# Timing of Quaternary volcanism and its relationship with tectonics in the central segment of the Ecuadorian Andes

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#### Abstract :

The unusually high number of volcanoes in the Ecuadorian Arc, located in the deformation zone of the continental North Andean Sliver, coincides with the projection of the major oceanic structures observed in the Nazca Plate, such as the Carnegie Ridge and the Grijalva fracture zone. Although the relationship between this tectonic setting and volcanism has been widely discussed in the literature, their temporal relationship has not been thoroughly investigated due to the lack of geochronological data. We present here 20 new KAr and 2 40Ar/39Ar ages obtained for 7 volcanoes of the central segment of the Ecuadorian arc, which together with previous data show that volcanism in this area started at ~1.3 Ma. A notable increase in volcanic activity occurred since ~0.6 Ma, when the formation of a dozen volcanoes occurred in a relatively small area of the central segment. While this arrangement of volcanoes, here referred to as a "volcanic cluster", appears to be controlled by crustal tectonic structures, the order of onset of these volcanoes and their eruptive activity does not show clear migration patterns over time. However, the presence of older volcanoes in the north of the central segment suggests a possible southward extension of volcanism between ~1.3 and ~ 0.6 Ma. Finally, based on the cumulative bulk volumes calculated for the volcanic edifices over time, we infer that the magmatic productivity rate has been roughly constant during the last ~550 kyr in this area.

## Highlights

▶ Volcanic activity in the central Ecuadorian Andes occurred since at least ~1.3 Ma ▶ An increase in volcanic activity took place to the south since ~0.6 Ma. ▶ The predominance of older volcanoes to the north suggests an extension of volcanism. ▶ Crustal tectonic structures had a key role in the spatial arrangement of volcanoes ▶ The overall volcanic output rate has been roughly stable during the last ~0.6 Ma.

Keywords : Ecuador, K-Ar dating, Quaternary, Eruptive history, Tectonics

#### 48 1. INTRODUCTION

49 The Northern Andean Volcanic Zone results from the subduction of the oceanic Nazca Plate 50 beneath the northwestern margin of South America (Fig. 1a). In contrast to the narrow array of nearly 51 40 Quaternary volcanoes in Colombia, more than 80 Quaternary eruptive centers (21 with Holocene 52 activity) form the broad Ecuadorian volcanic arc, which covers an area up to 130 km wide north of 2°S 53 latitude (Hall and Wood, 1985; Pedraza Garcia et al., 2007). Usually, these volcanoes are grouped 54 according to their distribution in along-arc alignments defined by their geographic relationship to the 55 two subparallel mountain ranges that form the Ecuadorian Andes (i.e., the Western and Eastern 56 Cordilleras), the tectonic depression that separates both ranges (i.e., the Inter-Andean Valley), and the sub-Andean Amazonian lowlands (Fig. 1b; e.g., Hall and Beate, 1991; Hall et al., 2008; Ancellin et al., 57 58 2017). Moreover, the distribution of volcanoes along the arc is not uniform. In fact, dozens of 59 independent edifices occur in areas of a few square kilometers, with distances between their summits 60 ranging from 6 to 12 km. These "volcanic clusters" alternate along the arc with a small 61 number of volcanoes, which define the three distinct segments of the Ecuadorian arc: northern, central, 62 and southern (Fig., 1c).

63 Almost all of the Ecuadorian volcanic overlaps the in-land projection of notable subducting 64 structures of the Nazca Plate (Fig. 1a), such as the Grijalva Fracture Zone, and the Carnegie Ridge, the 65 latter created by the motion of the Nazca Plate over the Galápagos hotspot (Meschede and Barckhausen, 66 2001; Lonsdale, 2005; O'Connor et al., 2007). The presence of these oceanic structures, together with 67 the convex shape of the continental margin, has been interpreted to be responsible for the slab flexure 68 described beneath the Ecuadorian arc (Yepes et al., 2016; Portner et al., 2020). In addition, the oblique 69 convergence of the Nazca Plate is responsible for the motion of the northwestern margin of South 70 America, forming the North Andean Sliver (Witt et al., 2006; Alvarado et al., 2016). This displacement 71 occurs through the Chingual-Cosanga-Pallatanga-Puná (CCPP) fault system (Fig. 1c), which traverses 72 the Ecuadorian Andes and extends northward into Colombia (Witt and Bourgois, 2010; Nocquet et al., 73 2014; Alvarado et al., 2016). Although several studies have been carried out on the slab structure (e.g., 74 Gutscher et al., 1999; Michaud et al., 2009; Yepes et al., 2016) and the kinematics along crustal faults

(e.g., Fiorini and Tibaldi, 2012; Alvarado et al., 2014, 2016; Baize et al., 2020; Jomard et al., 2021),
their relationship with the volcanism is under discussion.

