that the erosion rate affecting its flanks during its growth was 401 similar to the erosion rate calculated since the end of its construction, we obtain an eroded 402 volume of  $68 \pm 41$  km<sup>3</sup> between ~293 and 81 ka. This volume is added to the first volume of 403  $56 \pm 33$  km<sup>3</sup>, which provides a total volume of  $124 \pm 74$  km<sup>3</sup> of products emitted during the 404 ~212 ka of Tungurahua I construction (Table 3). As a result, the magmatic productivity rate of 405 this first edifice was  $0.6 \pm 0.3$  km<sup>3</sup>/ka. A quiescence period favoured the erosion of 406 Tungurahua I flanks between 80 and 33 ka (Fig. 10c). Then, the sudden loss of  $\sim 10 \text{ km}^3$  of 407 deposits (Bustillos, 2008) during the first western sector collapse at ~ 33 ka (Fig. 10d; Table 408 3) may have favoured the rise of magma (e.g., Hildenbrand et al., 2004) and the rapid 409 410 construction of Tungurahua II within the resulting amphitheatre (Fig. 10e). This second edifice culminated at about 5070 m, with a concave upward profile similar to the present 411 volcano. Although the volume of the emitted products  $(24 \pm 4 \text{ km}^3)$  is significantly lower than 412 the one calculated for the first edifice, its eruptive rate was similar  $(0.9 \pm 0.2 \text{ km}^3/\text{ka})$  given 413 the shorter duration of this stage, between  $29 \pm 2$  ka (Table 1) and  $2.96 \pm 0.03$  ka (Le Pennec 414 et al., 2013). A new flank failure occurred at ~3 ka (Fig. 10f), mobilizing around 3 km<sup>3</sup> of 415 deposits (Bustillos, 2008) from the western summit part. Finally, the third and still active 416 edifice was rapidly constructed in the depression left by this collapse (Fig. 10g). Tungurahua 417 III is characterized by the lowest volume of deposits  $(7 \pm 3 \text{ km}^3)$ , but displays a relatively 418 high eruptive rate of  $2.5 \pm 1.0 \text{ km}^3/\text{ka}$ . In addition, an erosion rate of  $0.2 \pm 0.1 \text{ km}^3/\text{ka}$  for the 419 eastern part of Tungurahua I not affected by the collapses is obtained, considering the eroded 420 volume of  $\sim 16 \text{ km}^3$  during  $\sim 80 \text{ ka}$ , i.e. since the end of the first edifice construction (Table 3). 421 As Tungurahua II collapsed rapidly after its construction without significant periods of 422

quiescence, and as Tungurahua III is still active, we cannot calculate erosion rates for theseedifices.

Based on these new results and field observations, we propose in Fig. 3 an update of the Tungurahua geological map (Hall et al., 1999; Bustillos, 2008). Tungurahua II not only consists of the lava flow sequence of the Tiacos unit (Fig. 2), but also crops out in the northern and southwestern flanks. We also propose that the Tungurahua I collapse scar is located to the west of the Tungurahua II scar, as suggested by the location of the upper parts of the Pondoa, Runtún and Ulba plateaux.

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#### 432 5. Discussion

433 5.1. New groundmass K-Ar ages

## 434 5.1.1 Comparison with previously published ages

The new K-Ar ages of Tungurahua I (Table 1 and Fig. 3b, c and d) are strikingly 435 younger than previously published whole-rock K-Ar ages of  $770 \pm 5$  and  $350 \pm 4$  ka (Barberi 436 et al., 1988), for samples from Tungurahua, but whose location is unknown. Such difference 437 can be explained by the analysis of whole-rock samples that include phenocrysts, which can 438 carry inherited radiogenic argon and/or weathering areas that have experienced loss of 439 potassium. Both phenomena will induce older K-Ar ages. Our results highlight the importance 440 of analysing the groundmass alone, after a thorough mineralogical separation, as previously 441 442 reported in different contexts, including arc volcanism (e.g., Samper et al., 2007; Germa et al., 2011; Zami et al., 2014). Although unpublished, four <sup>40</sup>Ar/<sup>39</sup>Ar ages obtained at the 443 Laboratoire Geoazur (Côte d'Azur University, Nice, France) support our K-Ar ages. Indeed, 444 inverse isochron ages of  $27 \pm 4$  and  $104 \pm 44$  ka (M. Fornari, pers. com.) agree with our ages 445 of  $29 \pm 2$  and  $153 \pm 14$  ka obtained for the same lava flows (PS-117 and PS-110 respectively; 446 Table 1). In addition, two distinct lava flows sampled in the same eruptive phase than PS-99 447

and PS-118 have  ${}^{40}$ Ar/ ${}^{39}$ Ar ages of 99 ± 2 and 252 ± 6 ka (M. Fornari, pers. com.), which are in the range of our K-Ar ages of 79 ± 3 and 293 ± 10 ka, respectively (Table 1). Moreover, most samples from Tungurahua II and III are younger than 15 ka (Table 1), in agreement with their emplacement after the Last Glacial Maximum (Hall et al., 1999; Clapperton, 1990). Although they display a large relative uncertainty, our ages are also consistent with previously published <sup>14</sup>C ages of less than ~3 ka for Tungurahua III deposits (Hall et al., 1999; Le Pennec et al., 2008, 2013, 2016).

In this southern part of the Ecuadorian arc, within the Inter-andean valley, radiometric ages are available only for Chimborazo and Carihuairazo volcanoes (Fig. 1b). Both were built up since 230 ka, and until Holocene for Chimborazo volcano (Samaniego et al., 2012; Barba et al., 2008). Further south, the construction of the Sangay volcano, the last active edifice of the Eastern Cordillera, started around 500 ka (Monzier et al., 1999; Fig. 1b). Hence, it appears that the construction of Chimborazo, Carihuairazo, Sangay and Tungurahua volcanoes are rather coeval, which suggests a recent development of this part of the arc.

