

# Geochronological evolution of the potentially active Iliniza Volcano (Ecuador) based on new K-Ar ages

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Santiago Santamaria, Xavier Quidelleur, Silvana Hidalgo, Pablo Samaniego, Jean-Luc Le Pennec, et al.. Geochronological evolution of the potentially active Iliniza Volcano (Ecuador) based on new K-Ar ages. Journal of Volcanology and Geothermal Research, 2022, pp.107489. 10.1016/j.jvolgeores.2022.107489. hal-03553857

# HAL Id: hal-03553857 https://uca.hal.science/hal-03553857v1

Submitted on 3 Feb 2022

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1 2	Geochronological evolution of the potentially active Iliniza Volcano (Ecuador) based on new K-Ar ages
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17	Keywords:
18 19 20 21 22 23	<ul> <li>Iliniza volcano</li> <li>Ecuador</li> <li>K-Ar dating</li> <li>Geomorphology</li> <li>Volcanic hazards</li> </ul>
24	Highlights:
25 26 27 28 29 30	<ul> <li>Iliniza volcano is formed by two late-Pleistocene edifices and their satellite vents.</li> <li>The North Iliniza edifice started growing at ~123 ka and ended at ~116 ka.</li> <li>The South Iliniza edifice was built from ~46 to ~25 ka and produced a VEI 5 event.</li> <li>Effusive eruptions took place during the Holocene from 2 southern satellite vents.</li> <li>Iliniza volcano should be considered as a potentially active volcano.</li> </ul>

31

# 32 ABSTRACT

The youngest volcanism of the Ecuadorian Volcanic Front (Western Cordillera) is mainly 33 dominated by highly explosive events, including the growth and violent destruction of lava domes, and 34 the formation of thick pyroclastic sequences. Deposits associated with such eruptive dynamics have 35 36 been identified at Iliniza, a compound volcano located in the Western Cordillera with a poorly defined 37 evolutionary history. We present the first K-Ar ages of Iliniza volcano combined with stratigraphic data, 38 numerical reconstructions, and geochemical analyses, providing a new perspective on its evolution. Our 39 results show that Iliniza volcano is much younger than previously proposed. The Iliniza twin-peaked shape is the result of the superposition of two andesitic to dacitic stratovolcanoes. (1) The North Iliniza 40 (NI) edifice was constructed by two lava successions and an intermediate satellite vent, showing a short 41 range of mainly effusive activity between  $123 \pm 6$  and  $116 \pm 2$  ka. (2) The South Iliniza (SI) edifice 42 43 began its construction through the Lower SI stage when massive lavas dated at ~45 ka formed a basal cone. During the Upper SI stage, the uppermost part of this edifice was destroyed by the highly 44 explosive Jatuncama phase (VEI 5) leaving a 30-40 m-thick ignimbrite sequence. The subsequent 45 extrusion of several dacitic lava domes reconstructed the South Iliniza summit at around 35 ka. The 46 47 Terminal SI stage corresponds to the emission of several and esitic lavas between  $31 \pm 4$  and  $25 \pm 3$  ka. The Iliniza eruptive activity extended into the Late Pleistocene and Holocene with the extrusion of the 48 Tishigcuchi lava dome, and the emission of the Pongo lava flow dated at  $6 \pm 4$  ka. Based on the proposed 49 50 eruptive history, we suggest that a revised volcanic hazard assessment of the potentially active Iliniza 51 volcano is required.

52

# 53 1. INTRODUCTION

Magmatism in subduction zones archetypically creates volcanic arcs formed by large composite 54 volcanoes whose erupted volumes reaches several tens of cubic kilometers (de Silva and Lindsay, 55 2015). After several geochronological studies, it seems that arc volcanoes grow in "spurts", i.e., 56 57 relatively short-term construction stages separated by long-term quiescence periods. Inside these 58 constructional periods, there are frequent "instantaneous" destruction events, such as sector collapses 59 and caldera-forming eruptions (e.g., Esser et al., 2004; Hildreth, 2007; Conway et al., 2016; Pure et al., 60 2020). Indeed, several case studies worldwide attest the potential for eruptive activity to occur even 61 after long-term quiescence periods (e.g., García-Palomo et al., 2002; Hora et al., 2007; Mariño et al., 62 2021). The study of the temporal, morphological and compositional records during the growth of a volcano provides insights into magmatic processes and eruptive behavior at various time scales, and 63 thus represents a key issue for hazard assessment (Gamble et al., 2003; Capra et al., 2008; Brenna et 64 65 al., 2012).

66 Although several suitable examples are found in the North and South American arcs, for instance, most studies are focused on recent time scales, leaving the oldest eruptive history poorly 67 68 studied. Along the Ecuadorian Andes, at least 84 Quaternary volcanoes have been identified (Bernard 69 and Andrade, 2011). These volcanic centers are arranged in north-south alignments, described from east 70 to west as the Volcanic Front, the Main Arc, and the Back-Arc (Fig. 1; Hall and Beate, 1991; Hall et 71 al., 2008). Each alignment shows distinctive characteristics in terms of magma composition, volcanic 72 edifice morphology and eruptive dynamics. In particular, the Volcanic Front includes the edifices 73 located on the Western Cordillera, with 15-20 km-wide composite volcanoes which showed several 74 cone-building stages and major sector collapses (e.g., Pichincha volcanic complex; Robin et al., 2010). 75 The formation of lava dome complexes is also recurrent, and often appears during the final eruptive stages following the transition from high-silica andesites to dacites (e.g., Hidalgo, 2006; Robin et al., 76 77 2010; Almeida et al., 2019; Bellver-Baca et al., 2020). Moreover, these stages also involve highly explosive eruptions (e.g., Hidalgo et al., 2008; Robin et al., 2008; Andrade et al., 2021), directed blast 78 events (e.g., Bernard et al., 2014), and the formation of two 3 km-wide calderas (i.e., Cuicocha and 79

Quilotoa calderas; von Hillebrandt, 1989; Mothes and Hall, 2008; Sierra et al., 2020). Notably, large
explosive eruptions occurred during the Holocene in the northern and central segments of the Volcanic
Front (Fig. 1), where large urban areas such as Quito (Ecuador's capital city) are nowadays surrounded
by a high number of volcanoes.

84 Iliniza is a twin-peaked compound volcano (5125 m asl) located 50 km south of Quito, in the central segment of the Ecuadorian Volcanic Front (Fig. 1a). Iliniza volcano exhibits volcanological 85 characteristics that are similar to other Volcanic Front edifices, including the presence of dacite lava 86 87 domes and a thick pyroclastic density current (PDC) deposit, both associated with its late eruptive stages 88 (Hidalgo et al., 2007). Although the geochemistry of the Iliniza volcano's magmas was previously investigated (e.g., Hidalgo et al., 2007, 2012; Schiano et al., 2010; Georgatou et al., 2018), its eruptive 89 90 chronology remained uncertain due to the lack of radioisotopic ages. Based on erosional geomorphology compared to other volcanoes in the Ecuadorian arc, Hidalgo et al. (2007) suggested 91 92 that the earliest Iliniza activity might be as old as  $\sim 1$  Ma, and Hall and Beate (1991) inferred an Holocene age for the Tishigcuchi satellite lava dome. Despite the lack of reliable chronological data, 93 Iliniza volcano was classified as potentially active (Bernard and Andrade, 2011). If confirmed, a 94 relatively young activity would increase the probability of a future reactivation and, consequently, 95 96 increase the threat that this volcano may represent for the populations living in the Inter-Andean valley.

97 Here, we define the main geomorphologic and volcanological units of Iliniza volcano and 98 present its first geochronological data, combined with new field observations and geomorphological 99 reconstructions. We aim to constrain the eruptive stages of Iliniza volcano through time, as well as its 100 growth and erosion patterns. In addition, geochemical data are used to describe the compositional 101 evolution of its eruptive products over time. Our results show that the construction period of Iliniza 102 volcano is shorter and younger than expected.

103

### 104 2. GEOLOGICAL CONTEXT

105 Iliniza volcano is part of the Northern Andean Volcanic Zone, which results from the 106 subduction of the Nazca plate beneath the South American plate (Fig. 1a). The tectonic processes related to the active margin in Ecuador caused the formation of two N-S mountain ranges separated by a 107 tectonic depression known as the Inter-Andean Valley (e.g., Tibaldi and Ferrari, 1992; Spikings et al., 108 109 2005; Winkler et al., 2005; Alvarado et al., 2016). Iliniza volcano (0°39.8'S, 78°43.0'W) is constructed on the boundary between the Western Cordillera and the Inter-Andean Valley. The Western Cordillera 110 mainly consists of deformed oceanic mafic rocks accreted to the continental margin during the Late 111 Cretaceous to Paleocene, which are covered by Paleogene sedimentary and volcano-sedimentary 112 sequences (Jaillard et al., 2004; Vallejo et al., 2009, 2019). These units are in turn overlain by the Silante 113 Formation, which is exposed to the northwest of Iliniza volcano. It is composed of volcanoclastic 114 115 sandstones, conglomerates and red mudstones derived from the erosion of the San Juan de Lachas 116 volcanic island arc, of Early Miocene age (Boland et al., 2000; Vallejo, 2007; Vallejo et al., 2020). Towards the southwest, the Zumbahua Formation constitutes an extensive volcanic and volcano-117 118 sedimentary sequence deposited in lacustrine and fluvial basins during the Late Miocene-Pliocene (Barberi et al., 1988; Hughes and Bermúdez, 1997; Vallejo et al., 2019). Although no radioisotopic ages 119 120 are reported, a Pliocene age is inferred for the volcanoclastic series forming the plains gullied by the 121 Jatuncama River, to the west of Iliniza (Hughes and Bermúdez, 1997).

122 The northern Andean geodynamics are dominated by the northeastward decoupling of the North Andean Sliver from the continental margin of South America (Freymueller et al., 1993; Witt et al., 123 2006; Egbue and Kellogg, 2010; Nocquet et al., 2014). Alvarado et al. (2016) observed that deformation 124 in Ecuador has progressively migrated eastward to its current location on the Chingual-Cosanga-125 Pallatanga-Puna (CCPP) fault system creating the Quito-Latacunga Microblock (QL-M). Iliniza 126 volcano is located along the NE-SW alignment created by the Machachi right-lateral strike-slip fault 127 (M-f; Soulas et al., 1991; Egüez et al., 2003), and is close to the northern extension of the Latacunga 128 129 reverse Fault System (Lavenu et al., 1995; Egüez et al., 2003). The M-fs is considered part of the Quito-130 Latacunga fault system which delineates the western boundary of the QL-M (Alvarado et al., 2016).

131

#### **3. METHODS**

#### **3.1.** Sampling strategy

Field work and sampling were carried out in 2019 and 2020 with the purpose to identify and 134 describe the main volcanic units, to establish their stratigraphic relationships, and to collect new fresh 135 136 rock samples for K-Ar dating and whole-rock geochemical analyses. In addition, in order to gather a 137 comprehensive stratigraphic record, we used previous field data, petrographic descriptions, and samples from Hidalgo (2001, 2006) and Hidalgo et al. (2007). As a result, we completed a dataset of 113 whole-138 rock analyses that cover the entire stratigraphic succession Sample locations are shown in Figure 2. All 139 140 maps and locations are projected using the Universal Transverse Mercator (UTM) coordinate system (Zone 17). 141

142 From the whole dataset, a total of nineteen new samples were selected for K-Ar dating from lava flows, monolithological breccias, and juvenile blocks from PDC deposits. Six samples belong to 143 the North Iliniza edifice, of which two correspond to monolithological breccias located at the base of 144 145 the northern flank (ILI 11, ILI 20), three to intermediate height lavas (ILI 16B, ILI 18, 19EQ17), and 146 one to a summit lava (19EQ24). Four lavas of South Iliniza edifice were sampled from the northern (19EQ18, 19EQ25), eastern (19EQ02), southern (20EQ72) and southwestern (19EQ20, 20EQ75) 147 148 flanks, as along with a lava dome sample (19EQ23b) and a massive lava block (ILI 29A, 20EQ79b) 149 from the summit area. Three juvenile blocks were sampled from PDC's deposits on the northern flank of Iliniza (19EQ16), Jatuncama river valley (19EQ19a) and Santa Rosa area (20EQ81a). Lastly, four 150 dacitic blocks were collected from the Pilongo (ILI 25) and Tishigcuchi (19EQ22, 19EQ70, 20EQ74) 151 satellite lava domes. In addition, three samples of the nearby Santa Cruz volcano were taken from its 152 153 southern (19EQ44) and northern (19EQ03, 20EQ69) flanks.