77 Volcanism in the central segment of the Ecuadorian arc occurs approximately between latitudes 78 0.1°S and 0.8°S, surrounding Quito, the capital of Ecuador. Twenty kilometers south of Quito, more 79 than a dozen of volcanoes stand in an area 70 km wide (E-W) and 40 km long (N-S) that defines the 80 central volcanic cluster of the Ecuadorian arc (Fig. 1c and 2). Although these volcanoes have been 81 studied individually and on a regional scale for geochemical and stratigraphic purposes (e.g., Chemin, 82 2004; Hidalgo et al., 2007; Hall and Mothes, 2008; Hall et al., 2017b; Ancellin et al., 2017; Chiaradia 83 et al., 2020; Santamaría et al., 2022), the geochronological data remain scarce and their eruptive 84 histories remain poorly studied (especially for the oldest edifices). In order to investigate the temporal 85 link between volcanism, tectonics and the geodynamic setting, we present here new geochronological 86 data together with new field observations for the volcanoes of the central segment of Ecuador, focusing 87 on its volcanic cluster. By combining the available ages, we describe for the first time the Pleistocene 88 eruptive history of this part of the Ecuadorian arc. Furthermore, this work aims to investigate the 89 relationship between ancient and recent tectonics and the development of volcanism in this area.

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### 91 2. GEOLOGICAL CONTEXT

## 92 **2.1. Ecuadorian geological setting**

93 The Ecuadorian continental margin consists of a series of allochthonous and para-94 autochthonous terrains containing several fault systems and sutures roughly parallel to the trench 95 (Cediel, 2019). The Oriente Foreland Basin (Fig. 1b) corresponds to a sedimentary sequence formed 96 since the Mesozoic that overlies the Precambrian Guyanese craton (Vallejo et al., 2021). The Eastern 97 Cordillera is formed by Paleozoic to Jurassic magmatic and metamorphic belts, whose protholites are 98 of both sedimentary and igneous origin (Litherland et al., 1994; Spikings et al., 2015). The Western 99 Cordillera consists of deformed Cretaceous mafic and ultramafic rocks which are overlain by sequences 100 of marine sediments and volcanic deposits (Vallejo et al., 2019). Further west, the Coastal Forearc

101 consists of several Mesozoic to Cenozoic sedimentary basins that were formed over an ultramafic 102 basement (Luzieux et al., 2006; Witt et al., 2006; Vallejo et al., 2019). These oceanic terrains are 103 interpreted as the remnants of an oceanic plateau accreted to the continental margin during the Late 104 Cretaceous-Paleogene (Spikings et al., 2010; Vallejo et al., 2019; Jaillard, 2022). The Pujilí suture (Fig. 105 1c) was formed after this accretionary event. The transition between the terrains of the Western and 106 Eastern Cordilleras is masked by the Inter-Andean Valley, an intramountain basin containing a thick 107 sequence of Miocene-Pliocene volcanoclastic sediments overlying a tectonic mélange composed of 108 continental and oceanic units (e.g., Aspden et al., 1995; Hungerbühler et al., 2002; Lavenu et al., 1995; 109 Winkler et al., 2005). The Quaternary volcanic arc overlies the Miocene-Pliocene volcanoclastic 110 deposits found in both Cordilleras and in the Inter-Andean Valley. In particular, the volcanoes of the 111 central segment were built on the sedimentary Silante (Late Oligocene-Middle Miocene) and 112 volcanoclastic Zumbahua (Middle Miocene) formations in the Western Cordillera (Vallejo et al., 2019, 113 2020), and the Pisayambo volcanics (Miocene) in the Eastern Cordillera (Barberi et al., 1988; Lavenu 114 et al., 1995; Egüez et al., 2017).

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#### 116 **2.2.** Volcanism in the central volcanic cluster of the Ecuadorian Andes

117The central segment of the Ecuadorian volcanic arc occurs roughly between latitudes 0.1°S and1180.8°S (Fig. 1c). Although this distinction primarily includes volcanoes such as Pichincha (Robin et al.,1192010), the Chacana caldera (Hall and Mothes, 2008b) and the group of edifices located in the Sub-120Andean zone (e.g., Hoffer, 2008; Mothes and Hall, 2008; Salgado et al., 2021), the present study focuses121on the volcanic cluster located between the Eastern and Western Cordilleras at 0.4-0.8°S latitudes (Fig.1222). Our study not only includes the volcanoes considered as active, but also those with confirmed or123estimated Quaternary activity. The geological background of these volcanoes is summarized below.

124 The Almas Santas volcano (3786 m asl; lat. 0°35'S; long. 78°51'W), located on the western 125 side of the Western Cordillera (Fig. 2), is one of the closest volcanic centers to the trench of the entire 126 Ecuadorian arc (~240 km). This volcano comprises a basal andesitic edifice built during a mostly effusive stage followed by the emplacement of dacitic to rhyolitic lava domes, such as Cerro Azul, a satellite lava dome located on the eastern flank of Almas Santas. A NW sector collapse partially destroyed the volcanic edifice, probably at the end of its eruptive history (Chemin, 2004; Eissen et al., 2005). No geochronological data are available for Almas Santas; a Middle Pleistocene age has been suggested based on its highly eroded morphology (Chemin, 2004; Eissen et al., 2005).