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## 463 5.1.2. Association between ages and volcanic phases

The distribution of our new ages is fairly homogeneous on the scale of the volcano 464 465 activity, apart from the end of the first edifice construction (Fig. 5). Indeed, the oldest basal lava flows of Tungurahua I have an age of 300 ka, and the edifice remained active until the 466 emplacement of lava flows forming the upper parts of plateaux, at around 80 ka. The edifice 467 collapsed around 33 ka (Le Pennec et al., 2013), but we do not have any sample with an age 468 between 80 ka and the 33 ka destabilization. Tungurahua I activity might have continued 469 470 between 80 and 33 ka if the lava flows were only emplaced in the summit area or in the western flank that have been destroyed by latter flank collapses, since the plateaus do not 471 472 seem covered by any younger deposits. Similarly, we did not observe any activity between

 $246 \pm 17$  and  $188 \pm 7$  ka (Fig. 5). Although it could be due to a sampling bias, these ~50 ka 473 474 quiescence periods would be the longest experienced by the volcano. Moreover, owing to the relatively high age-uncertainty of lavas younger than 15 ka (Table 1), and the similar 475 476 geochemistry observed for the two younger edifices, we cannot determine whether these lavas belong to Tungurahua II or III. Therefore, we rely on stratigraphic relationships observed in 477 the field to associate young samples with a given eruptive phase. Sample PS-109 (7  $\pm$  4 ka) is 478 older than 3 ka and corresponds to Tungurahua II activity (Fig. 3), probably as well as sample 479 PS-107 (5  $\pm$  8 ka), which belongs to a nearby lava flow. Hall et al. (1999) associated the 480 young lava flow at the bottom of the Ulba valley (sampled here as PS-111 and 16EQ19) to 481 Tungurahua III activity based on petrological similarities. However, there are very few 482 mineralogical differences between the two younger edifices (Appendix A). We associate 483 PS-111 and 16EQ19, as well as PS-119 and 16EQ13 (southwestern flank lavas), to 484 485 Tungurahua II activity (Fig. 3), because Tungurahua III deposits in the sector collapse depression are not thick enough to have overflown into the eastern and southern valleys. 486 487 Regarding the Baños lava flow (16EQ37;  $6 \pm 9$  ka), there is no place where a clear stratigraphic relationship could be observed between the lava and the ~3 ka collapse deposits 488 (namely the blast deposits associated with the sector collapse). Indeed, these Tungurahua II 489 blast deposits are dated between  $2640 \pm 45$  and  $3195 \pm 45$  BP (<sup>14</sup>C on charcoal and carbonized 490 twigs), crop out along the Chambo and Puela valleys (Fig. 2) and cover the northern flank of 491 the volcano (Le Pennec et al., 2013), especially Pondoa and Runtún plateaux around Baños 492 city (Fig. 2), but do not crop out above the Baños lava flow. The lava flow originated from a 493 lateral vent (Fig. 3b), and was later covered by an ash deposit dated at  $1470 \pm 85$  BP (<sup>14</sup>C on 494 charcoal; Hall et al., 1999). Assuming that the Baños lava flow is younger than the blast 495 496 deposits, we associate the Baños lava flow with the beginning of Tungurahua III activity, in agreement with Hall et al. (1999) and Le Pennec et al. (2016). 497

The Vizcaya lava flow is coeval with Tungurahua I activity  $(253 \pm 5 \text{ ka})$ , but its major and trace contents clearly differ from Tungurahua rocks (Fig. 7; Fig. 9). Hence, this flow cannot be associated with Tungurahua volcano and was rather erupted from an unknown volcanic centre, probably located to the north.

Unfortunately, the southeastern flank could not be sampled and dated in this study. Indeed, access to the Minsas plateau (Fig. 2) was not possible during the erupting period, when our last field trip took place. However, previous major and trace element analyses (Hall et al., 1999; Appendix B) indicate a composition close to those of Ulba upper part (16EQ17; Table 2). Minsas plateau lava geochemistry, morphology and erosion state therefore suggest that the flow is coeval with other Tungurahua I plateau lavas, and was erupted around 80 ka (Fig. 3).

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## 510 5.2. Location of the ~33 ka sector collapse scar

The succession of construction stages of the volcano and the erosion prevent to 511 accurately determine the location of the Tungurahua I collapse scar. However, morphology 512 analysis of the DEM, and observations made during field campaigns allow us to propose that 513 the northern part of the scar follows the western escarpment of the Pondoa plateau (Fig. 3). 514 Indeed, a "diamond-shaped" plateau, located west of Pondoa, is made of Tungurahua I 515 collapse deposits overlain by Tungurahua II lava flows (Fig. 11). This part of the volcano was 516 therefore destroyed by the first collapse, but was not affected by the second one. Note that 517 such observations are in agreement with the geological map of Hall et al. (1999). The 518 morphology of the southwestern flank, from Patacocha plateau to the second collapse scar, 519 seems to constitute a single unit filling a wide valley (Fig. 3d and Fig. 11d). Indeed, lava 520 flows cover a Tungurahua I breccia deposit, where sample 16EQ12 comes from (Fig. 3a), and 521 522 no dated lava is there older than 30 ka (Fig. 3d). We therefore propose that the top of the first

(~33 ka) collapse scar is located on the eastern flank at around 3900 m a.s.l., where plateaux
slopes change (Fig. 4) forming the lower boundary of the Tiacos unit, and located along the
summit part of the Patacocha plateau (Fig. 3).

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## 527 5.3. Geochemical evolution of the volcanic products

528 Overall, the lavas of the three successive edifices of Tungurahua volcano show quite 529 similar compositions. Indeed, their silica content varies between 52 and 62 wt.%, and their 530 Mg# between 40 and 60 (Fig. 12a), except for 16EQ17 sample, which is more differentiated 531 than the other lavas, and presents higher content of incompatible elements (Fig. 7; Fig. 9).

532 The La/Yb ratio varies depending on the depth, composition and nature of the magmas source, fractional crystallization and/or interaction with the mantle (Moyen, 2009). Temporal 533 evolution of the La/Yb ratio for Tungurahua samples (Fig. 12b) shows an overall decrease 534 between 300 and 100 ka, and a significant increase toward the end of Tungurahua I activity, 535 shown by samples younger than 100 ka. During Tungurahua II and III construction, La/Yb 536 537 contents are relatively scattered, and vary within the range observed for Tungurahua I lavas. Moreover, the La/Sm ratio provides information about the degree of partial melting, and the 538 Sm/Yb ratio is affected by the depth or nature of the magmatic source (e.g., Wilson, 1989; 539 540 Rollinson, 1993). Fig. 12b shows that these ratios are relatively constant through time for Tungurahua lavas, except a high Sm/Yb content after the ~33 ka collapse (PS-117) and a 541 relatively high La/Sm content towards the end of Tungurahua I construction (16EQ17). 542 Overall, these geochemical evolutions seem to be mainly due to the nature of the magmas. 543 544 The La/Sm and La/Yb ratios have the same trend than the SiO<sub>2</sub> content as a function of time, 545 except for sample PS-117. The higher ratios correspond to the most differentiated lava flows, such as sample 16EQ17, which is a dacite significantly enriched in the most incompatible 546 547 elements (LILE, HFSE and LREE; Table 2) compared to other andesite samples. Concerning

sample PS-117, the high La/Yb ratio is correlated with its high Sm/Yb ratio, due to its 548 depletion in Dy, Er, Y and Yb (Table 2) that could be related to the heterogeneity of the 549 mantle wedge composition. Large scale sector collapses occurring in volcanic islands may 550 551 cause an increase of the partial melting rate due to the pressure reduction affecting the magma chamber (e.g., Hildenbrand et al., 2004). On the other hand, the thick crust may prevent sector 552 collapses to affect the deep magmatic source in continental environments. In Ecuador, Robin 553 554 et al. (2010) observed large geochemical variations just after two major sector collapses in 555 Pichincha volcano lavas (Fig. 1b). The authors infer that new magma batches, associated with new magmatic cycles, may have triggered these sector collapses. We have fewer analyses for 556 557 Tungurahua volcano, and they are spread over a shorter time scale. However, the geochemistry of Tungurahua lava flows is rather homogeneous for the three edifices and does 558 not seem to be affected by the two observed collapses. 559