154

# 155 **3.2.** K-Ar dating

Eighteen samples were carefully selected based on their low weathering appraised from thin section examination (Appendix A). High groundmass abundance (relative to phenocrysts content), and

low vesicle content were also considered. Samples were dated by applying the K-Ar method on 158 groundmass, using the unspiked Cassignol-Gillot technique (Cassignol and Gillot, 1982). The latter 159 relies on the detection of tiny quantities of radiogenic argon (<sup>40</sup>Ar\*) diluted by <sup>40</sup>Ar from atmospheric 160 contamination. The mass spectrometer is used to measure the <sup>40</sup>Ar and <sup>36</sup>Ar electrical signals extracted 161 162 from a sample, and to compare them with an aliquot of pure air measured under the same analytical conditions. This approach renders the knowledge of the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio unnecessary for our 163 technique. The difference of the <sup>40</sup>Ar/<sup>36</sup>Ar isotopic ratios acquired from the sample and the atmosphere 164 is used to quantify the amount of <sup>40</sup>Ar\* produced by the <sup>40</sup>K radioactive decay since the closure of the 165 isotopic system. Thus, the independent measurement of K-content, the <sup>40</sup>K relative isotopic abundance 166 in nature and its decay constant (Steiger and Jäger, 1977; Min et al., 2000) allow to calculate the age of 167 the sample. The Cassignol-Gillot technique is adequate to date young calk-alkaline volcanic products 168 169 that typically exhibit low <sup>40</sup>Ar\* contents (Gillot et al., 2006). This technique was successfully applied to the Quaternary Ecuadorian volcanic arc (Alvarado et al., 2014; Bablon et al., 2018, 2019, 2020), in 170 the Andes (e.g., Germa et al., 2010; Samaniego et al., 2016; Grosse et al., 2018, 2020; Pallares et al., 171 2019; Mariño et al., 2021), and worldwide (e.g., Germa et al., 2011; Hildenbrand et al., 2018; Dibacto 172 173 et al., 2020). Groundmass fraction is preferred for dating since it is the potassium-enriched phase that crystallizes last following the eruption, and thus incorporated the initial argon with atmospheric isotopic 174 ratio. Furthermore, the use of groundmass avoids the possible contamination by inherited <sup>40</sup>Ar\* 175 176 contained in phenocrysts, which could skew ages in young volcanic products (e.g., Singer et al., 1998; 177 Harford et al., 2002; Renne et al., 2012; Lahitte et al., 2019). Samples were prepared following the 178 protocols detailed in Bablon et al. (2018), where analytical procedures, standards used, and uncertainty 179 calculations are also supplied. Potassium and argon isotopic measurements were carried out at the 180 GEOPS laboratory in Orsay (Paris-Saclay University, France). The reproducibility under 1-o confidence level was checked by performing the measurements at least twice. Fourteen new K-Ar ages 181 were acquired from the previous selected samples and are presented in Table 1. 182

183

### 184 **3.3.** Geochemical analyses

185 Nineteen additional samples were collected for geochemical analyses, following the sampling strategy previously described, to provide a dataset of 40 new analyses presented in Appendix B. Whole-186 rock contents of major and trace elements were measured from agate-grinded powders at the GEO-187 OCEAN laboratory, University of Bretagne Occidental (Brest, France) via Inductively Coupled Plasma-188 189 Atomic Emission Spectrometry (ICP-AES), following the procedure described by Cotten et al. (1995). 190 Relative standard deviations are <1% for SiO<sub>2</sub>, <2% for the other major elements, and <5% for trace elements. To provide a complete dataset covering as much of the volcanic history as possible, we 191 included 73 analyses from Iliniza volcano obtained in the same laboratory and published by Hidalgo et 192 al. (2007). 193

194

# 195 **3.4. Geomorphological reconstructions**

Numerical methods allow to model the primary geomorphology of a volcanic edifice despite 196 197 the presence of intense erosive features. They are used to calculate the bulk volume of an edifice at the 198 end of each construction stage, as well as the volume removed by erosion. The morpho-structural 199 analyses were carried out using field observations, Google Earth® satellite images, orthophotography, 200 and a 4-m spatial resolution digital elevation model (DEM) developed by the Sigtierras program from 201 the Ministry of Agriculture and Livestock of Ecuador (http://geoportal.agricultura.gob.ec). A regular 202 30-m resolution point cloud was extracted from it to facilitate numerical calculations. We followed the method developed in Lahitte et al. (2012) according to the descriptions provided by Germa et al. (2015) 203 and Dibacto et al. (2020), which are summarized below. The above-mentioned papers yield further 204 205 methodological details and comparisons with other numerical techniques.

The surface preceding the Iliniza construction  $(S_{t0})$  was calculated using an ordinary kriging interpolation method. Our approach uses the external points extracted from the basal outline of the edifice, and theorized profiles of the paleo-topography. The elevation uncertainty at each point is provided by the prediction standard error map resulting from ordinary kriging. We employed the ShapeVolc software (Lahitte et al., 2012) to model the post-cone-building surfaces  $S_{t1}$  based on control points extracted from reliable present-day remnants of pre-erosion topography such as the radial crests and *planèzes*. Uncertainty at each point is defined by  $\sigma_{St1-i} = \sqrt{\sigma_{mod}^2 + \sigma_{ed-i}^2}$ , where  $\sigma_{mod}$  is the elevation uncertainty of the modeled surface, and  $\sigma_{ed-i}$  is that derived from the spatial dispersion of the control points determined by a prediction standard error map.

The construction stage volume  $v_{cs}$  corresponds to the integration of the elevation difference between  $S_{t0}$  and  $S_{t1}$  surfaces multiplied by the pixel area, while the erosion stage volume  $v_{es}$  uses  $S_{t1}$ and present-day  $S_{t2}$  surfaces. Volume uncertainty  $\sigma_v$  is given by the combination of the height uncertainties of each point  $\sigma_{e-i}$  multiplied by the pixel area, where  $\sigma_{e-i} = \sqrt{\sigma_{Stf-i}^2 + \sigma_{Sti-i}^2}$ . Output  $(R_o)$  and erosion  $(R_e)$  rates are obtained by dividing the  $v_{cs}$  and  $v_{es}$  volumes by the eruptive  $\Delta T_{cs}$  and quiescent  $\Delta T_{es}$  period durations, respectively. Rate absolute uncertainty is defined by  $\sigma_{Ri} = \sqrt{\left(\frac{\sigma_v}{v}\right)^2 + \left(\frac{\sigma_T}{\Delta T}\right)^2}$ , where  $\sigma_T$  is the uncertainty of the period duration  $\Delta T$ .

222

#### **223 4. RESULTS**

# 224 4.1. Morphology

225 The twin peaks of Iliniza volcano correspond to two prominent superimposed stratovolcanoes 226 (Fig. 2). The North Iliniza edifice (5125 m asl), also called Tioniza (Hidalgo, 2001), stands on the 227 eastern edge of the Western Cordillera at 4000 m asl. This volcano has an elongated basal shape with a radius ranging from 4 km over the Western Cordillera side to 6 km in the Inter-Andean Valley side. 228 229 The summit's southeastern flank is not preserved. Only a narrow and steep amphitheater (750 m wide 230 and slope angle  $> 40^{\circ}$ ), probably formed by glacial erosion, remains in place (Fig. 2b). The North Iliniza lavas partially cover the Huayrapungo peak (4585 m asl), a narrow pinnacle located 2.5 km northeast 231 from the summit (Fig. 2b). The South Iliniza edifice (5248 m asl) covers the southeast flank of the 232 North Iliniza edifice. This stratovolcano has a well-defined semicircular shape of 7 km of radius, whose 233 summit is located 1.5 km to the southeast of North Iliniza's summit. The base of the volcano ranges 234 235 from 3300 m asl to 3600 m asl in the inter-Andean valley. Lastly, the Pilongo and Tishigcuchi satellite lava domes are located at the northern and southern flanks of Iliniza volcano, about 5.2 km from itshighest summit.

238 The late Pleistocene glaciations strongly modified the morphology of Iliniza volcano (Hidalgo, 2001), as shown by the different stages of glacial erosion exhibited by its two edifices. The northern 239 240 edifice is dissected by wide U-shaped valleys creating a steep central horn surrounded by a low-sloping plateau situated between 4100 and 4200 m asl, where its lowest points extend down to 3780 m asl. 241 242 Several well-defined ridges radiate from the central horn and separate each glacial valley (Fig. 3a). A 243 succession of moraines a few tens of meters thick is observable inside the main glacial valleys at 244 elevations ranging from 4100 m asl to 4500 m asl. The northwestern flank of the Huayrapungo peak is contoured by a succession of lateral moraines that form a glacial fan at the base of this structure, i.e., at 245 about 4100 m asl at the head of the Pilongo Valley (Fig. 3b). In contrast, the South Iliniza glacial valleys 246 are narrow and less incised preserving the conical shape of the edifice. The lowest frontal and lateral 247 248 moraines are recognizable at the base of the cone at about 3700 m asl on the eastern flank and 3800 m asl on the northern and southern flanks. Heine (2011) presented a summary of evidences describing 249 several glacial cycles in the Ecuadorian Andes (e.g., Clapperton, 1986, 1987; Heine, 1995, 2000). The 250 author inferred that the non-studied moraine sequences of the Iliniza, Cayambe and Antisana volcanoes 251 252 could include deposits from the Last Glacial Maximum (LGM; ~35-20 ka) and even from older cycles. This hypothesis is supported by the moraine associations identified at Rucu Pichincha volcano, where 253 LGM and Younger Dryas (~12.5-10.2 ka) moraine series were recognized via radiocarbon dating in the 254 255 interior of pre-existing wide glacial valleys between 4000 and 3800 m.asl. (Heine, 1995). Observed at 256 similar elevations, the moraine sequences described at Chimborazo volcano and in the Papallacta valley 257 (Chacana caldera; Fig. 1) have been attributed to the LGM and others possibly to previous glacial cycles 258 (Clapperton, 1987, 1990; Heine, 1995). Comparing the moraine elevations in the Ecuadorian Andes, 259 we also consider that those observed at Iliniza volcano were emplaced during the LGM (and possibly 260 during earlier glacial cycles), where its northern edifice suffered a more extended erosion, thus explaining its more conspicuous erosional morphology. Nonetheless, further documentation is required 261 262 to confirm the ages of these glacial deposits.

263

#### 264 **4.2. Eruptive Chronology**

The evolution stages of Iliniza volcano and its relationship with the nearby Santa Cruz volcano are presented below, together with a simplified geological map shown in Figure 4. Volcanic units description is based on the previous studies of Hidalgo (2001, 2002) and Hidalgo et al. (2007), and our new morphologic, stratigraphic, and geochronological data summarized in Table 2.

269

#### 270 4.2.1.Santa Cruz Volcano

Santa Cruz (SC), is a highly eroded stratovolcano (3978 m asl) mainly comprising successions 271 of andesitic lava flows (e.g., 19EQ44: 56.4 wt.% SiO<sub>2</sub>). It is located in the Inter-Andean valley, 10 km 272 273 east of the South Iliniza edifice (Fig. 2). Only the southern flank of the volcano is exposed, where the preserved gently dipping slopes (8-14°) are dissected by wide and deep valleys. Highly weathered and 274 altered dacitic lava domes are found in the summit area (e.g., 19EQ04: 65.6 wt.% SiO<sub>2</sub>). The northern 275 flank, where preserved, is covered by the Inter-Andean valley deposits (Qiv), which are 300 m higher 276 277 compared to the *Qiv* average elevation at the base of the southern flank. A K-Ar age of  $702 \pm 11$  ka is obtained from an andesitic lava flow of the southern ridge (19EQ44), representing an intermediate age 278 of the Santa Cruz edifice. 279

Loma Saquigua (LS) is an isolated summit peak (3839 m asl) of Santa Cruz volcano. The base of Loma Saquigua is formed by a dacite lava dome (LS<sub>D</sub>; 63.7 wt.% SiO<sub>2</sub>). A block taken in its eastern flank (20EQ69) yields a relatively young K-Ar age of  $79 \pm 2$  ka. The upper structure of Loma Saquigua consists of andesitic lava flows (LS<sub>A</sub>; 57.8 wt.% SiO<sub>2</sub>) dated at  $60 \pm 3$  ka (19EQ03). The Santa Cruz volcanic products, including those of Loma Saquigua, show a mineral assemblage composed of plagioclase, orthopyroxene, clinopyroxene, and Fe-Ti oxides, whereas amphibole is more common in the dacitic lavas.

287

#### 288 4.2.2.Iliniza Volcano

#### 289 4.2.2.1. Early satellite lavas

290	The Pilongo lava dome (Pi) is located on the lower north-western flank of Iliniza volcano,
291	along the western edge of the homonymous valley (Fig. 2). This satellite lava dome is 600 m in basal
292	diameter and reaches a height of 3935 m asl., i.e., 250 m above the valley floor. Due to its low elevation
293	and location, the lava dome does not show evidence of substantial glacial erosion. Erosion caused by
294	fluvial processes created steep slopes on its eastern and southern flank. The northern and western flanks
295	are surrounded by a gently sloping plain consistent in elevation and dip with the northern flank of
296	Iliniza. The Pilongo lava dome is formed by porphyritic rhyodacites (68-69 wt. % SiO <sub>2</sub> ; Table 2). A
297	sample taken from the southern base of the lava dome (ILI25) yields an age of $353 \pm 6$ ka.

298

# 299 4.2.2.2. North Iliniza edifice (NI)

This edifice is formed by two thick sequences of andesitic to dacitic (62-65 wt.% SiO<sub>2</sub>) lava flows, monolithological breccias and scarce proximal pyroclastic deposits (Fig. 4; Table 2). The highest portion of the edifice is characterized by widespread hydrothermal alteration. In addition, the lavas sourced from the Huayrapungo satellite peak appear interspersed between the two above-mentioned sequences of North Iliniza.

305 The Lower NI stage (NI-Ls) is defined by a sequence of monolithological breccias, 5-30 mthick lava flows, and scare pyroclastic successions, displaying andesite to dacite compositions (62-64 306 307 wt.% SiO<sub>2</sub>). This sequence is well exposed in the glacial ridges around the North Iliniza edifice specially on the Western Cordillera side (e.g., Quillotoro and Ninarrumi hills; Fig. 3a). The NI-Ls maximum 308 thickness is estimated at 200-300 m in the Western Cordillera side, and 700-800 m in the Inter-Andean 309 310 Valley side. The NI-Ls succession overlies the Mio-Pliocene volcano-sedimentary sequences of the Western Cordillera (i.e., Silante and Zumbahua Formations). Two blocks taken from two 311 monolithological breccia layers (ILI20, ILI11) in the northern flank give ages of  $122 \pm 6$  and  $123 \pm 6$ 312 313 ka.