132 To the east, four volcanoes are located on the eastern edge of the Western Cordillera, adjacent 133 to the Inter-Andean Valley (Fig. 2). La Carcacha edifice (3880 m asl; lat. 0°19'S; long. 78°36'W) is a 134 volcano dated at ~1.29 Ma (Hidalgo, 2006) associated with the Atacazo-Ninahuilca volcanic complex, 135 both located on the southern periphery of Quito. The Atacazo edifice (4455 m asl; lat. 0°21'S; long. 136 78°37'W), active between ~220 ka and ~83 ka (Hidalgo, 2006), partially covers La Carcacha edifice 137 and experienced a major sector collapse followed by the extrusion of several satellite lava domes around 138 70 ka (Hidalgo, 2006). At least six Plinian eruptions associated with the Ninahuilca dome complex, 139 formed within the sector collapse amphitheater of the Atacazo edifice, occurred during the Holocene 140 (Hidalgo et al., 2008). To the south, Corazón volcano (4784 m asl; lat. 0°32'S; long. 78°40'W) was 141 formed by andesite lava sequences and, like many other volcanic centers in the Western Cordillera, 142 exhibits a prominent sector collapse amphitheater opened to the west (Robles, 2013). A pyramidal peak 143 (glacial horn) created by the intense glacial erosion forms the summit of Corazón above 2800 m asl 144 (Fig. 2b). This structure consists of a thick sequence of monolithical breccias overlain by a sequence of 145 thin lavas. The satellite domes of Cerro Bomboli (with probable Holocene activity; Robles, 2013) and 146 La Moya are located on the northern and eastern flanks of Corazón volcano, respectively. Further south, 147 Iliniza volcano (5248 m asl; lat. 0°40'S; long. 78°43'W) is composed of two superimposed 148 stratovolcanoes active between ~124 and ~116 ka, and ~45 and ~25 ka, respectively. Iliniza volcano is 149 surrounded by the Pilongo (~353 ka) and Tishigcuchi (probably Holocene) domes (Hidalgo et al., 2007; 150 Santamaría et al., 2022). The Pongo lava flow (~6 ka) represents its most recent activity (Santamaría et 151 al., 2022).

Three highly eroded volcanoes are located in the Inter-Andean Valley (Fig. 2). East of Corazón,
the **Pasochoa** volcano (4199 m asl; lat. 0°28'S; long. 78°29'W) is made up of voluminous basaltic

and esite lava sequences. A groundmass  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  age of  $1.33 \pm 0.30$  Ma was obtained from a southwest 154 lava flow (Opdyke et al., 2006). To the south of Pasochoa, the Rumiñahui volcano (4722 m asl; lat. 155 0°35'S; long. 78°30'W) is formed by two lava sequences that differ in their andesitic composition of 156 157 mid- to high-potassium, respectively (Starr, 1984). Both volcanoes exhibit eroded collapse 158 amphitheaters on their western flanks. To the southwest, the Santa Cruz volcano (3978 m asl; lat. 159  $0^{\circ}39$ 'S; long. 78°38'W) is composed of andesitic lavas and dacitic domes dated at about 700 ka (Santamaría et al., 2022). Recent data suggest a renewed activity between ~79 and ~60 ka, forming the 160 161 Loma Saquigua dome (Santamaría et al., 2022). Between the Rumiñahui and Santa Cruz volcanoes 162 stands the *Tiopullo plateau*, a topographic high (3500 m asl.) within the Inter-Andean Valley that 163 divides the Machachi-Guayllabamba basin to the north and the Latacunga basin to the south. The 164 Tiopullo plateau has an elongated NW-SE shape approximately 10 km wide and 5 km long, reaching 165 an elevation of 400 m above the Inter-Andean Valley. The plateau shows flanks slopes of less than 7°, 166 with shallow fluvial incisions, and a flat summit with no significant uplifts. Tiopullo, as well as most 167 of the central segment, is covered by a thick sequence of tephra fall deposits associated with the 168 Cotopaxi volcano (Hall et al., 2017a), making sampling of Tiopullo rocks difficult in this area.