560 Several studies have focused on the evolution through time of Ecuadorian lavas geochemistry, notably for Atacazo (Hidalgo, 2006), Cayambe (Samaniego et al., 2005), 561 562 Iliniza (Hidalgo et al., 2007), Mojanda-Fuya Fuya (Robin et al., 2009), and Pichincha (Samaniego et al., 2010) volcanoes (Fig. 1b). These edifices are located in the northern part of 563 the Ecuadorian arc, in front of the Carnegie ridge (Fig. 1a). They were constructed since 564 1.3-1.0 Ma until the Holocene, except for Mojanda-Fuya Fuya and Iliniza, which are not 565 precisely dated yet. These edifices present a long-term evolution, between typical 566 calc-alkaline compositions for the oldest lavas, to adakitic compositions for the most recent 567 deposits, which is interpreted as a modification of the sources of the magmas induced by the 568 569 subduction of the Carnegie ridge, and the subsequent increase of the geothermal gradient. The relatively short duration of Tungurahua activity (about 300 ka), and its location in the 570 571 southern part of the arc (farther away from the Carnegie ridge than the northern volcanoes), prevent us to identify these long term deep processes, if present. This latter conclusion has 572

been corroborated by the recent work of Ancellin et al. (2017), who analysed the Sr-Nd-Pb isotopic signature of the Ecuadorian magmas and conclude that magmas from the southern part of the arc (as those of Tungurahua and Sangay volcanoes) do not display a clear subduction slab partial melting component.

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### 578 5.4. Magmatic productivity and erosion rates

579 *5.4.1. Tungurahua eruptive and erosion rates* 

The overall volume obtained for the present edifice of Tungurahua ( $108 \pm 30 \text{ km}3/\text{ka}$ ; 580 Table 3 and 4) is similar to the one obtained for Viejo Cayambe (Samaniego et al., 2005), and 581 582 seems to correspond to a medium size compared to arc volcanoes in general (Table 4; Grosse et al., 2009). However his volume is higher than Ecuadorian Antisana (Hall et al., 2017; Table 583 584 4), Imbabura (Le Pennec et al., 2011) and Chimborazo (Samaniego et al., 2012) volcanoes, which are more eroded or younger, and is lower than Rucu Pichincha (Robin et al., 2010) and 585 586 Mojanda (> 140 km3; Robin et al., 1997) volcanoes, located more to the north (Fig. 1b), and 587 significantly older. Our palaeotopographical reconstructions suggest that Tungurahua I was a volcano with lower sloping upper flanks, while Tungurahua II and III have an exponential 588 shape with a concave profile and steeper slopes (Fig. 4; Fig. 10). The nature of lavas 589 590 composing these three edifices is very similar and cannot explain this morphological difference. Tungurahua I has been subjected to erosion longer than Tungurahua II and III, and 591 592 the erosion mainly affected steep slopes of areas near the summit. Less eroded parts, in particularly flanks with low slopes, constitute the present planezes. Our model of 593 Tungurahua I morphology is based on the surface of these planezes, and it does not exclude 594 595 the possibility that Tungurahua I could have had a similar concave profile as the present edifice at the end of its construction. Assuming that the activity of Tungurahua I ended 596 ~80 ka, we determined the erosion rate by calculating the volume loss between our 597

topographic model at 80 ka and the present-day topography. This was performed only 598 considering the eastern flank, where the remnants of Tungurahua I not affected by sector 599 collapses crop out, and yielded a volume of  $16 \pm 4 \text{ km}^3$ , corresponding to an erosion rate of 600  $0.2 \pm 0.1$  km<sup>3</sup>/ka (Table 3). Assuming the long term erosion rate is constant over time, we 601 obtain a total eroded volume of  $68 \pm 41 \text{ km}^3$  during the construction of Tungurahua I, between 602 293 and 81 ka (PS-118 and PS-116 respectively; Table 1 and 3). Based on our models, the 603 volume of Tungurahua I corresponds to  $56 \pm 33 \text{ km}^3$  of deposits. In order to take into account 604 605 the erosion that affected the edifice during its construction phase, we have added the  $68 \pm 41 \text{ km}^3$  eroded volume to calculate the volume of emitted products and the magmatic 606 productivity rate. Our result of  $0.6 \pm 0.2$  km<sup>3</sup>/ka (Table 3) thus corresponds to a magmatic 607 production volume of  $124 \pm 74$  km<sup>3</sup> during a period of 212 ka. However, these values should 608 be considered with caution, as the basement elevation under Tungurahua volcano is not well 609 610 constrained, and the constant erosion rate applied over the whole construction period was most probably variable through time, as a function of the climatic conditions and the nature of 611 612 outcropping volcanic products. Moreover, we consider that the deep valleys have been dug by 613 erosion, which may have occurred mainly before 30 ka since Tungurahua II lavas outcrop at the bottom of these valleys (Fig. 3). However, these lavas are younger than 15 ka (e.g. sample 614 PS-111), and we cannot quantify the volume of deposits eroded by the Last Glacial 615 616 Maximum, which occurred between 25 and 15 ka in this region (Clapperton, 1990; Heine, 2000). Furthermore, tephra deposits can easily erode when they are not covered with lava 617 flows. It is possible that such deposits existed, but it is difficult to estimate and take into 618 619 account this volume in our calculations of erosion rates. Similarly, from a calculated volume of  $21 \pm 4 \text{ km}^3$  obtained for Tungurahua II, added with a volume of  $4 \pm 2 \text{ km}^3$  for erosion, we 620 obtain a volume of  $24 \pm 4$  km<sup>3</sup> of emitted products, giving an eruptive rate of  $0.9 \pm 0.2$  km<sup>3</sup>/ka, 621 similar to Tungurahua I. Finally, the magmatic productivity rate calculated for Tungurahua III 622

623  $(2.5 \pm 1.0 \text{ km}^3/\text{ka}; \text{Table 3})$  is consistent with the eruptive rate of ~1.5 km<sup>3</sup>/ka estimated by 624 Hall et al. (1999) over the last 2300 years, for a similar volume to ours. The relatively high 625 production rate calculated for Tungurahua III may be explained by its recent construction and 626 rather continuous activity, compared to the two older edifices, which are averaged over a 627 larger time scale, certainly including periods of quiescence.