314 The Huayrapungo stage (NI-Hs) is represented by an eroded peak formed by voluminous andesitic lavas (62 wt.% SiO<sub>2</sub>) cropping out in the northern NI flank. Huayrapungo lavas exhibit meter-315 scaled flow banding textures, well-exposed in the southern flank of the peak (Fig. 4b), whereas flow 316 foliation and subvertical columnar jointing are common close to the summit areas. Although field 317 318 relationships are unclear, it seems that Huayrapungo lavas, of at least 250 m in thickness, overly a pyroclastic succession probably related to the Lower NI stage clearly observed in the southern flank of 319 320 the Huayrapungo peak. Based on the morphological and structural characteristics of Huayrapungo and its stratigraphic position, we consider this peak as a satellite vent of the NI edifice. A sample (19EQ17) 321 collected south of the Huayrapungo peak is dated at  $121 \pm 2$  ka. 322

The Upper NI stage (NI-Us) consist of a 600–700 m-thick pile of viscous lava flows (30-60 323 m in thickness) that shape the upper structure of the North Iliniza edifice above 4400 m asl (Fig. 4a). 324 This lava succession is andesite to dacite in composition (62-65 wt.% SiO<sub>2</sub>). A notable feature is a 325 326 voluminous 100 m-thick lava exposed in the summit area which flowed down 1500 m northwestwards 327 (Fig. 3a). Erosion reveals the flow foliation structure and fractures associated with a secondary summit vent located at 4800 m asl. A sample collected at the base of this massive lava yields an age of  $116 \pm 2$ 328 ka (IL118). Another 90 m-thick lava is located on the western flank in the Quillotoro hill, overlying the 329 330 NI-Ls succession. It is cut by a glacial valley on its highest portion. We suggest an emplacement age similar to that of the ILI18 lava flow. 331

332

# 333 4.2.2.3. South Iliniza edifice (SI)

This edifice corresponds to a compound volcano formed by a basal stratovolcano discordantly overlain by a summit lava dome complex and massive lava flows (Fig. 5). These successions define the three cone-building stages of the South Iliniza edifice (Table 2). The lower flanks of the edifice are covered by a thick pyroclastic succession associated with the second stage.

338 The Lower SI stage (SI-Ls) corresponds to an early cone constructed on top of the NI 339 successions and the remnants of the Santa Cruz volcano. It consists of a 1100 m-thick succession of 340 dacitic (62-65 wt. % SiO<sub>2</sub>) massive lavas, sparse inter-layered breccias, and semi-consolidated PDC 341 deposits. Outcrops near the center of the edifice show moderated hydrothermal alteration. Two consistent ages of  $45 \pm 2$  ka and  $46 \pm 1$  ka are obtained from lavas located on the northern (19EQ18) 342 and eastern (19EQ02) flanks, respectively. Glacial striations preserved on the northern lava flow 343 344 confirm its pre-LGM age (roughly 35-20 ka; Clapperton, 1986; Heine, 2011). This basal stratovolcano is disrupted above 4700 m asl where the radial slope decreases top-down from 35° to less than 10° 345 forming a truncated cone. The change in slope is especially noticeable on the southern flank where a 346 347 saddle shape structure, called the Cantarilla height (Fig. 3a), marks a structural unconformity (Fig. 4a and 5b). 348

349 The Upper SI stage (SI-Us) incorporates a pyroclastic succession surrounding the lower flanks
350 of the basal cone, and the summit lava domes located above the Cantarilla unconformity (Table 2).

351 The Jatuncama ignimbrite (SI-Ji) is a widespread PDC succession that crops out at the lower flanks of the South Iliniza edifice (Fig. 6). Widespread outcrops occur in the Jatuncama valley, to the 352 353 southwest of Iliniza volcano (Fig: 4). The Jatuncama pyroclastic deposits overlie semi-consolidated pyroclastic deposits ascribed to the Lower SI stage to the east, and inorganic consolidated soils to the 354 355 south of the SI edifice. The Jatuncama ignimbrite consists of a thick multiple bedded block-and-ash 356 PDC sequence (SI-J<sub>BA</sub>) overlaid by pumice-and-ash flow deposits (SI-J<sub>PA</sub>). The SI-J<sub>BA</sub> deposits are 357 continuous, typically normal graded to massive, poorly sorted, slightly consolidated, and gray to pinkish 358 in color. No interlayered paleosoils are observed in the Jatuncama sequence. Degassing pipes are commonly observed in the upper beds (Fig. 6b). The SI- $J_{BA}$  deposits are constituted by poorly 359 360 vesiculated juvenile dacite blocks (63-67 wt.% SiO<sub>2</sub>; Table 2) showing radial and prismatical-jointed 361 structures, and varying amounts of pumice lapilli. Both clast types are supported in a fine-grained ashmatrix bearing glass shards and free crystals of plagioclase, amphibole, and scarce pyroxene. Low-362 density pumice lapilli are generally scarce in the lower beds of the SI-J<sub>BA</sub> deposit, whereas clasts with 363 textural banding of glassy and high-density pumice are common (Fig. 6c). The SI-J<sub>BA</sub> average thickness 364 is ~30-40 m with a maximum of 120 m in the Jatuncama valley. The reconstructed area covered by the 365 SI-J<sub>BA</sub> deposits reaches  $\sim 60 \text{ km}^2$  with an average thickness of 35 m, yielding an estimated volume of 366

367 2.1 km<sup>3</sup>. These values suggest an eruptive phase with a volcanic explosivity index (VEI) of at least 5. 368 We should stress that no tephra fallout deposits have been observed, thus the estimated volume should 369 be considered as a minimum. The high-density pumice sample (19EQ19a) collected from an 370 intermediate bed of the SI-J<sub>BA</sub> in the Jatuncama valley exhibit high atmospheric contamination 371 preventing K-Ar dating.

372 Two 7-10 m-thick pumice-and-ash PDC units (SI-JPA) overlie the SI-JBA deposits at the Jatuncama valley (site 20EQ92; Fig. 6d) and the northeastern SI flank (site 20EQ96). The SI-J<sub>PA</sub> units 373 are massive, poorly consolidated, and light gray to beige in color. They are composed of fibrous dacite 374 375 pumice lapilli (65-67 wt.% SiO<sub>2</sub>) and occasional high-density dacite blocks up to 10 cm in diameter (Fig. 6e), supported in a matrix formed by fine glass shards and crystals of plagioclase, amphibole, and 376 pyroxene. In addition, a 25 cm-thick rhyolite pumice-and-ash flow PDC deposit (71-72 wt.% SiO<sub>2</sub>) 377 crops out on the northeastern SI flank was described as the Santa Rosa pumice-and-ash PDC (SI-JSR) 378 379 by Hidalgo et al. (2007). We identified a  $\sim$ 1-2 m-thick matrix-supported deposit (site 20EQ81), with a poorly-sorted texture, outcropping on top of the northern SI-J<sub>PA</sub> (site 20EQ96). The collected samples 380 reveal a mixture of rhyolitic pumiceous blocks (20EQ81a) and poorly vesiculated dacite blocks 381 (20EQ81b, c) all ranging from 10-30 cm in diameter, suggesting a probable reworking of the primary 382 383 deposit described by Hidalgo et al. (2007).

384 The Jatuncama ignimbrite sequence is preserved as a gently sloping surface (4-12°) intersected by shallow fluvial channels. The heads of these streams are commonly covered by moraines or 385 intersected by glacial valleys at elevations above ~3750 m asl, i.e., above the LGM limit observed in 386 387 other volcanoes of the region (Clapperton, 1986, 1990; Heine, 2000, 2011). The Jatuncama succession 388 is overlain by a thick sequence of paleosoils, tephra fallout deposits from Cotopaxi, and other reworked 389 materials of broadly Holocene age (Fig. 5a). Notably, the Cotopaxi F2 and F4 rhyolitic tephra fall deposits ( $7770 \pm 70$  to  $5830 \pm 80^{-14}$ C yr BP; Hall and Mothes, 2008) were identified in the Planchaloma 390 and Pastocalle areas (Fig. 4). Minor landslide scarps affecting these shallow deposits are recognizable 391 392 on the eastern and southeastern SI flanks.

Two *consolidated PDC deposits (SI-U*<sub>CP</sub>) crop out east of the Cantarilla height, on the southwestern flank of the cone (Fig. 4b). These deposits, which are  $\sim 100$  m-thick each, overlie the Lower SI sequence forming the conspicuous Cantarilla angular unconformity. The summit lava domes and its related deposits overlie this pyroclastic sequence. Unfortunately, no samples could be collected due to the terrain roughness.

The Summit Lava Dome Complex (SI-USDC) is located on top of the remnants of the Lower SI 398 edifice (Fig. 5b), between 4710 and 5060 m asl, reaching a basal diameter of ~1.7 km. The SI-U<sub>SDC</sub> 399 400 vent, inferred as the geometrical center of the structure, occurs 250 m to the north with respect to that 401 of the basal cone. As a result of the erosion, only the main core of the summit lava domes has been 402 preserved. Multiple lava lobes and remnants of the SI- $U_{SDC}$  talus are exposed in the summit southern flank, forming a sequence of thinner strata lying unconformably upon the older cone in the Cantarilla 403 height (Fig 5b). The summit lava domes are dacitic in composition (64–67 wt.% SiO<sub>2</sub>) and. A sample 404 405 taken at the northern base of the SI-U<sub>SDC</sub> (19EQ23b) yields an age of  $34 \pm 1$  ka. The higher sections of the South Iliniza edifice are covered by undifferentiated dacitic breccias (SI-U<sub>DL</sub>) interpreted as 406 reworked PDC deposits related to the SI-U<sub>SDC</sub> dome-forming eruptive activity. 407

The Terminal SI stage (SI-Ts) is represented by several massive lava flows and 408 409 monolithological breccias that overlie the SI-U<sub>SDC</sub> deposits and descend mainly along the western flank 410 into the Providencia valley (Fig. 4b and 5). This lava succession shapes the SI edifice summit above 5000 m asl, reaching a thickness of ~250 m. The SI-Ts lavas are mostly andesitic in composition (SI-411  $T_A$ ; 61–63 wt.% SiO<sub>2</sub>). Two voluminous lava flows, called the Termancucho lavas (Hidalgo, 2001), 412 413 outcrop on the summit's western flank and can be traced 3 km downslope into the upper Providencia 414 valley (Fig. 3a and 4b). The lower 70 m-thick lava flow (20EQ79) is composed by a porphyritic dacite (SI-T<sub>D</sub>; ~67 wt.% SiO<sub>2</sub>), whereas the upper 50 m-thick lava flow (ILI 29) has an andesitic composition 415  $(\sim 62 \text{ wt.}\% \text{ SiO}_2)$  consistent with the overlying SI-T<sub>A</sub> series (Table 2). A sample collected from the lower 416 417 Termancucho lava (20EQ79a) was discarded for K-Ar measurements due to its high phenocryst and 418 low groundmass contents. Another andesitic lava flow outcrops on the southern SI flank at the headwaters of the Tiliche river (site 20EQ72; Fig. 4), is partially overlaid by a LGM moraine. The 419

420 upstream trace of the Tiliche lava flow is intersected by the Providencia valley, hiding the source of this 421 flow. Nevertheless, we relate this lava flow to the summit's terminal lavas given their similar 422 petrological characteristics and stratigraphic position (Table 2). A sample taken from the base of the 423 Tiliche lava flow (20EQ72) yields an age of  $31 \pm 4$  ka. A comparable, albeit younger, age of  $25 \pm 3$  ka 424 was obtained from an andesitic block (19EQ25) collected from a monolithological breccia on the 425 northern SI flank.

426

# 427 4.2.2.4. Late satellite lavas

Tishigcuchi (T), also called Rasuyacu (Hall and Beate, 1991), is a satellite dome *coulée* located 428 429 on the southern flank of the South Iliniza edifice (Fig. 7a). It is composed of a 1100 m-wide lava dome (4185 m asl), and at least 3 viscous lava flows reaching 90 m-thick and 1800 m-long. The lava SI-J<sub>BA</sub> 430 was constructed over a 7° slope at 3850 m asl formed by the SI- $J_{BA}$  and the Tiliche lava flow (Fig. 4). 431 The Tishigcuchi lava *coulée* is andesitic in composition (62-63 wt.% SiO<sub>2</sub>). No collapse or explosion 432 433 crater structures are observed, and no pyroclastic deposits related to the Tishigcuchi lava dome are 434 found in our study. The dome shows no evidence of glacial erosion and is covered by soils intercalated with Cotopaxi's rhyolitic Holocene lapilli and ash fall deposits. Attempts to obtain a K-Ar age from the 435 436 selected samples (19EQ22, 20EQ74) were unsuccessful due to the high atmospheric contamination 437 exhibited by the groundmass.

Pongo (Pg) is a voluminous lava forming a 4 km-long terrace between the Pongo and 438 Providencia rivers, in the Jatuncama valley (Fig. 7b). The erosion caused by the Pongo river has exposed 439 a 60-m-high cliff with columnar jointing at the southwestern edge of the lava. Exposures of the 440 441 Jatuncama ignimbrite are observed on the valley walls next to the Pongo lava . The Pongo lava is composed by aphanitic andesites (59 wt.% SiO<sub>2</sub>). Although the sample collected at the Providencia 442 River (19EQ20) is highly contaminated by atmosphere, a second sample taken at the base of the 443 columnar jointing exposures (20EQ75) provides an age of  $6 \pm 4$  ka. The source of the lava flow cannot 444 445 be clearly identified upstream into the glacially carved Providencia valley. Given the size of the Pongo

lava and its Holocene age, its upper parts should be still observable as they could not have been
completely eroded or covered by younger deposits. Thus, an origin from a satellite vent located at the
southwestern base of Iliniza volcano is suspected.

449

### 450 **4.3. Reconstructed morphology for volume estimations**

#### 451 4.3.1.Basement surface reconstruction

452 Defining the substratum morphology is an essential step for volume calculations, as minor 453 changes in the basement morphology could lead to volume errors greater than 50% in stratovolcanoes (e.g., Ceboruco volcano; Frey et al., 2004; Tungurahua volcano; Bablon et al., 2018). The basement 454 shape of Iliniza volcano ( $S_{I-t0}$  surface) was reconstructed using a theorized topographic profile 455 modeled from four parallel auxiliary profiles located to the north and to the south of the volcano . The 456 auxiliary profiles intersect the hills of Ninarrumi and Quillotoro to the north, and Chilcapamba to the 457 south of the Iliniza volcano (Fig. 2 and 8a), which form the northwestern-southeastern ridge of the 458 Western Cordillera. Further to the east, at the eastern and southeastern foothills of the South Iliniza 459 460 edifice, the auxiliary profiles intersect a slight elevation of the Santa Cruz volcano and the Loma La 461 Cruz ridge (Fig. 8a).