169 East of Pasochoa, on the western edge on the Eastern Cordillera (Fig. 2), the Sincholagua 170 volcano (4873 m asl; lat. 0°32'S; long. 78°22'W) is an eroded edifice for which no geochronological or 171 geochemical data are available. Further south, Cotopaxi (5897 m asl; lat. 0°41'S; long. 78°26'W) is the 172 only volcano of this volcanic cluster whose Holocene activity has been thoroughly studied (Cotopaxi 173 II edifice; e.g., Mothes et al., 1998; Hall and Mothes, 2008; Pistolesi et al., 2013; Tsunematsu and 174 Bonadonna, 2015; Vezzoli et al., 2017; Sierra et al., 2019). Its eruptive history began with an ancient 175 rhyolitic volcanic center (Cotopaxi I - Barrancas stage), whose products are preserved on Cotopaxi's 176 present-day southern flank. The remnants of the Cotopaxi-I caldera are overlain by a sequence of andesite lavas and breccias associated with the Morurco Edifice (Cotopaxi I - Morurco stage), located 177 178 to the south of the ancient caldera rim. A voluminous andesite lava sequence, that flowed ~40 km 179 northward from source through the Pita River valley, is associated with this stage (Hall and Mothes, 180 2008). The ages of the rhyolite and andesite sequences are not fully constrained. Two fission-track ages

181 of  $0.56 \pm 0.04$  and  $0.54 \pm 0.05$  Ma were obtained from biotite-rich obsidians by Bigazzi et al. (1997), 182 but unfortunately the sampling sites were not provided. The Cotopaxi-I series and the southern flank of 183 Sincholagua are covered by a thick ignimbrite deposit corresponding to the Chalupas caldera-forming 184 eruption that occurred southeast of Cotopaxi (lat. 0°47'S; long. 78°20'W). The Chalupas eruption, dated 185 at  $216 \pm 5$  ka (Bablon et al., 2020b), was followed by the construction of the Quilindaña and esite 186 edifice (4876 m asl) dated at ~184 and ~169 ka (Hammersley, 2003; Córdova et al., 2020). Several 187 tephra fall deposits older than 43 ka represent its most recent dated activity (Córdova et al., 2020). 188 Huañuña (4197 m asl; lat. 0°37'S; long. 78°14'W) and Chaupiloma (also called Rio Valle; 4126 m 189 asl; lat. 0°40'S; long. 78°16'W) are rhyolitic domes located to the north of the Chalupas caldera. Based 190 on stratigraphic evidence, these volcanic centers have been assigned an Holocene age (Mothes and Hall, 191 2008; Hall et al., 2017b). Northeast of Sincholagua and Huañuña, the Antisana volcano (5758 m asl; 192 lat. 0°29'S; long. 78°08'W) consists of three successive andesite edifices constructed since ~400 ka 193 (Hall et al., 2017b), including the voluminous Cuyuja lava sequence dated at 0.21  $\pm$  0.03 Ma (groundmass <sup>40</sup>Ar/<sup>39</sup>Ar; Opdyke et al., 2006). Stratigraphic evidence suggests that the most recent 194 195 activity at Antisana may have occurred prior to 800 yr BP (Hall et al., 2017b).

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#### **197 3. METHODS**

## 198 **3.1.** Sampling strategy

Field campaigns were conducted between 2016 and 2020 to identify and describe the main volcanic units, to establish their stratigraphic relationships, and to collect fresh rock samples for K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar dating, and whole-rock geochemical analyses. A sledgehammer was used to sample inner parts that were not exposed to ambient air and located away from the outer weathered crust. Due to the scarce information on the stratigraphy of some of the volcanoes in the central cluster, we studied the global structure of each edifice as explained below. In order to cover the maximum number of cone building stages, we sampled, whenever possible, the units located at the summit, mid-altitude, and base

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of the studied volcanoes. Considering the arrangement of the access routes, our sampling was performed on several flanks of each volcano to ensure an adequate spatial and stratigraphic distribution of the data.

208 At Almas Santas volcano, one sample was recovered from the Tangan columnar jointed lava 209 flow (19EQ36), located in a lower section of its southern flank, near the Río Toachi canyon (Fig. 2a). 210 Based on its stratigraphic position, it corresponds to an early stage of Almas Santas. An additional 211 sample was collected from a metrical andesitic block found at the base of the Cerro Azul satellite cone, 212 on the eastern flank of Almas Santas (19EQ43). A total of thirteen samples were collected from Corazón 213 volcano. Samples 19EQ05, 19EQ07 and 19EQ10 correspond to massive lava flows that form the 214 southern and southwestern summit ridges of the volcano (Fig. 2b). These ridges were probably formed in a late stage of Corazón's history, as they are relatively well preserved from erosion. In addition, 215 216 sample 19EQ11 was collected from the uppermost section of a lava sequence from the Quitasol river 217 canyon, located at the base of the Bomboli satellite cone (northern foothills of Corazón; Fig. 2a). Further 218 south, a massive lava flow exposed on the northern flank of Corazón was sampled (19EQ13). A juvenile 219 block was collected from a nearby pyroclastic density current (PDC) deposit (19EQ14a). Two samples 220 were taken from a sequence of tephra fall deposits exposed on the northern flank of Corazón (19EQ15a, 221 19EQ15b), probably corresponding to a recent activity at Cerro Bómboli. Finally, an andesitic block 222 was recovered from the monolithological breccias at the base of the pyramidal peak of Corazón 223 (19EQ09), as well as an interlayered lava flow (19EQ08). These breccias are overlain by a thick sequence of thin lava flows (~1-5 m) that form the upper part of the summit. These lavas were sampled 224 225 at sites 20EQ83 and 20EQ84. Additionally, a dacite block was collected from an avalanche deposit on 226 the northwestern flank (20EQ50) near Atacazo-Ninahuilca volcano.