628

### 629 5.4.2. Comparison between eruptive rates of Tungurahua volcano and other studies

Many phenomena may impact on the magmatic productivity, such as the geodynamic 630 context, the nature and thickness of the crust, or the period of time considered. In a 631 compilation of the magmatic productivity calculated over the world, White et al. (2006) 632 obtained an average rate of  $4.4 \pm 0.8 \text{ km}^3/\text{ka}$  for continental crust volcanoes and 633  $2.3 \pm 0.8$  km<sup>3</sup>/ka for andesitic edifices. Our eruptive rate of 2.5 km<sup>3</sup>/ka, corresponding to 634 Tungurahua III activity (Table 3 and 4), falls within this latter range. Note that the rates of 0.6 635 and 0.9 km<sup>3</sup>/ka, obtained here for Tungurahua I and II, respectively (Table 3 and 4), are 636 comparable to the ones obtained on Chimborazo (0.1 to 1 km<sup>3</sup>/ka; Samaniego et al., 2012) and 637 Pichincha (~0.6 km<sup>3</sup>/ka for both Rucu and Guagua Pichincha; Robin et al., 2010) volcanoes, 638 both also from Ecuador (Fig. 1). Tungurahua eruptive rates are also similar to those from 639 other arc volcanoes, for instance in Chile at Parinacota (~0.3 and 1 km<sup>3</sup>/ka for the whole 640 edifice and the young cone, respectively; Hora et al., 2007), Puyehue-Cordón Caulle 641 (0.42 km<sup>3</sup>/ka; Singer et al., 2008) and El Misti (0.63 and 2.1 km<sup>3</sup>/ka for the whole edifice and 642 peak eruptive rates, respectively; Thouret et al., 2001) volcanoes, which were active since less 643 than 320 ka, or with Ceboruco volcano in Mexico (~0.5 km<sup>3</sup>/ka; Frey et al., 2004). However, 644 Tungurahua eruptive rates are significantly higher than at Aucanquilcha volcano in Chile 645  $(0.04 \text{ and } 0.16 \text{ km}^3/\text{ka} \text{ for the whole edifice and the highest eruptive rate stage, respectively;}$ 646 Klemetti and Grunder, 2008) and at Tequila volcano in Mexico (0.13 and > 0.24 km<sup>3</sup>/ka for 647

the whole field constructed during the last million years and the youngest cone, respectively; 648 Lewis-Kenedi et al., 2005). These data show that eruptive rates may vary significantly in the 649 same geodynamic context. Moreover, volcanoes which experienced a long period of activity 650 651 (in the order of one million years) seem to have lower eruptive rates than younger edifices, averaged over shorter times (e.g., Klemetti and Grunder, 2008). The magmatic productivity 652 rates also vary during construction stages of a single edifice, where a few thousand years 653 period of high activity will display a higher eruptive rate than the one averaged on the whole 654 655 eruptive history of the volcano. Indeed, stratovolcanoes grow in spurts (e.g., Hildreth and Lanphere, 1994; Lewis-Kenedi et al., 2005), with sporadic eruptive pulses, separated by long-656 time periods of quiescence, producing most of the volcano volume. The magmatic 657 productivity rates averaged over the whole period of construction are therefore systematically 658 lower, such observed for Tungurahua with ~0.4 km<sup>3</sup>/ka for the whole volcano (Table 3), while 659 the eruptive rate of the three individual edifices is higher than 0.6 km<sup>3</sup>/ka. Magmatic 660 productivity rates of Tungurahua I, II and the whole edifice arelong-term averaged eruptive 661 662 rates, which include quiescence periods, whereas Tungurahua III, younger than 3 ka, 663 represents a « peak » of activity with a significantly higher eruptive rate (Table 3). A similar picture seems to occur in Peru at Ampato-Sabancaya volcanic complex. Ampato, the older 664 edifice, has an eruptive rate of 0.08-0.09 km<sup>3</sup>/ka, whereas it is of 0.6-1.7 km<sup>3</sup>/ka for the 665 666 younger edifice Sabancaya, constructed since 6-10 ka (Samaniego et al., 2016).

As expected, Tungurahua magmatic productivity rates are lower than in a subduction context where the velocity of the plate is faster  $(5 \text{ km}^3/\text{ka} \text{ for Mount Fuji in Japan; Crisp},$ 1984), and higher than in a subduction context where the convergence rate is slower, as for instance in the Lesser Antilles. Indeed, eruptive rates there vary between 0.13 km<sup>3</sup>/ka in Martinique (Mount Pelée; Germa et al., 2015), 0.15 km<sup>3</sup>/ka at Montserrat (Harford et al., 2002), and 0.04 to 0.7 km<sup>3</sup>/ka in Guadeloupe (Lahitte et al., 2012; Ricci et al., 2015a; 2015b; Table 4). Finally, Tungurahua eruptive rates are lower than those obtained in Argentina for Payún Matrú volcano ( $4 \text{ km}^3/\text{ka}$ , averaged over the last 300 ka; Germa et al., 2010), where back-arc extension may have favoured the magma ascent.

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#### 677 5.4.3. Comparison between erosion rates of Tungurahua volcano and other studies

Since only a few studies have investigated erosion rates, their relationship with the 678 geodynamic context or the climate variability is still poorly understood. Our erosion rate for 679 volcano of  $0.2 \pm 0.1$  km<sup>3</sup>/ka, equivalent to  $6.5 \pm 1.7$  t/km<sup>2</sup>/ka and 680 Tungurahua I  $2.4 \pm 0.6$  mm/a, calculated for the last 80 ka, is significantly higher than rates obtained in the 681 arid central Andes and in Peru (between 0.01 and 0.11 mm/a; Karátson et al., 2012) or in 682 tropical environments, such as in the Lesser Antilles with  $0.05 \pm 0.02$  km<sup>3</sup>/ka in Martinique 683 (Germa et al., 2015), and between  $0.2 \pm 0.2$  and  $1.4 \pm 0.6$  t/km<sup>2</sup>/ka in Guadeloupe (Ricci et al., 684 2015a; 2015b) islands. This difference could be explained by the succession of glacial and 685 interglacial periods experienced by Tungurahua volcano, whereas the Antilles islands were 686 only subject to rainfalls. However, morphology and extreme rainfalls experienced by La 687 Réunion island, as well as the faster weathering of basaltic than andesitic lavas (e.g., Gislason 688 et al., 1996; Louvat and Allègre, 1997), may explain its high erosion rate of  $1.2 \pm 0.4$  km<sup>3</sup>/ka 689 (Salvany et al., 2012), compared to the one of Tungurahua volcano. 690