462

# 463 **4.3.2.Iliniza volcano paleosurface reconstruction and volume calculations**

The total reconstructed area for Iliniza volcano is 127 km<sup>2</sup>, which corresponds to a present-day bulk volume of  $34 \pm 14$  km<sup>3</sup>. This volume represents the amount of volcanic products preserved between the present-day topography and the modeled basement surface  $S_{I-t0}$ . Considering an activity range of  $98 \pm 7$  kyr, corresponding to the growth of the North and South Iliniza edifices between  $123 \pm 6$  ka and  $25 \pm 3$  ka, an apparent bulk output rate of  $0.35 \pm 0.14$  km<sup>3</sup>/kyr was determined. Nevertheless, our results have shown that the eruptive activity of Iliniza volcano was seemingly interrupted by long-term quiescence periods between each construction stage. Therefore, volume calculations, and growth or 471 output rates, require to be adjusted for each construction and erosion stages (Table 2). Appendix C
472 provides several topographic profiles comparing the modeled cones of the Iliniza edifices, the modeled
473 basement surface, and the present-day surface.

474 The first construction stage of the Iliniza volcano corresponds to the extrusion of the Pilongo lava dome, which has a present-day volume of  $18 \pm 5 \times 10^{-3}$  km<sup>3</sup>. The next stage corresponds to the 475 construction of the North Iliniza edifice. The modeled cone  $S_{NI-t1}$  has a semicircular base with a 476 477 concave profile that reached 5200 m asl. The symmetry axis is located 200 m southwest of the present-478 day summit and is coincident with the narrow amphitheater of the eastern flank. The volume of the modeled cone  $v_{NI-cs}$  is  $28 \pm 9$  km<sup>3</sup>, a relatively small value compared to the volcano's heigh of ~1700 479 480 m above the Inter-Andean Valley. This value is explained by the presence of the Western Cordillera 481 basement, which makes its base level ~400 m higher than the Inter-Andean valley. Considering a period of activity occurring between  $124 \pm 5$  ka and  $116 \pm 2$  ka, the output rate obtained  $R_{NI-o}$  is  $3.5 \pm 2.6$ 482 km<sup>3</sup>/kyr. 483

La Virgen plain (LV), located northeast of Iliniza volcano (Fig. 2 and 5), was originally 484 interpreted as part of the South Iliniza edifice (Hidalgo et al., 2007). However, a detailed analysis of its 485 geometry reveals that the slope gradient direction of La Virgen points to a source located to the west, 486 coinciding with the location of the North Iliniza edifice. We support this hypothesis by the discordant 487 position of the northern lava flow from the SI-Ls stage (19EQ18, ILI 34). This lava flowed into the 488 489 Pilongo valley between La Virgen plain and the Huayrapungo peak (Fig. 4), implying a pre-South Iliniza construction for the northeastern sector. Overlapping of other products of the South Iliniza 490 edifice is not excluded during the formation of La Virgen plain. 491

The reconstruction of the eastern sector of the North Iliniza edifice at ~45 ka (i.e., before South Iliniza construction) was not straightforward given that this area is covered by the South Iliniza deposits. This area completes the surface  $S_{NI-t2}$  corresponding to the relief at the end of the quiescence period between growth of both edifices. We used two auxiliary topographic profiles based on radial sections of the present-day northeastern sector La Virgen and the southwestern sector Pongo alto (Fig. 8b) to compute the surface  $S_{NI-t2}$ . The eroded volume  $v_{NI-es}$ , calculated between the modeled cone  $S_{NI-t1}$  and the eroded surface  $S_{NI-t2}$ , is  $6 \pm 2 \text{ km}^3$ . Only the western sector was exposed to non-stop weathering during the ~116 kyr quiescence of North Iliniza. Then, the eroded volume in the western sector  $v_{es-W}$ is  $3 \pm 1 \text{ km}^3$ , implying an erosion rate  $R_{NI-e-W}$  of  $0.03 \pm 0.01 \text{ km}^3/\text{kyr}$ .

501 The construction of the South Iliniza edifice comprises the lower cone-building, the upper conebuilding, and the terminal effusive stages. The former two cones were modeled independently as a first 502 503 approach, but we selected a simpler geometry involving a single cone given the poor geometric constrains. A volume  $v_{SI-cs}$  of  $18 \pm 6$  km<sup>3</sup> was obtained for the modeled cone  $S_{SI-t1}$ . As in the case of 504 the North edifice, this volume appears to be rather small given the volcano height of ~1850 m measured 505 from the Inter-Andean valley bottom. The modeled paleo-summit is located 250 m east of the current 506 summit and reaches 5300 m asl. Considering a  $21 \pm 3$  kyr-long cone-building period (from  $46 \pm 1$  to 25 507  $\pm$  3 ka), the South Iliniza edifice yields an output rate  $R_{SI-o}$  of  $0.8 \pm 0.3$  km<sup>3</sup>/kyr. The volume difference 508 509 between the present-day surface  $S_{SI-t2}$  and the reconstructed cone  $S_{SI-t1}$  gives an eroded volume  $v_{SI-es}$ of  $6 \pm 2 \text{ km}^3$  implying an erosion rate  $R_{SI-e}$  of  $0.24 \pm 0.09 \text{ km}^3/\text{kyr}$ . Figure 8c shows that the northern 510 contact between the South Iliniza modeled cone and the partially eroded North Iliniza edifice occurs 511 along the Rio Blanco valley in the northern sector and along the Pongo Alto valley in the southern sector 512 (see also Fig. 11c-f). Lastly, the Tishigcuchi lava dome yields a present-day volume of  $339 \pm 41 \times 10^{-3}$ 513 km<sup>3</sup>, whereas the Pongo lava flow reaches a volume of  $73 \pm 18 \times 10^{-3}$  km<sup>3</sup>. 514

515

# 516 4.4. Geochemical characterization

The Iliniza volcanic products are classified in the SiO<sub>2</sub> vs. K<sub>2</sub>O diagram (Fig. 9a; Peccerillo and Taylor, 1976) as medium-K andesites and dacites, which are similar to those observed in other Volcanic Front edifices (VF, Fig. 1b). Some scarce andesites and rhyolites, corresponding to the Pongo and Santa Rosa units, fall outside the VF field. Each construction stage shows narrow silica content ranges. Negative correlations are observed in Harker diagrams including MgO, Fe<sub>2</sub>O<sub>3</sub>\*, CaO, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> *versus* silica, used as differentiation index, while K<sub>2</sub>O and Na<sub>2</sub>O show positive correlations (Fig. D.1). The North Iliniza and South Iliniza eruptive products typically form well-defined trends. Samples from the Pilongo and Santa Rosa units plots along or near the prolongation of the Iliniza trend. In contrast,
the eruptive products of Tishigcuchi and Pongo show K<sub>2</sub>O enrichment and Na<sub>2</sub>O depletion compared
to the andesitic lavas of the Terminal SI stage(SI-T<sub>A</sub>).

527 Variations in trace element contents in relation to silica increase for the North and South Iliniza 528 tend to form well-correlated trends (Fig. D.2). Some transition metals (e.g., V, Sc) show a marked 529 compatible behavior as well as Heavy Rare-Earth Elements (HREE; e.g., Yb) and Y. However, the 530 Large-Ion Lithophile Elements contents (LILE; e.g., Rb, Ba) remain relatively constant, except for 531 South Iliniza edifice which shows an overall incompatible behavior with the andesitic SI-Ts values 532 being the lowest. High contents of Light Rare-Earth Elements (LREE; e.g., La, Ce), Th and Sr are observed in the products of Santa Rosa, Tishigcuchi and Pongo. Cr and Ni are also high for these 533 samples, as well as in the andesitic SI-Ts lavas. Only a few samples are available for lower South Iliniza 534 edifice, making its geochemical signature poorly constrained. Its northern lava flow (19EQ18, ILI 34) 535 536 exhibits unusually high LREE, Th and Sr contents.

537 Incompatible elements and Rare-Earth Elements (REE) spider diagrams normalized to primitive mantle/chondrites (Sun and McDonough, 1989) are shown in Figure 9b-e. Overall, the 538 chondrite-normalized REE diagram for North and South Iliniza dacites exhibit similar, slightly 539 540 fractionated patterns with LREE enrichment and HREE depletion, and no Eu anomaly. The South 541 Iliniza samples present an overall, albeit slight, REE depletion relative to North Iliniza, except for the 542 northern Lower SI stage lava flow (19EQ18, ILI 34) which has a strong LREE enrichment. The highest HREE depletions are observed for the most evolved products of Iliniza volcano, i.e., the dacitic 543 544 Termancucho lava (dacitic SI-Ts), Pilongo and Santa Rosa units. The primitive mantle-normalized plot 545 reveals a similar pattern for all samples with positive Ba, K and Rb anomalies and negative Nb and P. Lower Ti, Dy, Y and Yb signatures characterize the dacitic SI-Ts, Pilongo and Santa Rosa units. The 546 low HREE (e.g., Yb<0.61 ppm) and Y (<7.8 ppm) concentrations observed in the Pilongo and Santa 547 Rosa units, coupled with the high LREE (e.g., La>12 ppm) contents, result in elevated La/Yb ratios 548 compared to other units (Fig 10e). Conversely, samples from the Tishigcuchi and Pongo eruptive 549 products show similar ratios but also higher mafic signatures (e.g., SiO<sub>2</sub><63 wt.%, Mg#>50). Overall, 550

the La/Yb ratio show a slight increase over time (excluding Pilongo), whereas fluid-mobile to fluidimmobile ratios (e.g., Ba/Th) decrease (Fig. 10b, d). Further detailed descriptions regarding the geochemistry and petrography of Iliniza volcano are provided in Hidalgo (2001, 2002) and Hidalgo et al. (2007).

555

#### 556 5. DISCUSSION

557 5.1. Iliniza and Santa Cruz geochronological evolution

Although a rather limited number of ages have been obtained here, their key stratigraphic 558 position allows us to propose a complete geochronological evolution of Iliniza and Santa Cruz 559 volcanoes. Our stratigraphic, geochronological, and geochemical data suggest that the Iliniza volcano 560 561 had a relatively short lifetime span. We propose that Iliniza volcano was constructed in short eruptive intervals separated by long repose periods throughout late Pleistocene (from ~350 ka to the Holocene) 562 as summarized below. Prior to the construction of the Iliniza volcano, the Santa Cruz volcano was 563 constructed in the Inter-Andean valley. The predominantly effusive activity of the Santa Cruz volcano, 564 dated at  $702 \pm 11$  ka, is represented by the thick lavas exposed on its southern flank and the dacitic lava 565 domes present in the summit area. We found no other evidence of volcanic activity in this area until the 566 extrusion of the Pilongo lava dome, the earliest stage of Iliniza volcano, which took place close to the 567 Machachi fault (Fig. 3) at  $353 \pm 6$  ka. 568

569 After an apparent quiescence period of ~230 kyr, the North Iliniza volcano started the 570 construction of a  $\sim 1600$  m-high edifice, in the southern prolongation of the Machachi fault (Fig. 11a). 571 Two lava successions characterize the effusive activity occurring between  $123 \pm 6$  and  $116 \pm 2$  ka (Table 572 1), after the Penultimate Glacial Maximum (Shackleton et al., 2003). Nevertheless, we interpret this age 573 range with caution as no basal lava could be sampled. Based on morphological and stratigraphic evidence, we attribute the formation of the Huayrapungo peak to a satellite vent contemporary with the 574 lower lava sequence. Later, the erosion caused by Pleistocene glaciations, presumably from pre-LGM 575 glacial cycles (>49 ka; Heine, 2011), shaped the wide radial glacial valleys around the North Iliniza 576

summit, and incised the Pilongo and Providencia-Pongo paleo-valleys (Fig. 4). After an apparent ~620 kyr-long quiescence period, activity resumed on the Santa Cruz volcano when the dacitic lava dome of Loma Saquigua was extruded at  $79 \pm 2$  ka, followed by the emission of andesitic lavas at  $60 \pm 3$  ka (Fig. 11b).