Eight samples were collected at Pasochoa volcano. Four lava flows were sampled from the upper (19EQ31, 19EQ32, 19EQ33) and middle (19EQ34) sections of the radial ridges on the northern flank of the volcano (Fig. 2). Sample 19EQ37 belongs to a lava flow found at the bottom of the Millipaso ravine in the foothills of Pasochoa's southern flank. Samples 19EQ30 and 19EQ38 correspond to two voluminous lava flows observed in the margins of the southeastern and southwestern flanks of the volcano. The scarce exposure of massive lava flows in the summit area precluded sampling; instead, 233 we collected a sample (19EQ42b) for geochemical analysis from one of the numerous dykes that occur 234 between the uppermost monolithological breccias. Likewise, the summit outcrops of Rumiñahui 235 volcano consist mostly of weathered monolithological breccias and rare massive lava flows intersected 236 by several andesitic dikes, which is suggestive of a highly eroded ancient edifice. An andesitic block 237 was collected from a monolithological breccia exposed near the lower section of the central peak 238 (19EQ35). Samples 19EQ27 and 19EQ39 correspond to massive lava flows observed on the 239 southeastern and northwestern flanks, respectively, whose surface morphology is partially identifiable 240 nowadays. Sample 19EQ28 corresponds to an eroded lava flow observed on the southeast ridge of the 241 volcano, which underlies the 19EQ27 lava flow.

242 The scarcity of access roads and trails to Sincholagua, together with its eroded morphology and 243 thick cover of Holocene deposits (soils and tephra fall deposits), prevented adequate sampling of this 244 volcano. One sample was collected from a lava flow outcropping on the uppermost section of the 245 southwestern ridge (19EQ41) and another from a distal lava flow located on the northeastern flank 246 (20EQ86). Only sample 19EQ40 belongs to a lava flow from the basal section of the summit area. 247 Following the description of Hall et al. (2008), we collected five samples from the older stages of 248 Cotopaxi volcano. Sample 20EQ77 corresponds to a massive mica-rich obsidian flow (Cotopaxi I -249 Barrancas stage) outcropping at the base of Morurco peak. Two massive lavas (20EQ76, 20EQ78) were 250 sampled from the overlying sequence composed of andesitic lava flows and monolithological breccias 251 (Cotopaxi I - Morurco stage) outcropping in the upper section of the Morurco river canyon. Finally, 252 two samples of the voluminous lava flow that filled the Pita River valley were collected in the Bocatoma 253 (19EQ29) and Tanipamba (20EQ88) areas.

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## 255 **3.2.** K-Ar dating

Twenty unaltered samples from the central volcanic cluster were selected on the basis of meticulous thin-section examinations (Appendix A) for K-Ar dating using the unspiked Cassignol-Gillot technique (Cassignol and Gillot, 1982). This technique has also been applied to date young 259 volcanic rocks from the Ecuadorian volcanic arc (e.g., Bablon et al., 2018, 2019, 2020a; Santamaría et 260 al., 2022; Samaniego et al., 2022), as well as from other Andean volcanic arc segments (e.g., Germa et 261 al., 2010; Pallares et al., 2016, 2019; Grosse et al., 2018) and worldwide (e.g., Germa et al., 2011; 262 Hildenbrand et al., 2018; Dibacto et al., 2020). All analyses were performed on groundmass, except one 263 on plagioclase phenocrysts (19EQ27) and one on obsidian shards (20EQ77). Samples were manually 264 crushed with a steel mortar and sieved to the 63-80, 80-125, or 125-250 µm fraction sizes, according to 265 their phenocrysts-to-groundmass size ratio. Following a 15 min cleaning in an ultrasonic bath with a 266 10% HNO<sub>3</sub> solution, they were rinsed with de-ionized water. Magnetic and heavy liquids (bromoform) 267 separation methods were then used to extract the groundmass in a narrow density range, removing phenocrysts potential carriers of excess <sup>40</sup>Ar\* and any undetected weathered fraction. The Cassignol-268 Gillot technique was preferentially applied to the groundmass as it is the latest phase assumed to 269 270 crystallize in equilibrium with the atmosphere, and thus would provide the most probable age of the 271 sample and the emplacement of volcanic deposits.