691

## 692 6. Conclusions

This study allows us to refine the eruptive history of Tungurahua volcano, which was built in three stages since the last 300 ka. The overall volume calculated for the remaining edifice is ~110 km<sup>3</sup>, which corresponds to a mean eruptive rate of ~0.4 km<sup>3</sup>/ka. Tungurahua I was a ~125 km<sup>3</sup> and esitic to dacitic stratovolcano, built between 293 ± 10 and 79 ± 3 ka with a magmatic productivity rate of  $0.6 \pm 0.2$  km<sup>3</sup>/ka. Pondoa, Runtún, Ulba, Minsas and

Patacocha plateaux are present-day remnants of this first edifice. After a ~50 ka long period 698 of quiescence, the first western sector collapse occurred at ~33 ka (Le Pennec et al., 2013). 699 Tungurahua II was built between  $29 \pm 2$  and  $\sim 3$  ka (Hall et al., 1999; Le Pennec et al., 2013). 700 Around 25 km<sup>3</sup> of volcanic products filled the collapse amphitheatre, with an eruptive rate of 701  $0.9 \pm 0.2$  km<sup>3</sup>/ka, similar to those of Tungurahua I. They mainly crop out in the southwestern 702 flank and around Juive Grande area, in the northwestern flank (Fig. 2). Collapse of 703 Tungurahua II western flank was followed by rapid construction of Tungurahua III during the 704 last 3 ka. This third and still active edifice constitutes the western flank of the present-day 705 volcano, and is being built with a relatively high productivity rate of  $2.5 \pm 1.0 \text{ km}^3/\text{ka}$ . We 706 also estimated that around 16 km<sup>3</sup> of Tungurahua I volcanic material was eroded since the end 707 of its construction, corresponding to an erosion rate of  $0.2 \pm 0.1$  km<sup>3</sup>/ka. The composition of 708 709 Tungurahua lavas is rather homogeneous, and the magmatic signature of the three edifices do 710 not seem to have been affected by the two sector collapses experienced by the volcano. Moreover, the geochemistry do not show changes in the deep magmatic source as observed 711 712 for northern Ecuador volcanoes.

713

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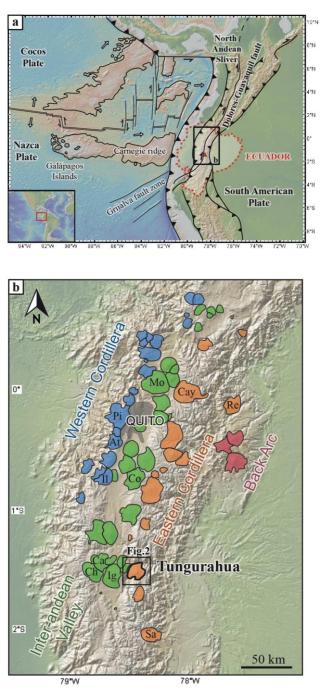
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## 1016 Figure captions

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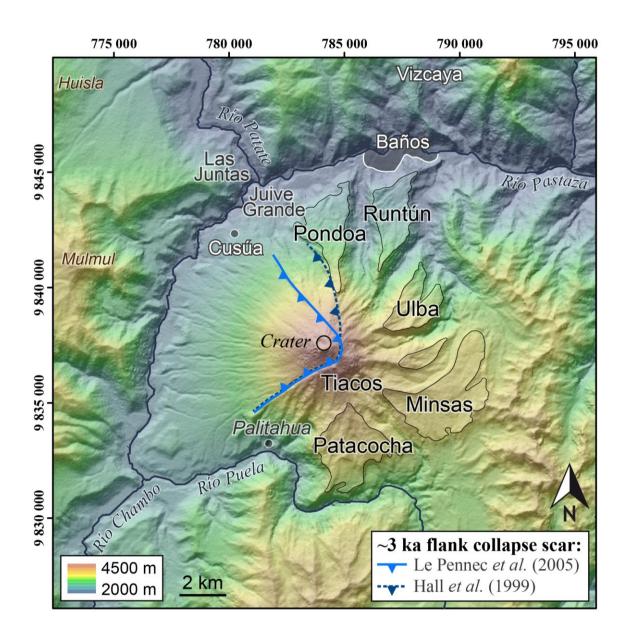
# 1018 **Fig. 1**:

1019 a) Regional setting of Ecuador, showing main tectonic structures and geodynamic context of the Northern 1020 Volcanic Zone of the Andes. Arrows indicate the direction of plate motion (DeMets et al., 1990). Bathymetry 1021 image is from GeoMapApp, using data of Smith and Sandwell (1997). Red triangle represents location of 1022 Tungurahua volcano. b) Map of Ecuadorian volcanic arc, modified from Hall et al. (2008). Volcanoes are 1023 distributed along the Western Cordillera (volcanic front, represented in blue), the Inter-andean valley (green), the 1024 Eastern Cordillera (orange) and the back arc (red). Quito, the capital city, is represented in grey. Tungurahua 1025 volcano is surrounded by heavy black borders. At: Atacazo; Ca: Carihuairazo; Cay: Cayambe; Ch: Chimborazo; 1026 Co: Cotopaxi; Il:Iliniza; Mo: Mojanda; Pi: Pichincha; Re: Reventador; Sa: Sangay.



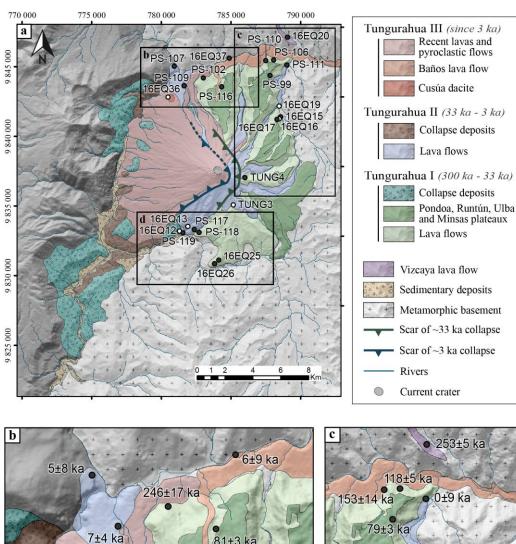
# 1029 Fig. 2:

Shaded view of the Shuttle Radar Topography Mission (SRTM) Digital Elevation Model (DEM; 30-m resolution) of Tungurahua volcano and places mentioned in the text (location is indicated on Fig.1b).
Coordinates are in Universal Transverse Mercator (UTM; zone 17). Mulmul and Huisla are neighbour volcanoes located in the Inter-andean valley. Blue lines represent main rivers and thin black lines the boundary of plateaux upper surfaces. Tiacos unit corresponds to a 80-100 m-thick sequence of Tungurahua II lava flows that cover older lavas of Tungurahua I (Hall et al., 1999). Vizcaya lava flow extends over at least 5 km along the valley north of Tungurahua, from an unknown source.