581 The South Iliniza edifice was constructed on top of the partially eroded North Iliniza. A conspicuous structural unconformity marks the two growth phases of this edifice. The earliest phase 582 583 corresponds to the emplacement of the Lower SI stage eruptive products, which are constituted by thick 584 lavas and pyroclastic successions dated at about 45 ka, forming a basal edifice (Fig. 11c). Remnants of 585 this edifice are exposed in the southern flank and in the center of the South Iliniza edifice. According to the stratigraphic position of the Jatuncama ignimbrite deposits covered by LGM moraines, and its 586 radial distribution fanning away from the South Iliniza edifice, we propose that this unit represents an 587 explosive phase prior to the second growth phase of this edifice (Fig. 11d). As discussed below, the 588 589 geochemistry of the dacitic components of the Jatuncama ignimbrite is comparable to the SI summit 590 lava domes (SI-U<sub>SDC</sub> unit), thus supporting our hypothesis. During the second growth phase, a summit lava dome complex and its related pyroclastic deposits subsequently filled the depression caused by the 591 Jatuncama eruption (crater rim, Fig. 4) and reconstructed the volcanic cone since  $34 \pm 1$  ka. Then, a 592 593 final mostly effusive stage involved the emission of several andesitic lavas covering the uppermost parts of the volcanic cone (Fig. 11e). Our K-Ar ages suggest that this activity extended up to  $25 \pm 3$  ka. 594

595 The Tishigcuchi lava dome coulée and Pongo lava flow extrusions represent the youngest eruptive stages of the Iliniza volcano (Fig. 11f), as previously suggested (Hall and Beate, 1991). The 596 597 Tishigcuchi lava dome was extruded on the southern flank of the volcano along the southern 598 prolongation of the Machachi fault. Although no radiometric age could be obtained, a stratigraphic age 599 between 20 to 8 ka can be proposed due to the presence of the underlying Tiliche lava flow dated at 31  $\pm$  4 ka, the lack of LGM glacial erosion or associated deposits (maximum extents reached at 34.8-27.9 600 601 ka and 19.2 ka; Heine, 2011), and the overlying Cotopaxi F2 and F4 fallout deposits (~8.5 and ~6.7 cal ka; Hall and Mothes, 2008). Finally, the age obtained from the Pongo lava flow  $(6 \pm 4 \text{ ka})$  demonstrates 602 that Iliniza volcano was still active during the Holocene. 603

604 The available ages in the central part of the Ecuadorian arc point to the existence of two types of volcanism based on the extent of their eruptive chronology. The long-lived volcanic complexes, 605 which exhibit multiple edifices and cone-building stages as old as 1 Ma, extending their activity to more 606 recent times even up to the Holocene (e.g., Pichincha and Cayambe volcanic complexes; Samaniego et 607 608 al., 2005; Robin et al., 2010), and the short-lived compound volcanoes, which were rather formed in briefer cone-building stages of few tens of ka and were mostly emplaced in relatively recent times (e.g., 609 Cotacachi and Imbabura volcanoes; Le Pennec et al., 2011; Almeida et al., 2019). Our new K-Ar ages 610 reveal that the age and extent of Iliniza volcanic activity is in good agreement with this group of young 611 612 short-lived volcanoes, whereas Santa Cruz could be considered as a long-lived volcano.

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# 5.2. The Jatuncama explosive phase

615 The Jatuncama ignimbrite samples exhibit a dacitic composition similar to that of the South Iliniza upper stage (Fig. 12). However, the compositional dispersion of the SI-J<sub>BA</sub> points to a more 616 617 intricate deposit, as indicated by the SiO<sub>2</sub> content ranging between 63 and 67 wt.%. Figures 12a and 618 12b show the geochemical distribution of the SI-J<sub>BA</sub> dacitic juvenile clasts compared to the South Iliniza units. For similar SiO<sub>2</sub> and Mg# values, the low-density pumices are slightly enriched in K<sub>2</sub>O compared 619 620 to the high-density pumices and dacites. Furthermore, the high-density pumices generally fall within 621 the SI-U<sub>SDC</sub> field, while low-density pumices are more correlated with the SI-T<sub>D</sub> pole. The few glassy juvenile clasts available are relatively scattered without any clear relationship. The  $SI-J_{BA}$  composition 622 623 also shows slight variations according to the location of the sampling site (Fig. 12d). A relatively higher dispersion degree is observed in the Jatuncama valley and on the southern flank (sites 7-9) compared to 624 625 the southeastern flank where low  $K_2O$  samples seem to be absent (sites 3-5). This difference may be 626 explained by the fact that the lower SI- $J_{BA}$  beds, with higher participation of high-density pumices and dacites, are not well exposed on the southeastern flank. In addition, the plots of the SI-J<sub>PA</sub> units 627 (20EQ92, 20EQ96) fall in the fields of slightly K<sub>2</sub>O enriched clasts. Therefore, on the basis of this 628 629 geochemical evidence, the petrographic descriptions provided above, and the fact that neither 630 discordances, nor interlayered paleosoils are observed in the Jactuncama succession, we argue that the Jatuncama ignimbrite units correspond to an intricate deposit formed during an explosive dome-forming eruption followed by a pumiceous phase both associated with the upper SI stage, as suggested by Hidalgo et al. (2007). The Jatuncama eruption was followed by the extrusion of the Summit Lava Dome Complex (SI-U<sub>SDC</sub>). Based on the estimated volume of the Jatuncama deposits, we infer the formation of a 1.5-2 km-wide crater (Figures 4 and 11d) related to the Jatuncama explosive phase (minimum VEI ~5), which agrees with the top surface diameter of the truncated basal cone (i.e., SI-Ls). The Cantarilla discordance marks the inferred crater rim created during the Jatuncama explosive phase (Fig. 11d).

638 In the lack of direct measurement, geomorphological, stratigraphic, and geochemical data can 639 provide an approximate age for the Jatuncama ignimbrite. Considering that the SI-Ji sequence overlies the SI-Ls deposits and its distribution around the basal SI edifice, a lower bound is defined by the Lower 640 SI stage at  $45 \pm 2$  ka. The overlaying Tiliche lava flow (20EQ72) constrains the upper bound at  $31 \pm 1$ 641 ka. Such pre-LGM age is supported by the glacial morphology affecting the highest sections of the 642 643 ignimbrite deposit, and by the thick Holocene tephra fallout sequence. Finally, considering the geochemical affinity with the SI- $U_{SDC}$  unit, we propose that the Jatuncama explosive phase, and the 644 formation of the SI-Ji pyroclastic sequence, occurred shortly before the extrusion of the summit lava 645 domes dated at  $34 \pm 1$  ka (19EQ23b). 646

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648 5.3. Growth and erosion patterns of Iliniza Volcano

Volcanic edifices are composed of a wide variety of eruptive products including lava flows, lava domes, PDC successions, and fallout deposits accumulated around a central vent. The destruction of part of the volcanic edifice during highly explosive events and/or sector collapses, and the remobilization of unconsolidated materials are other factors to consider during or in between the growth phases. Therefore, the bulk volume of the main edifice does not represent the entire volcanic products emitted and thus the calculated values should be considered as minima. Nevertheless, volumes obtained in numerical reconstructions provide a first-order approximation, allowing recognition of fluctuations in its spatial and temporal output patterns, and allowing comparison with other eruptive centers, asdiscussed below.

658 According to our numerical reconstructions both Iliniza edifices reached similar heights and 659 volumes. The combined  $v_{cs}$  volumes of the Iliniza edifices and satellite lava domes reaches a total bulk volume of  $46 \pm 15$  km<sup>3</sup> of accumulated material (Table 2). This value includes the volume of material 660 661 removed by erosion during the quiescence periods ( $v_{es}$ ). About 61 vol.% of this volume belongs to the North Iliniza edifice, 38 vol.%. to the South Iliniza edifice, and the remaining 1 vol.% to the satellite 662 lavas. Due to the complex topography of the Iliniza basement, our results exhibit a relatively high 663 uncertainty of ~35 vol.%. The volume of the SI-Ji deposits is implicitly included in our calculations as 664 665 its estimated value is within the volume uncertainty range.

666 The bulk volume of Iliniza volcano is similar to those reported for the other compound volcanoes located at the Ecuadorian northern cross-arc segment, e.g., Cushnirumi, Cusin, Fuya-Fuya 667 668 and Imbabura, which range from  $31 \pm 19$  km<sup>3</sup> to  $61 \pm 24$  km<sup>3</sup> (Bablon et al., 2020). Large volcanic 669 complex such as Pichincha, Cayambe and Mojanda accumulated larger volumes ranging from  $115 \pm 5$ 670 to ~160 km<sup>3</sup> (Robin et al., 2010; Samaniego et al., 2005; Bablon et al., 2020), which is not the case of 671 Iliniza volcano. In contrast, Antisana has a bulk volume of  $\sim 61 \text{ km}^3$ , but has a lifespan longer than 400 ka (Hall et al., 2017b). Volcanoes with volumes similar to those of Iliniza volcano are also found in the 672 southern cross-arc segment. Effectively, each Iliniza edifice is comparable in volume to the Mulmul or 673 674 Huisla stratovolcanoes, which show values of  $22 \pm 7$  and  $25 \pm 11$  km<sup>3</sup> (Bablon et al., 2018, 2020). Nevertheless, Iliniza volcano has a smaller volume relative to Chimborazo (Samaniego et al., 2012) and 675 the whole Tungurahua (Bablon et al., 2018) volcanoes. Compared to other worldwide volcanoes, Iliniza 676 could be considered as a medium-size compound volcano, whose volume and shape are typical of 677 continental arcs (Grosse et al., 2009). Similar bulk volumes to Iliniza are found in volcanoes such as 678 Parinacota (Hora et al., 2007), Ampato-Sabancaya (Samaniego et al., 2016), Yucamane-Calientes 679 (Rivera et al., 2020), Ceboruco (Frey et al., 2004), or Katmai (Hildreth et al., 2003b) volcanoes. 680 681 Nonetheless, the lifespans of these volcanoes differ by several tens of thousands of years.

682 The output rates calculated for the North Iliniza  $(3.5 \pm 2.6 \text{ km}^3/\text{kyr})$  and South Iliniza  $(0.8 \pm 0.3 \text{ km}^3/\text{kyr})$ km<sup>3</sup>/kyr) edifices are quite variable, although both structures show comparable volumes and shapes. 683 The higher growth rate of North Iliniza is explained by the short range of activity displayed by our 684 radiometric ages. The lack of outcrops and/or sampling of the lower units might have biased the activity 685 686 range towards the late-stage ages, then, the impact on output rates can be significant. Nevertheless, the sampling distribution and the small age range observed do not exclude a short-term (few tens of ka) 687 construction of the North Iliniza edifice. In fact, high growth rates have also been documented for 688 689 several Ecuadorian volcanoes such as Cubilche, Cusin, Imbabura (Bablon et al., 2020), Tungurahua III (Bablon et al., 2018), Cotopaxi (Hall and Mothes, 2008), and Guagua Pichincha (Robin et al., 2010) 690 691 volcanoes, with  $R_o$  values ranging from 2.0 ± 1.5 to 3.6 ± 2.1 km<sup>3</sup>/kyr. In contrast, the South Iliniza 692 growth rate is comparable to those of other Ecuadorian arc volcanoes.  $R_o$  values between  $0.6 \pm 0.3$  and 693  $0.8 \pm 0.2$  km<sup>3</sup>/kyr were reported for volcanoes such as Pichincha (Robin et al., 2010), Tungurahua I and 694 II (Bablon et al., 2018), Mulmul (Bablon et al., 2019), and Chimborazo (Samaniego et al., 2012). Similar 695 output rates were reported for other Andean volcanoes such as Misti (Thouret et al., 2001), Parinacota 696 (Hora et al., 2007), and Ampato-Sabancaya (Samaniego et al., 2016); although they are comparatively higher than in other continental arc systems such as the Cascades Range, Central Andes, Mexico, Japan, 697 or Alaska (e.g., Crisp, 1984; Hildreth et al., 2003a, 2003b; Frey et al., 2004; Ownby et al., 2007). Output 698 rate comparisons should be taken with caution as  $R_o$  values (> 1-2 km<sup>3</sup>/kyr) are typical of short-term 699 700 growth episodes (of few ka), whereas low values are typical of bulk eruptive rates (i.e., long periods including the quiescensde periods; Bablon et al., 2020). 701

The eruptive history of the Iliniza edifices developed separately in time, in contrast to other twin-peaked volcanoes such as Mojada-Fuya Fuya (Robin et al., 2009) in the Ecuadorian arc, or Yucamane-Calientes (Rivera et al., 2020) in the Peruvian arc. In fact, the evolution of Iliniza and Santa Cruz volcanoes included long-lasting quiescence periods, which is also the case for other volcanoes in the Ecuadorian Andes such as Cotopaxi (Hall and Mothes, 2008), Pichincha (Robin et al., 2010), Atacazo-Ninahuilca (Hidalgo, 2006), and Tungurahua (Bablon et al., 2018). Long resting periods (several tens of thousands of years) are also reported in other twin volcanoes and compound volcanoes in the region and worldwide such as San Pedro-San Pablo (Bertin and Amigo, 2015; González-Maurel
et al., 2019), Ampato-Sabancaya (Samaniego et al., 2016), Yucamane-Calientes (Rivera et al., 2020),
and Colima (Robin et al., 1987; Cortés et al., 2010). These observations suggest that eruptive hiatuses
are also common in this type of compound volcanoes from volcanic arcs, contrasting with models of
sustained eruptive activity throughout their lifetimes (e.g., Conway et al., 2016; Pure et al., 2020), while
increasing the potential for reactivation in present-day dormant volcanoes.

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### 716 5.4. Overall geochemical nature

Overall, samples from the North and South Iliniza (NS-I) edifices exhibit rather little 717 718 geochemical variability along a single evolutive trends (Fig. A.1) suggesting neither a change in 719 magmatic sources nor in the magmatic process active at crustal levels. In contrast, important differences rise when NS-I trace element contents are compared to the early and late satellite lavas and the Santa 720 721 Rosa rhyolites, in which HREE depletions and LREE enrichments were identified. Notably, the Iliniza 722 rocks do not show a continuous increase in SiO<sub>2</sub> or decrease in Mg# over time (Fig. 10a) as observed 723 at other volcanoes from the central segment of the arc (e.g., Pichincha volcano; Robin et al., 2010). The 724 silica-poor units (i.e., SI-T<sub>A</sub>, T and Pg units) occur during the late evolutionary stages of Iliniza.