272 The Cassignol-Gillot technique is suitable for the detection of minute amounts of radiogenic argon (<sup>40</sup>Ar\*) produced by the radioactive decay of <sup>40</sup>K, which may be diluted in <sup>40</sup>Ar derived from 273 atmospheric contamination. The difference in the <sup>40</sup>Ar/<sup>39</sup>Ar ratios obtained from the sample and from 274 275 an air aliquot, measured under identical conditions using a 180° sector multi-collector mass spectrometer, allows quantification of the <sup>40</sup>Ar\* content (%). The detection limit of the mass 276 spectrometer, close to 0.1% for <sup>40</sup>Ar\* (Quidelleur et al., 2001), allows dating volcanic products even of 277 Holocene age with a relatively small uncertainty (Gillot et al., 2006). The <sup>40</sup>Ar signal is regularly 278 279 calibrated with systematic measurements of the HD-B1 standard with an age of  $24.18 \pm 0.09$  Ma 280 (Schwarz and Trieloff, 2007). The potassium (K) concentration was measured by flame absorption 281 spectroscopy, in conjunction with the standards MDO-G (Gillot et al., 1992) and BCR2 (Raczek et al., 2001) for comparison and correction. Then, the <sup>40</sup>K/K ratio in nature and the <sup>40</sup>K decay constant (Steiger 282 283 and Jäger, 1977) allow the age of the sample to be calculated. Both potassium and argon measurements 284 were carried out at the GEOPS laboratory (Paris-Saclay University, France) and were performed at least 285 twice to verify their reproducibility within a 1- $\sigma$  uncertainty range. For a full description of sample

preparation, analytical procedures, and age and uncertainty calculations, the reader is recommended tosee Bablon et al. (2018).

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289 **3.3.** <sup>40</sup>Ar/<sup>39</sup>Ar dating

290 For the sake of comparison with the K-Ar technique, groundmass aliquots of samples 19EQ07 and 20EQ84 from the Corazón volcano were also dated using the <sup>40</sup>Ar/<sup>39</sup>Ar technique. This exercise 291 292 allows us to verify the accuracy of our dating and to highlight the presence or absence of external factors 293 such as alteration and isotopic fractionation that could disturb the K-Ar clock (cf. Schaen et al., 2020). 294 Both samples were irradiated for 60 min in the CLICIT facility of the TRIGA reactor at the Oregon 295 State University. The Alder-Creek Sanidine standard ACs-2 with an age of 1.189 Ma (Niespolo et al., 296 2017) was used for neutron fluence determination. The complete experimental procedure is described 297 in detail in Guillou et al. (2011). Samples were loaded into a double-vacuum resistance furnace for mid-298 temperature (~600°C) pre-degassing under pumping, followed by a nine-step incremental heating 299 experiment from approximately 700 to 1200°C. The extracted gases were purified using a Ti 300 sublimation pump and two GP-MK3 SAES Zr-Al getters operating at 400°C. Analyses of the five argon 301 isotopes were performed using a GV5400 instrument. Mass discrimination was calculated from repeated analyses of air pipettes using an <sup>40</sup>Ar/<sup>36</sup>Ar ratio of 298.56 (Lee et al., 2006). Interfering isotope 302 303 corrections, as well as other constants used are reported in Appendix B.

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#### 305 **3.4. Whole-rock geochemical analyses**

Whole-rock major and trace element contents were measured for all dated samples as well as for the other 15 additional samples collected specifically for geochemical analyses, completing a dataset of 35 new analyses. Agate-crushed powders were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), at the Geo-Ocean Laboratory, Université de Bretagne Occidental (Brest, France), following the analytical procedure described in Cotten et al. (1995). Relative uncertainties are lower than 1% for SiO<sub>2</sub>, and 2% for the other major elements, and 5% for trace elements. Major element concentrations were recalculated to a total of 100% on a water-free basis andare presented in Appendix C.

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### 315 **3.5.** Numerical reconstructions of paleotopographies for volume calculations

316 Numerical reconstructions of paleotopography provide a useful tool in the comprehension of 317 the size and shape reached by a volcanic edifice while eluding its erosional features (e.g., Grosse et al., 318 2009, 2020, 2022; Lahitte et al., 2012; Germa et al., 2015; O'Hara and Karlstrom, 2023). Here, we 319 consider the numerical reconstructions as a first approximation of the bulk volume of material 320 accumulated by the volcanic edifice at the end of its construction stage, as well as the amount of material 321 removed since the end of the volcanic activity. For this purpose, we used a 4-m resolution digital 322 elevation model (DEM) developed by the Sigtierras program of the Ministerio de Agricultura y 323 Ambiente de Ecuador (www.sigtierras.gob.ec). The structural features were mapped using a slope map 324 obtained from this DEM, as well as field observations, Google Earth® satellite imagery and 325 orthophotography.