# **Fig. 3**:

a) Revised geological map of Tungurahua volcano reported on shaded SRTM DEM after considering our new ages and field observations. Sample locations presented in this study are indicated by a black (K-Ar dated samples) or a white (non-dated samples) symbol. All samples have been analysed for major and trace elements.
Geological units are updated from Hall et al. (1999), and the collapse deposits cartography is presented in Bustillos et al. (2011). b), c), and d) are detailed views of the northern, southern, and eastern flanks respectively, showing location of the new K-Ar ages.



 246±17 ka
 81±3 ka

 7±4 ka
 0±9 ka

 79±3 ka
 79±3 ka

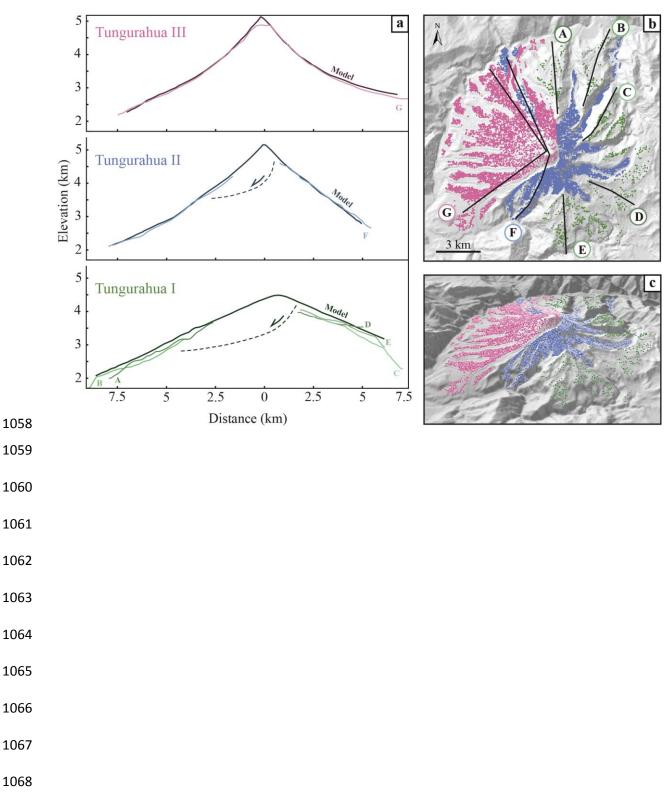
 92±1 ka
 92±1 ka

 92±1 ka
 92±1 ka

# 1052 Fig. 4:

a) Current elevation profiles of the three edifices, with their respective topographic models before erosion. The
location of the profiles is indicated in Fig. 4b. Asymmetrical altitude is due to the basement located higher to the
west. b) Selected points used for reconstructions reported on shaded DEM of Tungurahua volcano. c) 3D view
with the same selected point.

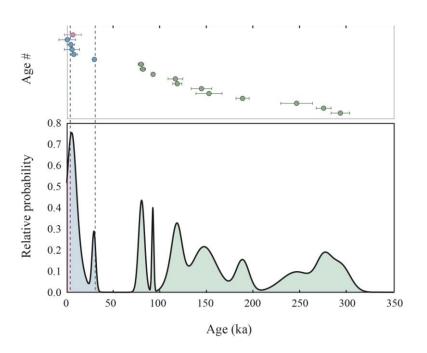




1069 Fig. 5:

Age-probability spectrum, outlining potential gaps of activity between 78 and 33 ka for Tungurahua I, and
between 27 and 15 ka for Tungurahua II. The method used to calculate the relative probability is detailed in
Deino and Potts (1992). The ages are plotted above with their 1σ uncertainty error bars. Green dotted line: ~33 ka
collapse; blue dotted line: ~3 ka collapse.

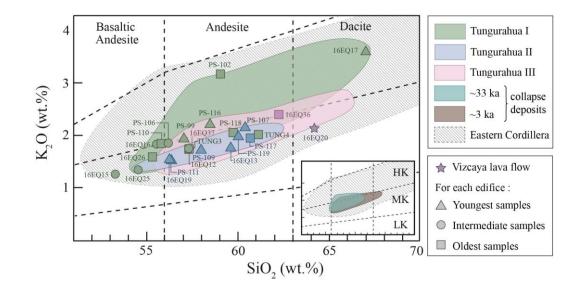
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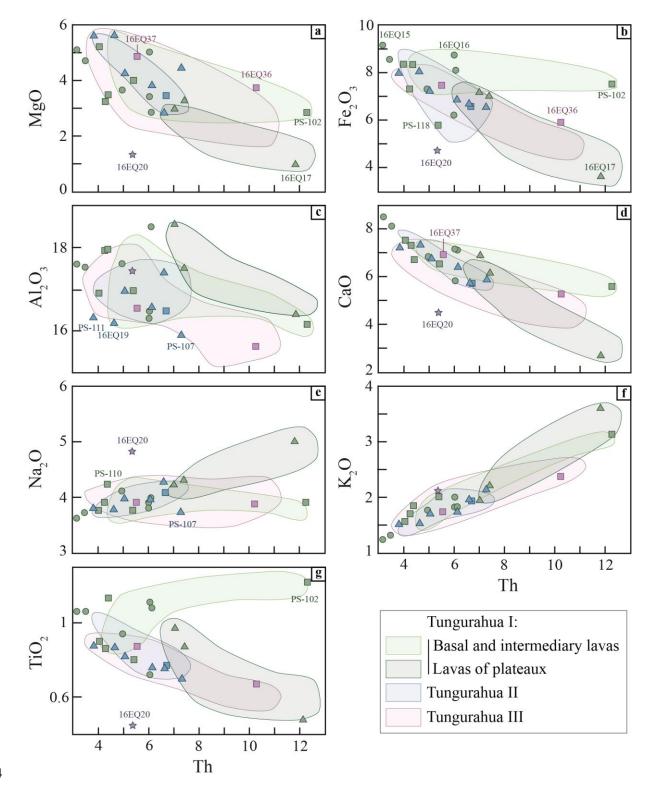
1076 **Fig. 6**:

1077 K<sub>2</sub>O vs. SiO<sub>2</sub> diagram (Peccerillo and Taylor, 1976). Hatched gray domain represent whole rock data of Eastern 1078 Cordillera volcanoes, from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/; using Samaniego et al. 1079 (2005), Bryant (2006), Hidalgo et al. (2012) and Chiaradia et al. (2014) studies). Data for Tungurahua I (green 1080 field), Tungurahua II (blue) and Tungurahua III (pink) originate from Schiano et al. (2010); Samaniego et al. 1081 (2011) and Le Pennec et al. (2013), and new data presented in Appendix B. Due to small amount of 1082 Tungurahua II outcrops, the blue domain was drawn from a smaller number of measurements. The inset 1083 represents the compositional fields of blocks belonging to Tungurahua I (turquoise) and II (brown) sector 1084 collapse deposits. HK: high-K calc-alkaline serie, MK: medium-K calc-alkaline serie, LK: low-K calc-alkaline 1085 serie. .