As presented in Table 2, the common mineral assemblages exhibit by the North Iliniza lavas 725 726 include plagioclase, orthopyroxene, clinopyroxene, Fe-Ti oxides and scarce amphibole, whereas the South Iliniza eruptive products include plagioclase, amphibole, clinopyroxene, Fe-oxides and rare 727 orthopyroxene. Based on a geochemical modelling approach, Hidalgo et al. (2007) and Schiano et al. 728 (2010) proposed that the NS-I magmatic series could result from an amphibole-dominated fractional 729 730 crystallization process of typical calc alkaline arc magmas. Their models also showed that the silica-731 rich products of Pilongo and Santa Rosa units require more complex petrogenetical models. In fact, the 732 trace element contents of these units were unable to be reconciled with a parental melt with NS-I 733 composition through a single fractional crystallization process, thus, implying the occurrence of an 734 additional parental melt and a mixing process involving both magmas. The petrogenetic processes 735 related to the origin of such silica-rich magmas are widely discussed as they could be produced by several processes including partial melting of the subducted slab and the metasomatism of the mantle 736 wedge caused by the derived silicate melts (e.g., Bourdon et al., 2003; Samaniego et al., 2005, 2010; 737 Hidalgo et al., 2007, 2012), crustal melting and/or assimilation of the lower crust (Garrison and 738 739 Davidson, 2003; Garrison et al., 2006; Sainlot et al., 2020), and intra-crustal fractionation of the required high-pressure assemblages (e.g., Bryant et al., 2006; Chiaradia et al., 2009; Bellver-Baca et al., 2020). 740 However, a comprehensive analysis of these petrogenetic processes and their temporal behavior is 741 beyond the scope of this paper. Nonetheless, the whole Iliniza magmatic series could be thus explained 742 by a fractional crystallization process coupled with magma mixing between mafic and silica-rich end-743 members (Hidalgo et al., 2007; Schiano et al., 2010); where the geochemical signatures of both end-744 745 members seem to occur throughout the geochronological evolution of Iliniza volcano, rather than being 746 restricted to its final stages.

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# 748 5.5. Exploring the implications for the hazard assessment

749 Unlike other active and potentially active volcanoes from the Volcanic Front (e.g., Pululahua, Guagua Pichincha, Ninahuilca), whose eruptions involved dacitic magmas and dome-forming eruptive 750 751 dynamics, the Holocene activity of Iliniza mainly released andesitic lavas. Based on the proposed 752 eruptive chronology, we infer that the most probable eruptive scenario could be dominated by the emission of lava flows and/or the formation of low-viscosity lava domes, whose subsequent collapse 753 may produce PDCs and regional tephra fallout deposits. The apparent migration of the active vents 754 755 through time, from northern to southern locations, favors an eruptive scenario possibly taking place on 756 the southern flank of Iliniza volcano. However, an active vent located in higher areas close to the summit 757 cannot be discarded. In such case, an eruption in these steeper slope areas would favor the destabilization of the newly emitted lavas increasing the risk of PDC formation, potentially 758 759 accompanied by explosive phases and widespread tephra fallouts (Voight et al., 2002; Harnett et al., 760 2018). Such events could affect the 200,000 inhabitants living within 20 km of the volcano (INEC, 761 2010), including the populations of Chaupi, Pastocalle and Toacazo (Fig. 2).

762 Although a high explosive phase was identified at Iliniza volcano, this event was unique throughout its eruptive history and are absent in the Holocene eruptive chronology. Therefore, we 763 764 expect that a scenario involving a highly explosive eruption (e.g., VEI 5), such as the Jatuncama event, is less probable in the short term. In addition, the Iliniza eruptive history does not include any major 765 766 flank collapse, as no avalanche deposits or morphological remains suggesting a collapse amphitheater were identified. However, the occurrence of the Iliniza volcano above an active strike-slip fault system, 767 768 the potential weakening of its flanks caused by weathering and hydrothermal alteration, and the steeply inclined slopes of its uppermost areas increase the risk of a potential collapse promoted by a tectonic 769 770 event.

Finally, the Cotopaxi fallout deposits covering the Iliniza volcano slopes is an additional hazard 771 to consider, although it is not intrinsically related to the Iliniza activity. The Holocene tephra layers 772 deposited on the flanks of Iliniza could be easily remobilized, especially during the rainy season 773 774 (December to April), forming secondary lahars that flow into the ravines of the volcano. The Cotopaxi tephra sequence, reaching up to 10 m in thickness, may slide due to the low cohesion of the lower and 775 thicker tephra layers. This hazard is supported by the multiple landslide deposits observed on the 776 777 southern flank of the Santa Cruz volcano (Hall et al., 2017a), and by the small scarps observed on the 778 east and southeast slopes of the South Iliniza edifice.

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# 780 6. CONCLUSIONS

This work provides the first geochronological data for the Iliniza volcano and allows to establish a comprehensive overview of its development over time. The first volcanic manifestations in the area correspond to the adjacent Santa Cruz volcano dated at  $702 \pm 11$  ka. After a long quiescent period, its activity resumed at  $79 \pm 2$  ka and  $60 \pm 3$  ka forming the small-volume Loma Saquigua lava dome.

785Iliniza shows a young episodic activity that began with the extrusion of the rhyodacite Pilongo786lava dome occurring at  $353 \pm 6$  ka. The Iliniza compound volcano ( $46 \pm 15$  km<sup>3</sup>) comprises two andesitic787to dacitic edifices formed in several cone-building stages. The older North Iliniza edifice ( $28 \pm 19$  km<sup>3</sup>)

was first constructed by a succession of thin lavas and breccias during the Lower NI stage at 123-122 ka, followed by the formation of the Huayrapungo satellite peak at  $121 \pm 2$  ka. Then, thick viscous lava sequence dated at  $116 \pm 2$  ka built the higher portion of the edifice through the Upper NI stage. The North Iliniza edifice showed a relatively high output rate of  $3.5 \pm 2.6$  km<sup>3</sup>/kyr.

792 After a  $\sim$ 70 kyr quiescence period, the South Iliniza edifice (18 ± 6 km<sup>3</sup>) grew over the remnants 793 of the North Iliniza edifice in three main cone-building stages, with an output rate of  $0.8 \pm 0.3$  km<sup>3</sup>/kyr. A basal edifice was constructed during the Lower SI stage by a series of massive lavas of dacitic 794 composition, dated between  $46 \pm 1$  and  $45 \pm 2$  ka. The Upper SI stage started with the Jatuncama 795 796 explosive phase, in which the uppermost portion of the basal stratovolcano was destroyed and a 30-40 797 m-thick dacitic pyroclastic succession was deposited. The estimated minimum bulk volume of the Jatuncama ignimbrite deposits is 2.1 km<sup>3</sup>, corresponding to a VEI ~5 eruption. The subsequent eruptive 798 activity rebuilt the South Iliniza edifice with the emplacement of a summit lava dome complex and its 799 800 related PDC deposits. The Terminal SI stage corresponds to the emission of several lava flows of 801 and esitic composition dated between  $31 \pm 4$  and  $25 \pm 3$  ka. Finally, higher K and esite magmas were emitted from satellite vents located to the south of Iliniza forming the Tishigcuchi lava dome probably 802 in the Holocene, and the Pongo lava flow dated at  $6 \pm 4$  ka. Contrary to other volcanoes of the volcanic 803 804 front, the Iliniza magmas show a compositional transition from dacites (63-67 wt.% SiO<sub>2</sub>) to andesites (60-63 wt.% SiO<sub>2</sub>) in the later eruptive stages. Based on these lines of geological and geochronological 805 evidences, we support the hypothesis that the Iliniza volcano must be considered as a potentially active 806 volcanic center. 807

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# 809 Acknowledgments

The authors wish to thank Brad Singer and Georges Boudon, and an anonymous reviewer, for their detailed reviews, constructive comments, and suggestions, which helped us to improve this manuscript. The authors are grateful to the "Reserva Ecológica Ilinizas" members for sampling authorization and logistics. We also thank Patricio Ramon for useful discussions and for authorizing

the use of his aerial photographic material, as well as Valérie Godard for having manufactured all the 814 815 thin sections. This work is part of an Ecuadorian-French cooperation program carried out between the Instituto Geofísico, Escuela Politécnica Nacional (IGEPN), Quito, Ecuador, and the French Institut de 816 817 Recherche pour le Développement (IRD), thought the Laboratoire Mixte International "Séismes et Volcans dans les Andes du Nord" (LMI-SVAN) program. This work was supported by the CNRS/INSU 818 TelluS and the LMI-SVAN programs. The first author's PhD grant was funded by the "Secretaria 819 820 Nacional de Educación Superior, Ciencia, Tecnología e Innovación" (SENESCYT), Ecuador. This is 821 Laboratoire de Géochronologie Multi-Techniques (LGMT) contribution number 169 and Laboratory of 822 Excellence ClerVolc contribution number XXX.

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## 1204 FIGURES

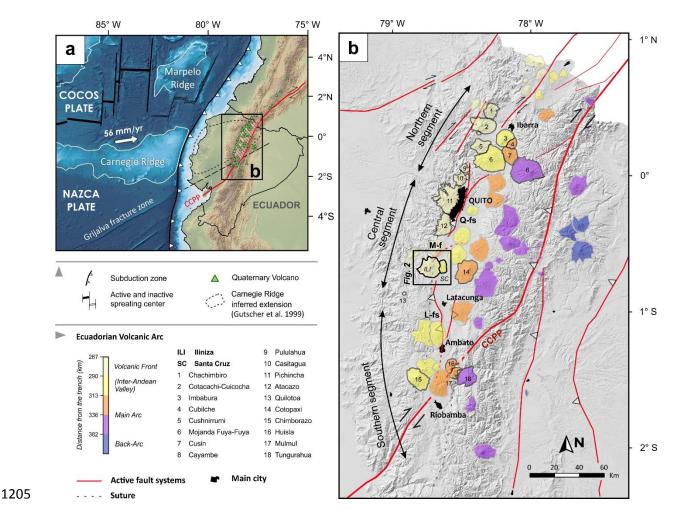


Figure 1. a) Geodynamic setting of the Ecuadorian arc (Modified from Gutscher et al., 1999). 1206 Arrows indicate the direction of the Nazca plate motion relative to the South American 1207 continental margin according to DeMets et al. (2010). b) Schematic map of the Ecuadorian 1208 volcanic arc. Volcanoes are colored according to their distance from the trench comprising the 1209 N-S alignments of the Volcanic Front (Western Cordillera), Inter-Andean Valley, Main Arc 1210 (Eastern Cordillera), and Back-Arc. Variability in the number of volcanic centers is represented 1211 by the northern, central, and southern across-arc segments. Iliniza (ILI) and Santa Cruz (SC) 1212 1213 volcanoes, as well as those mentioned in the text, are outlined with black and grey borders, respectively. Active fault systems are represented with red lines according to Alvarado et al. 1214 (2016). CCPP: Chingual-Cosanga-Pallatanga-Puná Fault System; Q-fs: Quito Fault System; 1215 M-f: Machachi Fault; L-fs: Latacunga Fault System. 1216

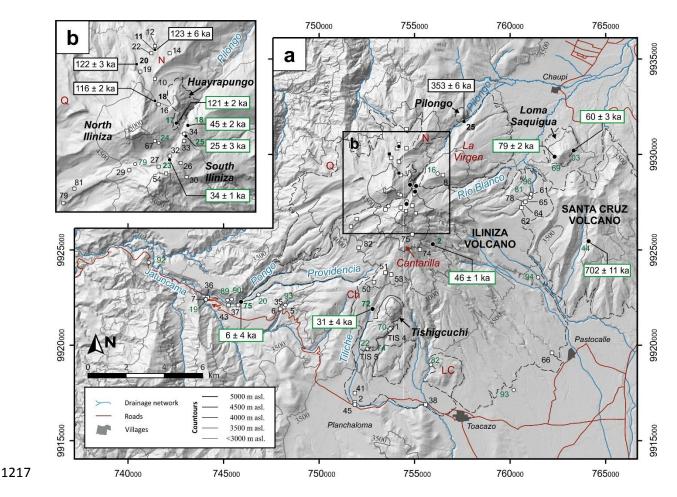


Figure 2. Hill-shaded digital surface model of Iliniza volcano showing the locations of new
samples (circles; green numbers) and those from Hidalgo et al. (2007) (squares; black
numbers). K-Ar dated samples are represented with solid symbols. Volcanic peaks shown as
black letters. Ridges and hills shown as red letters. Ch: Chilcapamba; LC: Loma La Cruz; N:
Ninarrumi; Q: Quillotoro. Rivers and valleys are labelled with blue letters.

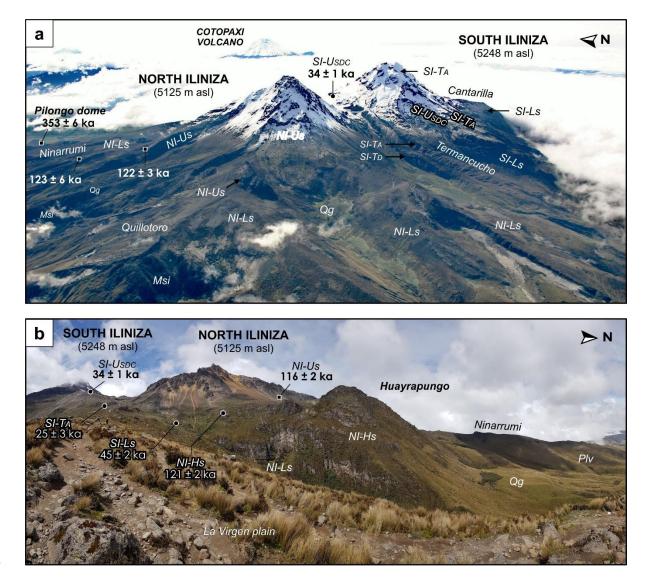


Figure 3. a) Aerial view of Iliniza volcano, looking east (photography by Patricio Ramon, IGEPN). b) Panoramic view of the North Iliniza edifice, looking west from La Virgen plain.