326 Due to the limited stratigraphic constraints of most of the volcanoes studied, we opted for a 327 simple procedure to reconstruct the volcanic edifices. Therefore, we followed the method described by 328 Germa et al. (2015), Bablon et al. (2018, 2020a), and Santamaria et al. (2022), which is summarized as 329 follows. The basal surface of each edifice  $S_{t0}$  was modeled using an ordinary kriging interpolation of 330 the ArcGIS® software, which follows the surrounding topography starting from the basal outline of the 331 edifice. We manually draw the basal outline of each volcanic edifice based on available geological 332 maps, slope breaks, curvature maps and satellite imagery. The Kriging interpolation used points of known elevation within 1 km around the basal outline to get a better fit of the modeled  $S_{t0}$  surface. A 333 334 regular 100 m point cloud was extracted from the Sigtierras DEM for each volcanic edifice. Based on 335 previous results from other volcanoes in the region (Bablon et al., 2018, 2020a; Santamaría et al., 2022; 336 Samaniego et al., 2022), we chose a conical model with a circular base and a concave profile shape, interpreted as the surface reached at the end of the construction stage  $S_{t1}$ . Such profile corresponds to 337

338 the exponential trend line obtained by plotting the elevation of the preserved points against their 339 distance from a vertical symmetry axis. This trend line was shifted to obtain the best fit. Points located 340 in highly eroded areas, such as deep glacial and fluvial valleys, were discarded for profile modeling. 341 Thus, the points preserved in crests or interfluves (planèzes) were interpreted as low erosion surfaces. 342 The surface uncertainty at each point  $\sigma_{S_{tn}-i}$  is provided by the prediction standard error map resulting 343 from ordinary kriging. The present-day surface topography  $S_{t2}$  is interpreted as the result of the erosion of the modeled cone  $S_{t1}$  after the quiescence period, including possible large sector collapses, thus 344 345 maximizing the eroded volume. The construction stage volume  $v_{cs}$  and the erosion stage volume  $v_{es}$ were calculated by integrating the elevation difference between  $S_{t0}$  -  $S_{t1}$ , and  $S_{t1}$  -  $S_{t2}$  surfaces 346 347 multiplied by the pixel area, respectively. The volume uncertainty  $\sigma_v$  corresponds to the combination 348 of the elevation uncertainties of each point  $\sigma_{e-i}$  multiplied by the pixel area, where  $\sigma_{e-i}$  =

$$349 \quad \sqrt{\sigma_{S_{tn}-i}^2 + \sigma_{S_{tn+1}-i}^2}.$$

350

351 **4. RESULTS** 

## 352 **4.1. K-Ar dating**

Twenty new K-Ar ages are presented in Table 1 and shown in Figure 2. K contents range from 0.76 to 1.75 wt.% for groundmass, reaching a minimum of 0.51 wt.% in plagioclase and a maximum of 2.4 wt.% in obsidian fractions. Radiogenic argon contents range from 0.5% to 28.9%, with a maximum of 47.7% for plagioclase.

357 Samples from the eastern and southern flanks of Almas Santas volcano yielded similar ages of 358  $374 \pm 7$  ka (19EQ43) and  $364 \pm 7$  ka (19EQ36), respectively. Considering the sampling bias favoring 359 the upper exposed sections of the edifice, this narrow age range probably represents the youngest cone-360 building stage of the volcano.

Further east, the Corazón volcano exhibits a wider range of ages between  $178 \pm 32$  and  $67 \pm 4$ ka. Notably, sample 19EQ08, taken from the base of the pyramidal peak was dated at  $178 \pm 32$  ka and 363 probably represents an older phase of the volcano. A second sample taken slightly higher (Fig. 2b) and 364 dated at  $175 \pm 30$  ka (20EQ84) supports this result. However, we treat both ages with caution due to 365 their high atmospheric contamination and low radiogenic argon content, reflected in their large uncertainty range. An age of  $149 \pm 6$  ka was obtained for a dacite block (20EQ50) collected from a 366 367 debris avalanche deposit located at the base of the northeastern flank of Corazón volcano. Finally, the 368 ages obtained from the lavas with fresh morphologies at the top of the ridges sampled on the northern 369 and southern flanks define a consistent range between  $95 \pm 3$  ka and  $67 \pm 4$  ka, the latter age being the 370 youngest age obtained for this volcano.

371 In the Inter-Andean Valley, the five ages obtained for Pasochoa volcano exhibit a narrow range 372 between  $472 \pm 8$  and  $423 \pm 20$  ka (Table 1). This range includes the voluminous lava flow outcropping in the Pita River valley (19EQ30), on the eastern flank of Pasochoa volcano, dated at  $450 \pm 7$  ka. Further 373 374 south, the highly weathered state of the Rumiñahui volcanic products precluded groundmass analyses. 375 Therefore, we analyzed plagioclase phenocrysts recovered from the less weathered sample 19EQ27, 376 which yielded an age of  $207 \pm 9$  ka. This sample corresponds to a massive porphyritic lava flow from 377 the eastern flank of the volcano, which belongs to the late volcanic stage characterized by high-K lavas 378 (Starr, 1984). Given the possible presence of inherited radiogenic argon in plagioclase crystals (e.g., 379 Singer et al., 1998), this result should be considered as a maximum value for the eruption age.