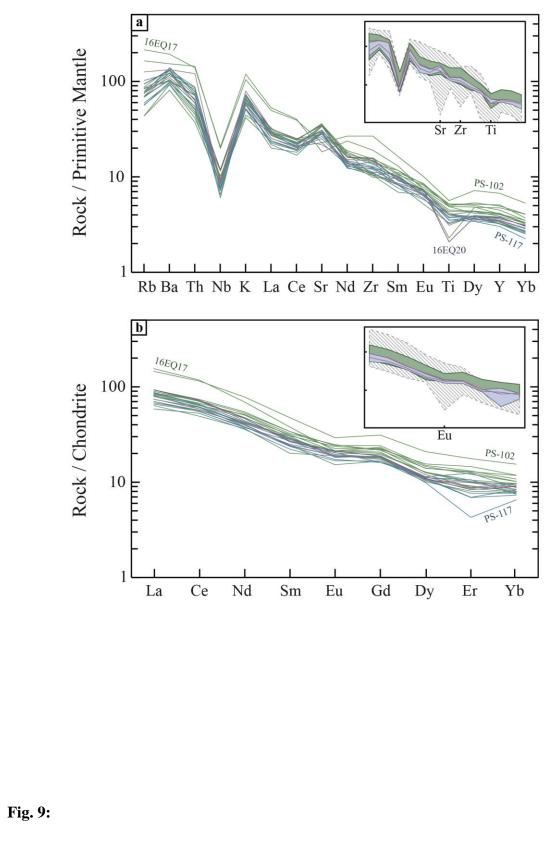


1089 Variation diagrams showing the evolution of major elements (in wt. %) as a function of Th (in ppm). Symbols
 1090 are the same used in Fig. 6. Coloured fields have been obtained from data published in Schiano et al. (2010) and
 1091 analyses given in Appendix B. Samples from the latter have been associated to a unit considering their location
 1092 and stratigraphical position.

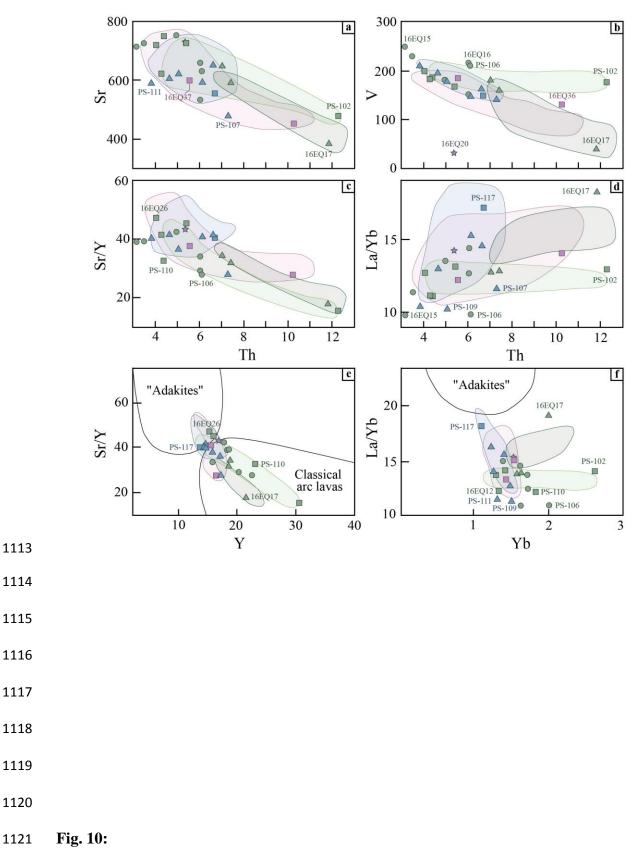


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1096 Fig. 8:
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a) Incompatible elements normalized to primitive mantle spider diagram (Sun and McDonough, 1989). Hatched
grey domain represent Eastern Cordillera data. Analysed samples are represented in green (Tungurahua I), blue
(Tungurahua II), pink (Tungurahua III) and purple (Vizcaya lava flow). b) Rare Earth Elements normalized to
chondrites diagram (Sun and McDonough, 1989). Symbols are the same used in Fig. 8a.



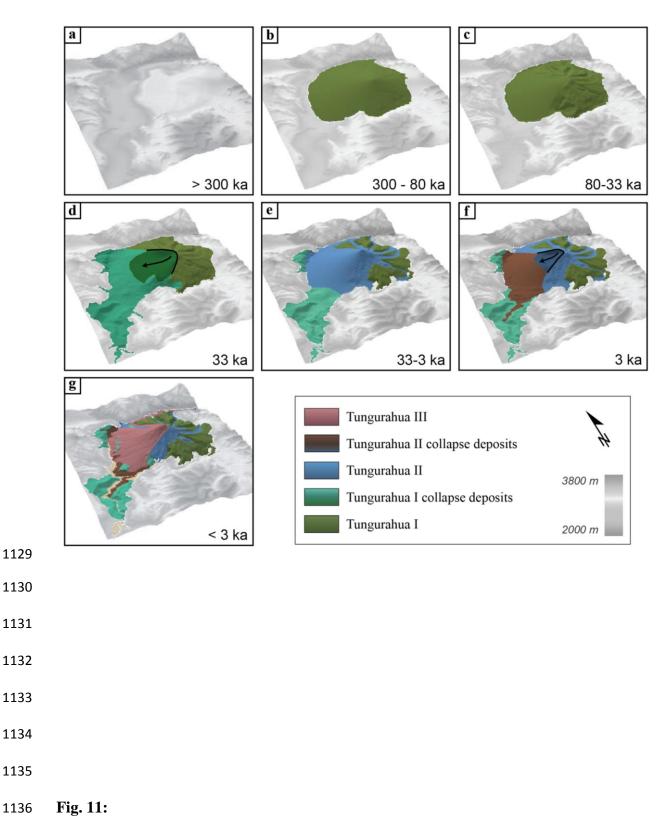
Variation diagrams of trace elements (in ppm). a-b) Sr and V vs. Th. c-d) (Sr/Y) and (La/Yb) vs. Th. e-f) (Sr/Y)
vs. Y and (La/Yb) vs. Yb. "Adakite" and classical arc lavas fields from Castillo et al. (1999). Symbols, caption
and references are the same used in Fig. 7.