1226 Geological unit abbreviations as in Figure 4.

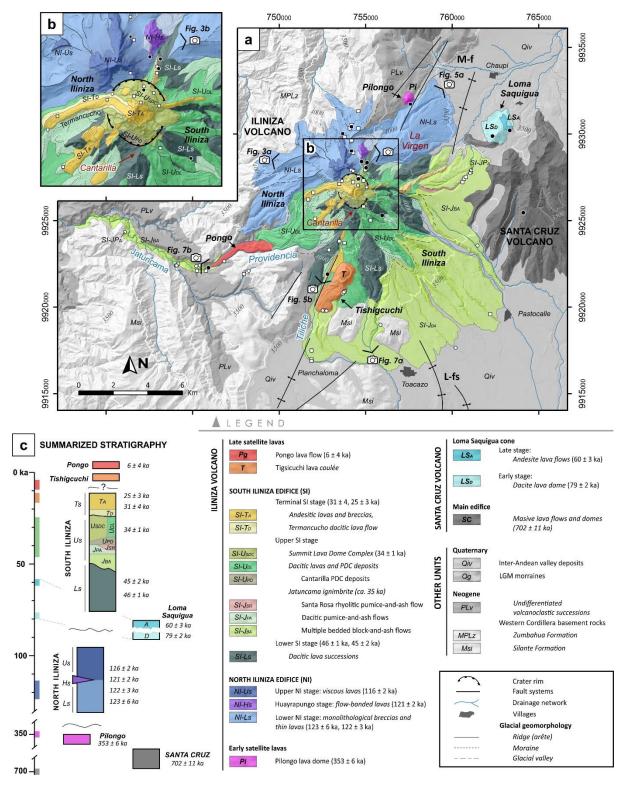
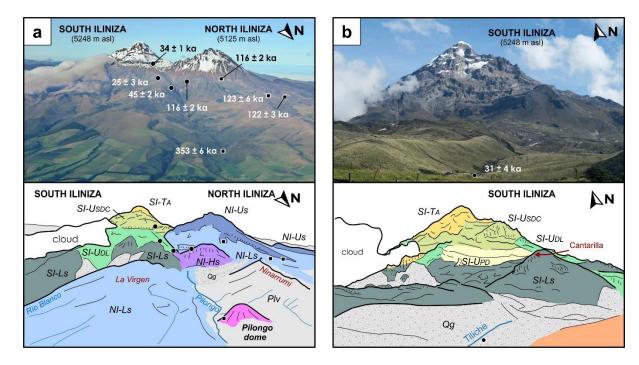


Figure 4. Simplified geological map of Iliniza volcano after considering our new ages (Table
1) and field observations, as well as those from Hidalgo (2001) and Hidalgo et al. (2007).
Sample sites are shown according to figure 2 caption. Local fault systems are symbolized with
black lines. M-f: Machachi Fault; L-fs: northern segment of Latacunga Fault System.



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**Figure 5.** View of **a**) Iliniza volcano, looking south (photography by Patricio Ramon, IG-EPN),

and b) South Iliniza edifice, looking north, showing the relationships between the main

stratigraphic units represented according to Figure 4.

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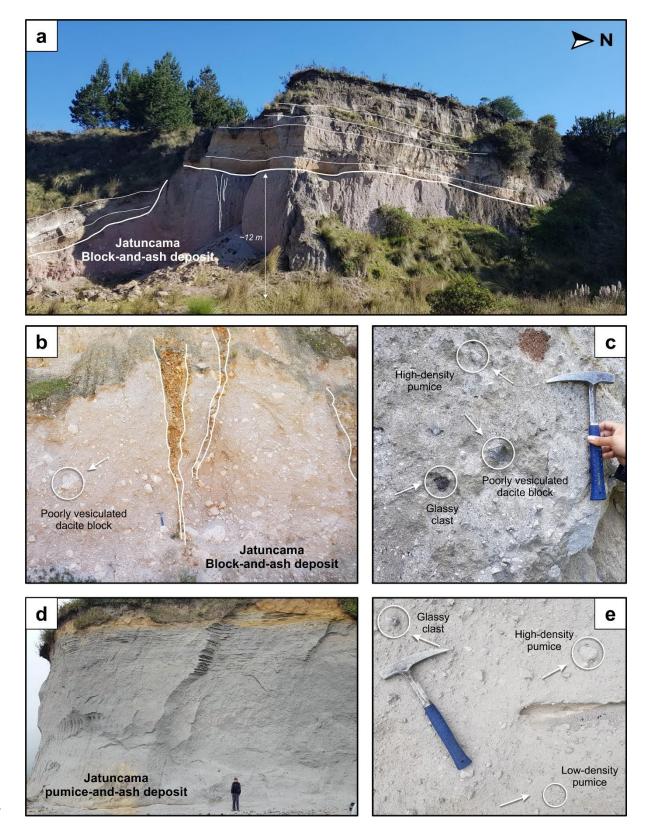
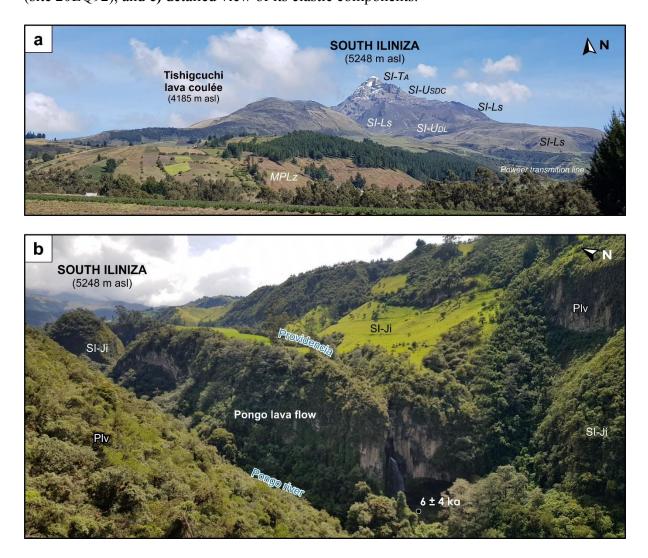




Figure 6. a) Jatuncama ignimbrite deposit at Planchaloma (site ILI 2), and b) detailed view of
its degassing pipes structures. The deposit is discordantly overlain by lahars, Cotopaxi tephra
fallouts, and soils. c) Types of clasts observed in a lower section of the ignimbrite deposit at

the Jatuncama valley (site 19EQ19). d) Pumice-and-ash flow observed at Jatuncama valley 1241 (site 20EQ92), and e) detailed view of its clastic components. 1242



- 1243
- Figure 7. a) Panoramic view of the Tishigcuchi lava dome and the South Iliniza, looking north. 1244
- b) View of the Pongo lava flow from the Jatuncama valley. Volcanological unit abbreviations 1245
- as in Figure 4. 1246

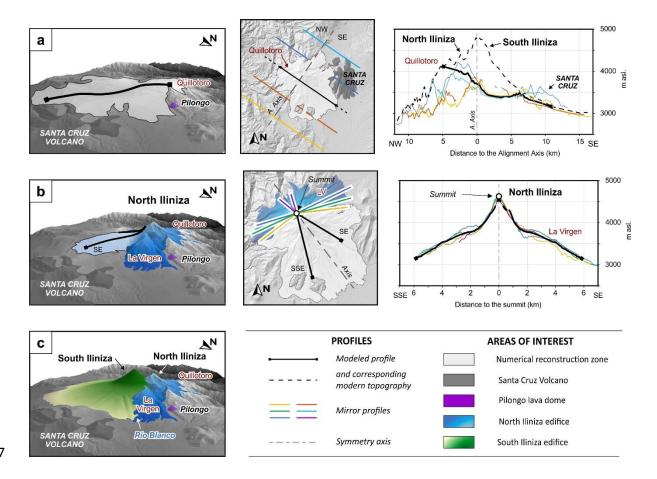
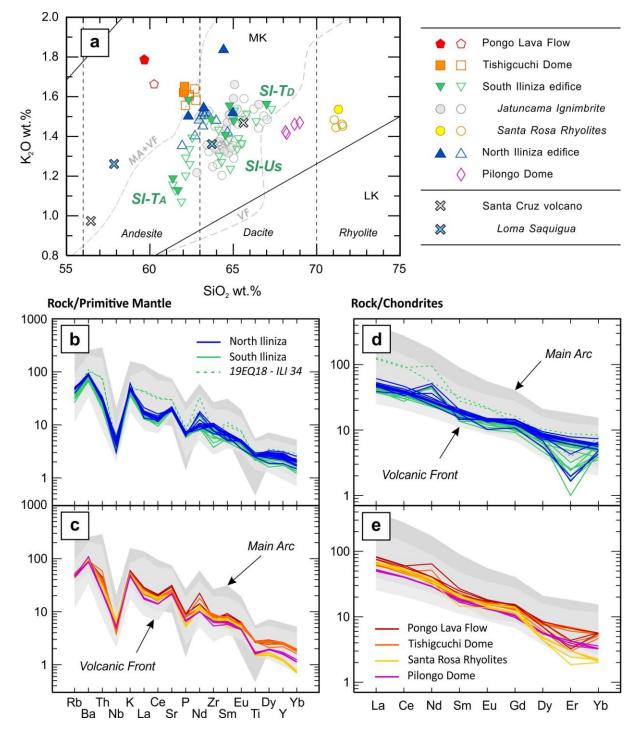


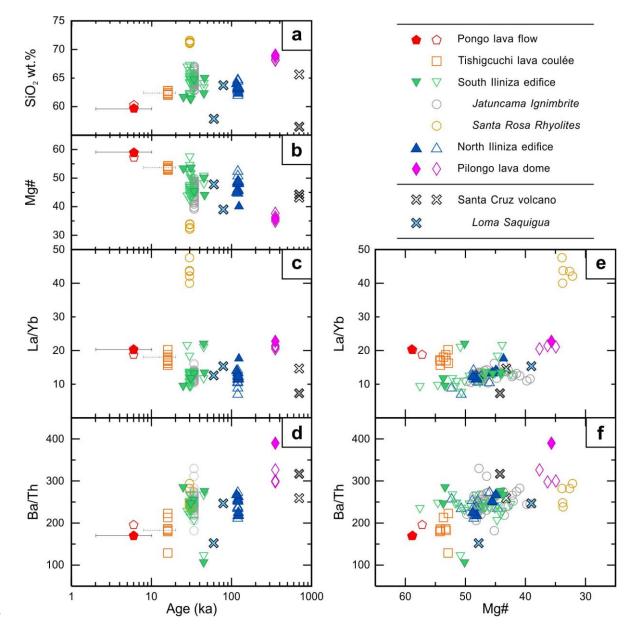
Figure 8. Model topographic profiles used for the reconstruction of the basement surface area of a) North Iliniza and b) South Iliniza edifices. Figures correspond, from left to right, to perspective and plan views of the reconstructed area, and to the mirror profiles used to create the modeled profile. c) Aerial view of the South Iliniza modeled cone fitted next to the partially eroded North Iliniza edifice.



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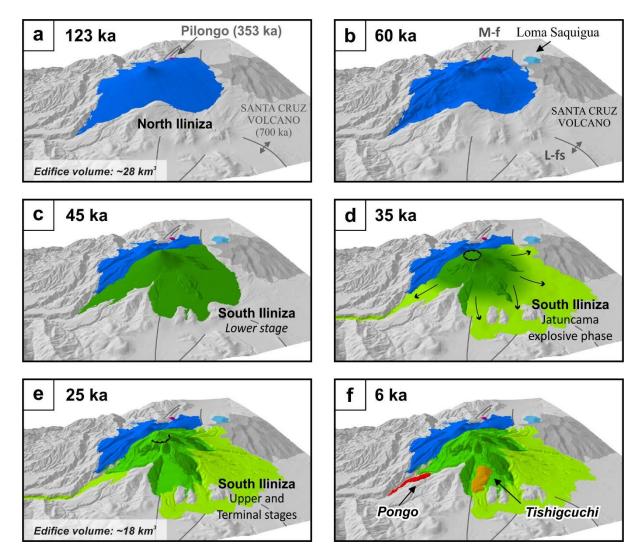
**Figure 9. a)** K<sub>2</sub>O vs SiO<sub>2</sub> diagram (Peccerillo and Taylor, 1976) for eruptive products of Iliniza and Santa Cruz volcanoes. MK: medium-K, and LK: low-K calc-alkaline series. The late evolutionary stages of the South Iliniza edifice are shown with green symbols. Volcanological unit abbreviations as in Figure 4. Gray dashed lines indicate the composition fields created by the Volcanic Front (VF) and Main Arc (MA) whole-rock data obtained from the Georoc database. Open symbols are for data from Hidalgo et al. (2007). **b-c)** Incompatible trace elements normalized to primitive mantle spider diagrams (Sun and McDonough, 1989) for

North and South Iliniza edifices, and Iliniza satellite lavas and the SI-J<sub>SR</sub> units, respectively. de) Rare Earth Elements normalized to chondrites diagram (Sun and McDonough, 1989) for the
same arrangements. Dark grey and light grey areas represent the composition fields depicted
by the Volcanic Front and Main Arc whole-rock data (Georoc database), respectively.



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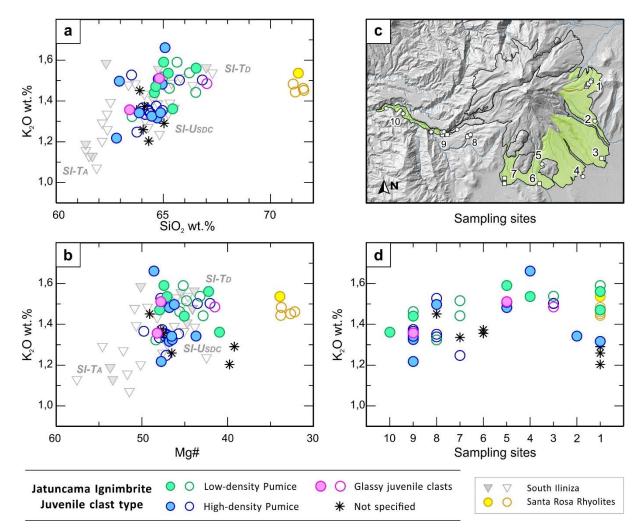
**Figure 10.** Temporal variations of **a**) Mg# (= $100*Mg/(Mg+Fe^{2+})$ ), **b**) SiO<sub>2</sub> (wt.%), and **c**) La/Yb and **d**) Ba/Th ratios. Horizontal axis represents the timeline (ka) in logarithmic scale. **e**) La/Yb and **f**) Ba/Th ratios plotted against Mg#. Filled symbols are for dated samples (Table 1). The 1 $\sigma$  age uncertainty is shown with a solid line for Pongo lava flow, while the age estimation range is shown as a dashed line for Tishigcuchi lava coulée.