Morphological reconstruction of Tungurahua volcano: a) before the onset of activity, b) at the end of Tungurahua I construction, c) after the quiescent period preceding the first flank collapse (note that the western flank no longer crops out today, this is therefore a modelling based on the volumes of the deposits, and does not consider incised valleys), d) after the first western sector collapse, e) at the end of Tungurahua II construction, f),

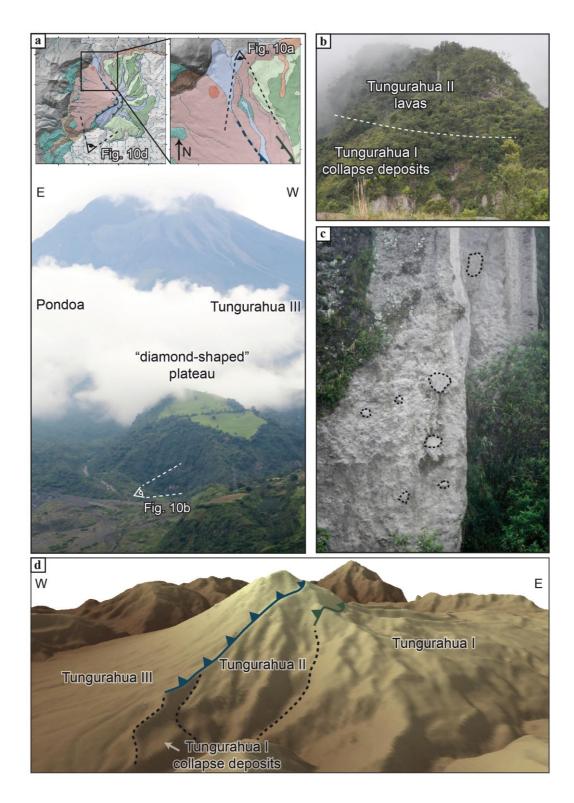
1126 after the collapse of the summit of Tungurahua II, and g) the current morphology, with the construction of

1127 Tungurahua III.



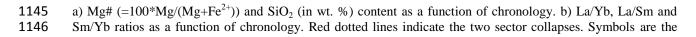
a) Overview of the "diamond-shape" plateau, located between Pondoa and Tungurahua III deposits. b)
Cross-sectional view of the plateau, composed of Tungurahua I collapse deposits overlaid by Tungurahua II lava
flows. c) Detailed view of Tungurahua I collapse deposits, showing blocks in a light breccia matrix. Most

- 1140 massive blocks are highlighted by black dotted lines. d) 3-D view of the southwestern flank. Green line: ~33 ka
- 1141 collapse scar; blue line: ~3 ka collapse scar. Dotted lines delimit the three edifices.



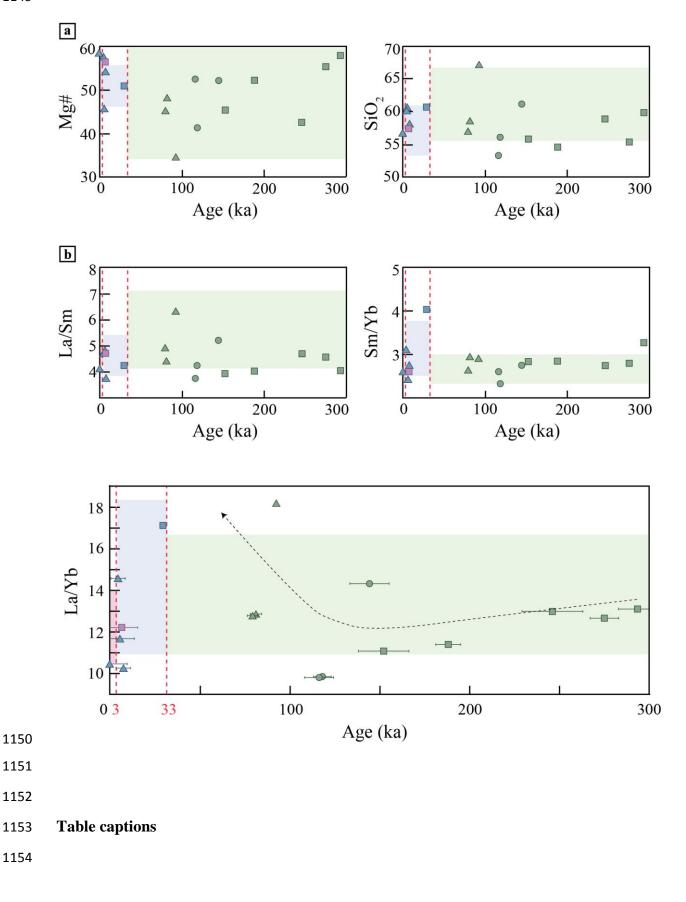
#### 1143

# 1144 Fig. 12:



1147 same used in Fig. 6. Coloured fields represent the range of Mg#,  $SiO_2$  and REE ratios obtained from our non-1148 dated samples and analyses given in Appendix B.





### 1155 **Table 1:**

New K-Ar ages obtained on groundmass in this study. Results are listed from the oldest to the youngest. Column headings indicate sample name, detail of the outcrop location, sample coordinates projected using the Universal Transverse Mercator (UTM) coordinate system (Zone 17), potassium concentration in percent, radiogenic argon content in percent and 10<sup>11</sup> atoms per gram, ages and weighted mean age in ka, with 1-sigma accuracy. Ages marked with an asterisk (\*) were calculated using unweighted average.

1161

#### 1162 **Table 2:**

Major and trace element composition of whole-rock samples. All major data were brought down to a total of
100%. Samples marked with an asterisk (\*) have not been dated.

1165

#### 1166 **Table 3:**

1167 Results of volumes, magmatic productivity and erosion rates calculations, given at 1-sigma accuracy, obtained 1168 from the palaeosurfaces modelling. Raw volume corresponds to the volume calculated from the surface model 1169 without taking into account erosion that occurred during the construction. Total volume corresponds to the sum 1170 of the raw volume and the volume eroded during the construction, based on the erosion rate. Min-max values 1171 were calculated by dividing the minimum volume by the maximum time period, and the maximum volume by 1172 the maximum time period, respectively. Erosion rate in T/km2/ka was calculated considering a rock mean 1173 density of 2.7. Ages marked with an asterisk (\*) are previous 14C published ages (Le Pennec et al., 2013).

- 1174
- 1175 **Table 4:**
- 1176 Summary of Tungurahua eruptive and erosion rates, compared to rates from other published studies.
- 1177
- 1178
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- 1180

## 1181 Appendix captions

#### 1182

### 1183 Appendix A:

1184 Thin sections of all samples (in alphabetical order), observed under an optical microscope. Photographs in
1185 left-hand column were taken with a polarized light, and in right-hand column with a natural light.
1186

1100

### 1187 Appendix B:

Major and trace element composition of Tungurahua whole-rock samples, presented in Hall et al. (1999) and in
Bustillos (2008). All major data were brought down to a total of 100%. Column headings indicate edifice,
sample name, outcrop coordinates projected using the Universal Transverse Mercator (UTM) coordinate system
(Zone 17) and given within 100 meters, and volcanic unit. Results are listed in two parts: lavas, from potentially
oldest to youngest, then blocks belonging to sector collapse deposits. pl : plateau.

1193

## 1194 Appendix C:

1195 KMZ file containing the location of the samples described in this article.