1272

1273 Figure 11. Synthetic charts showing the evolution of Iliniza and Santa Cruz volcanoes through time based on our numerical reconstructions. a) North Iliniza edifice construction; b) Santa 1274 Cruz volcano reactivation with the Loma Saquigua lavas emission; c) South Iliniza Lower Cone 1275 1276 construction; d) the Jatuncama highly explosive eruptive phase creating a thick pyroclastic deposit; e) South Iliniza Upper cone construction and terminal lavas emission; and f) Holocene 1277 1278 Tishigcuchi lava coulée and Pongo lava flow. Note that illustrations of phases c and d are mostly schematic, see text for details. Local fault systems are symbolized with black lines. M-1279 f: Machachi Fault; L-fs: northern segment of Latacunga Fault System 1280





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Figure 12. Geochemical diagrams for Jatuncama pyroclastic samples classified by clast type. K<sub>2</sub>O versus a) SiO<sub>2</sub> and b) Mg# (=100\*Mg/(Mg+Fe<sup>2+</sup>)) diagrams. SI-U<sub>SDC</sub>: South Iliniza upper cone; SI-T<sub>D</sub>: Dacite Terminal Lavas; SI-T<sub>A</sub>: Andesite Terminal Lavas. C) Geographical distribution of sampling sites around the base of South Iliniza and d) their variation in K<sub>2</sub>O content. Open symbols are for data from Hidalgo et al. (2007).

## 1290 TABLES

## **Table 1.** (caption provided bellow the table)

Sample	Location and Unit	Longitude (m)	Latitude (m)	K (%)	<sup>40</sup> Ar* (%)	<sup>40</sup> Ar* (10 <sup>11</sup> at/g)	Age ± 1σ (ka)	Mean age (ka)
	VOLCANO							
Pilongo la	iva dome							
8	Lava dome, Pilongo							
ILI 25	valley	757550	9931731	1.641	10.0%	6.0596	$354 \pm 6$	$353\pm 6$
					16.4%	6.0422	$352 \pm 5$	
North Ilin	niza edifice							
ILI 11	Monolithological breccia,	754150	9930434	2 404	2.0%	3.0594	$122 \pm 6$	132 + (
ILI II	N flank, NI-Ls	/34130	9930434	2.404				$123\pm 6$
	Monolithological breccia,				2.1%	3.1022	$124 \pm 6$	
ILI 20	N flank, <i>NI-Ls</i>	753648	9930031	2.148	5.5%	2.7666	$123 \pm 3$	$122 \pm 3$
	,				5.0%	2.6825	$120 \pm 3$	
	Lava flow, Huayrapungo							
19EQ17	peak, NI-Hs	754734	9928425	2.226	7.3%	2.8472	$122 \pm 2$	$121 \pm 2$
					6.8%	2.7715	$119\pm2$	
H I 10	Lava flow, N flank, NI-	754151	000000	1.070		2 2007	117 . 0	116 . 0
ILI 18	Us	754151	9929036	1.8/8	8.6%	2.2906	$117 \pm 2$	$116 \pm 2$
					8.7%	2.2671	$116 \pm 2$	
	niza edifice							
19EQ02	Lava flow, E flank, SI-Ls	755922	9925321	1.728	3.7%	0.8557	$47 \pm 1$	$46 \pm 1$
					3.1%	0.8006	$44 \pm 2$	
19EQ18	Lava flow, N flank, SI-Ls	755052	9928362	1.667	1.9%	0.7908	$45 \pm 2$	$45 \pm 2$
					1.9%	0.7826	$45\pm2$	
1050001	Lava dome, summit area,	754550	0007404	0.000	2 10/	0.0144	24 + 1	
19EQ23b	SI-U <sub>SDC</sub>	754550	9927424	2.302	3.1%	0.8144	$34 \pm 1$	$34 \pm 1$
	Lava flow, S flank				3.1%	0.8078	$34 \pm 1$	
20EQ72	(Tiliche river), $SI-T_A$	752778	9921934	1.206	0.8%	0.3788	$30 \pm 4$	$31 \pm 4$
	(), ~				0.9%	0.3921	$31 \pm 4$	•• - •
	Monolithological breccia,				0.970	0.3921	51 - 1	
19EQ25	N flank, $SI-T_A$	754997	9928069	1.311	0.9%	0.3273	$24\pm3$	$25 \pm 3$
					0.9%	0.3631	$27 \pm 3$	
Pongo lav	va flow							
20EQ75	Lava flow, Pongo valley	745904	9922305	1.534	0.2%	0.0922	$6 \pm 4$	$6 \pm 4$
					0.2%	0.1017	$6 \pm 4$	
SANTA	CRUZ VOLCANO					/		
19EQ44	Lava flow, S flank, SC	764061	9925476	1 096	14 7%	7.9746	$697 \pm 11$	$702 \pm 11$
	2	, 51001	<i>,,</i> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	1.070	15.4%	8.0858	$706 \pm 11$	, v <b>u</b> - 11
Loma Car	miana				т <i>Э</i> .т/0	0.0000	100 - 11	
Loma Saq		760005	0020001	1 400	5 00/	1 2222	70 + 2	70 - 2
20EQ69	Lava dome, <i>LS-d</i>	762285	9929891	1.480	5.8%	1.2233	$79 \pm 2$	79 ± 2
105055	T A 37A		000000000		6.8%	1.2283	$79 \pm 2$	~~
19EQ03	Lava flow, N flank, <i>LS-a</i>	763281	9930218	1.417	1.8%	0.8927	$60 \pm 3$	$60\pm3$
					2.2%	0.8868	$60 \pm 3$	

**Table 1.** K-Ar ages obtained in this study for Iliniza and Santa Cruz volcanoes listed in decreasing order from oldest to youngest. Column headings indicate sample name, outcrop and relative location, volcanological unit (abbreviations as in Figure 4), sample coordinates, potassium (K) content in percent, radiogenic argon content ( $^{40}$ Ar\*) in percent and in 10<sup>11</sup> atoms per gram, age obtained for each measurement, and weighted mean age in ka given with a 1- $\sigma$ uncertainty.

Edifice	Cone-building stage/Unit Age (ka) Volcanology		Petrography			
Late satellite lavas	Pongo lava flow $6 \pm 4$		Effusive eruption: voluminous lava flow	Aphanitic andesite (59 wt.% SiO pl, opx and cpx, ± pl		
	Tishigcuchi lava >20 an dome <8 ka		Lava dome-forming eruption	Andesite (62-63 wt.% SiO <sub>2</sub> ): pl, amp, opx, ± cpx		
South Iliniza	Terminal stage $31 \pm 4$ $25 \pm 3$		Mainly effusive activity: voluminous lava flows and related pyroclastic deposits	Mostly andesites (61–63 wt.% SiO <sub>2</sub> ): pl, opx, cpx, ± amp		
	Summit lava dome complex	34 ± 1 ka	Lava dome-forming eruptions and related PDC	Dacites (64–67 wt.% SiO <sub>2</sub> ): pl, am ± Fe–Ti oxides, ± cpx		
	Upper stage Jatuncama explosive phase	~35 ka	Explosive dome-forming eruption followed by a pumiceous phase: - Dacitic and rhyolitic pumice- and-ash flows - Multiple bedded block-and-ash flows	<ul> <li>Scarce rhyolites (71-72 wt.% SiO<sub>2</sub>): pl, ± cpx (aegirine), ± Fe-7 oxides</li> <li>Dacites (63-67 wt.% SiO<sub>2</sub>): pl, amp, ± cpx</li> </ul>		
			Cantarilla unconformity			
	Lower stage	$45 \pm 2$ to $46 \pm 1$ ka	Mainly effusive activity: basal edifice construction	Dacites (62-65 wt. % SiO <sub>2</sub> ): pl, ar cpx, ± opx, ± Fe-oxides		
North Iliniza	Terminal stage $116 \pm 2$ ka		Mainly effusive activity: viscous lava flows	Acid-andesites to dacites (62-65 wt.% SiO <sub>2</sub> ): pl, cpx, opx, ± Fe-T oxides, ± amp		
	Huayrapungo stage $121 \pm 2$ ka		Mainly effusive activity: voluminous flow-banded lava flow	Andesites (62 wt.% SiO <sub>2</sub> ): pl, opx and scarce cpx, ± Fe-Ti oxides		
	Lower stage	$122 \pm 6 \text{ to}$ $123 \pm 6$ ka	Mainly effusive activity: thin lava flows	Acid-andesites to dacites (62-64 wt.% SiO <sub>2</sub> ): pl, opx, cpx, ± amp, = Fe-Ti oxides		
Early satellite lavas	Pilongo lava dome	353 ± 6 ka	Lava dome-forming eruption	Porphyritic rhyodacite (68-69 wt. SiO <sub>2</sub> ): pl, amp, opx, ± cpx, ± Fe-T oxides		

**Table 2.** Generalized chronostratigraphy showing the main stages of the Iliniza volcano

1301 Abbreviations: pl=plagioclase, amp=amphibole, cpx =clinopyroxene, opx=orthopyroxene.

**Table 3.** Construction and erosion volumes calculated based on numerical reconstructions together with their corresponding rates. Numerical results given with a 1- $\sigma$  uncertainty (see text for details).

Output							Erosion	
Volume	Period	Duration	rate			Duration	rate	
(km <sup>3</sup> )	(ka)	(kyr)	(km³ kyr <sup>-1</sup> )	(km <sup>3</sup> )	(ka)	(kyr)	(km <sup>3</sup> kyr <sup>-1</sup> )	
$28\pm9$	124 - 116	$8 \pm 5$	$3.5\pm2.6$	$6 \pm 2$				
				$3 \pm 1$	116 - 0	$116 \pm 2$	$0.03 \pm 0.01$	
$18 \pm 6$	46 - 25	$21 \pm 4$	$\textbf{0.8} \pm \textbf{0.3}$	6 ± 2	25 - 0	$25 \pm 3$	$0.24 \pm 0.09$	
$18 \pm 5 \times 10^{-3}$ 339 ±								
41 × 10 <sup>-</sup> 3								
$73 \pm 18$ × 10 <sup>-3</sup>								
24 + 14	102 05	0.0 1 7	0.2 + 0.1					
	(km <sup>3</sup> ) $28 \pm 9$ $18 \pm 6$ $18 \pm 5 \times 10^{-3}$ $339 \pm 41 \times 10^{-3}$ $73 \pm 18 \times 10^{-3}$	(km <sup>3</sup> ) (ka) $28 \pm 9$ 124 - 116 $18 \pm 6$ 46 - 25 $18 \pm 5 \times 10^{-3}$ $339 \pm 41 \times 10^{-3}$ $373 \pm 18$	(km <sup>3</sup> )       (ka)       (kyr) $28 \pm 9$ $124 - 116$ $8 \pm 5$ $18 \pm 6$ $46 - 25$ $21 \pm 4$ $18 \pm 5 \times$ $10^{-3}$ $339 \pm$ $41 \times 10^{-3}$ $373 \pm 18$ $\times 10^{-3}$	Volume (km <sup>3</sup> )         Period (ka)         Duration (kyr)         rate (km <sup>3</sup> kyr <sup>-1</sup> ) $28 \pm 9$ $124 - 116$ $8 \pm 5$ $3.5 \pm 2.6$ $18 \pm 6$ $46 - 25$ $21 \pm 4$ $0.8 \pm 0.3$ $18 \pm 5 \times$ $10^3$ $339 \pm$ $41 \times 10^{-3}$ $373 \pm 18 \times 10^{-3}$ $\times 10^{-3}$	Volume (km <sup>3</sup> )         Period (ka)         Duration (kyr)         rate (km <sup>3</sup> kyr <sup>-1</sup> )         Volume (km <sup>3</sup> ) $28 \pm 9$ $124 - 116$ $8 \pm 5$ $3.5 \pm 2.6$ $6 \pm 2$ $18 \pm 6$ $46 - 25$ $21 \pm 4$ $0.8 \pm 0.3$ $6 \pm 2$ $18 \pm 5 \times 10^{-3}$ $339 \pm 41 \times 10^{-3}$ $373 \pm 18 \times 10^{-3}$ $\times 10^{-3}$ $\times 10^{-3}$	Volume (km <sup>3</sup> )         Period (ka)         Duration (kyr)         rate (km <sup>3</sup> kyr <sup>-1</sup> )         Volume Period (ka) $28 \pm 9$ $124 - 116$ $8 \pm 5$ $3.5 \pm 2.6$ $6 \pm 2$ $3 \pm 1$ $116 - 0$ $18 \pm 6$ $46 - 25$ $21 \pm 4$ $0.8 \pm 0.3$ $6 \pm 2$ $25 - 0$ $18 \pm 5 \times 10^{-3}$ $339 \pm 41 \times 10^{-3}$ $339 \pm 18 \times 10^{-3}$ $10^{-3}$ $310^{-3}$	Volume         Period         Duration         rate         Volume         Period         Duration $(km^3)$ $(ka)$ $(kyr)$ $(km^3 kyr^{-1})$ $(km^3)$ $(ka)$ $(kyr)$ $28 \pm 9$ $124 - 116$ $8 \pm 5$ $3.5 \pm 2.6$ $6 \pm 2$ $3 \pm 1$ $116 - 0$ $116 \pm 2$ $18 \pm 6$ $46 - 25$ $21 \pm 4$ $0.8 \pm 0.3$ $6 \pm 2$ $25 - 0$ $25 \pm 3$ $18 \pm 5 \times 10^3$ $339 \pm 41 \times 10^{-3}$ $339 \pm 18 \times 10^{-3}$ $10^{-3}$ $10^{-3}$ $10^{-3}$	

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