Similar to Rumiñahui, the Sincholagua lavas show intense weathering in most outcrops. However, a fresh lava sampled on the eastern flank (19EQ41) yielded a groundmass K-Ar age of 316  $\pm 6$  ka. Regarding Cotopaxi-I volcano, the obsidian flow at the base of the Morurco peak yielded an age of 537  $\pm$  11 ka (20EQ77), which is the oldest value obtained in this study. Finally, a lava flow exposed south of Morurco (20EQ78), and the voluminous Pita lava flows (20EQ88) yielded ages of 334  $\pm$  5 ka and 295  $\pm$  10 ka, respectively.

386

**4.2.** <sup>40</sup>Ar/<sup>39</sup>Ar dating

Plateau ages, isochron regressions and probability of fit were calculated using ArArCalc (Koppers, 2002) following the criteria of Sharp and Renne (2005). An isochron includes the maximum number of consecutive steps with a probability of fit  $\geq 0.1$ . It consists of at least three or more steps that contain  $\geq 60\%$  of the <sup>39</sup>Ar released and it defines a trapped <sup>40</sup>Ar/<sup>36</sup>Ar ratio not statistically different from 298.56. Retained criteria for acceptable age plateau are: (1) it must have a minimum of 3 or more consecutive steps that contain 60% or more of the <sup>39</sup>Ar released, (2) no resolvable slope at 1 $\sigma$  analytical uncertainty, (3) no outliers or age trends within the initial and final steps.

395 The step-heating experiments conducted on these two samples allow the calculation of age 396 plateaus with 87.5% (sample 20EQ84) to 97.0% (sample 19EQ07) of total gas released (Fig.3, 397 Appendix B). This is evidence that the K-Ar clock of these samples is not disturbed and that the 398 calculated ages are reliable. Indeed, according to the lost on ignition (LOI) values (-0.09 and 0.64%, 399 Appendix C), both samples are considered unaltered but with a slightly higher value of LOI for sample 400 20EQ84. This would explain that its apparent age spectrum appears more scattered, with ages ranging from  $72 \pm 41$  to  $170 \pm 97$  ka. Although two consecutive steps (5 and 6) are slightly discordant, we 401 402 calculated a plateau age of  $115.1 \pm 15.2$  ka for sample 20EQ84. The inverse isochron age of  $148.1 \pm$ 403 48.3 ka appears to be poorly constrained due to the very high atmospheric contamination of this sample, with radiogenic <sup>40</sup>Ar content below 3% for all steps. The experiment of sample 19EQ17 yielded a 404 405 relatively well constrained plateau age of  $94.3 \pm 4.9$  ka and an inverse isochron age of  $87.9 \pm 11.9$  ka. There is no evidence of <sup>40</sup>Ar\* excess or mass fractionation, as the <sup>40</sup>Ar/<sup>36</sup>Ar intercept values calculated 406 407 for the two inverse isochrons (Fig.3) are within uncertainties the current atmospheric value. Therefore, 408 the equivalent but more precise plateau ages will be used in our study.

409

## 410 **4.3.** Construction and erosion volumes of the central volcanic cluster

The numerical reconstructions allowed us to calculate the bulk volume of the volcanic edifices within the central volcanic cluster, as well as the volume of the material removed by erosion. It should be noted that the surface models used do not take into account the amount of material lost during the construction stages due to erosion or possible sectoral collapses, nor do they take into account far415 reaching products such as tephra fall deposits. Therefore, the edifice volumes obtained here 416 (construction and present-day volumes) are considered as minimum values, while the erosion volumes 417 are considered as maximum solely for their last quiescence period. On the other hand, the heterogeneity 418 of the volcanic materials prevents us from expressing our values as dense rock equivalent (DRE) 419 volumes, and therefore they are reported as bulk volumes. The calculated volumes are presented in 420 Table 2, together with previous volume estimates published for other volcanic centers. Our calculations 421 show that the most voluminous edifice (reconstructed volume) is the Almas Santas volcano with a bulk value of  $90 \pm 14$  km<sup>3</sup>, while the smallest is La Carcacha volcano with a value of  $8 \pm 1$  km<sup>3</sup>. The average 422 423 volume reached by the volcanoes of the central volcanic cluster is  $43 \pm 12$  km<sup>3</sup>, with Almas Santas 424 being the largest  $(90 \pm 14 \text{ km}^3)$  and Carcacha the smallest  $(8 \pm 1 \text{ km}^3)$ . The present-day volumes of the 425 studied edifices range from  $5 \pm 1 \text{ km}^3$  (Carcacha volcano) to  $44 \pm 5 \text{ km}^3$  (Pasochoa volcano), with an 426 average value of 20 km<sup>3</sup>. The minimum uncertainty in the volumetric calculations is 10 vol.%, with a 427 maximum of 24 vol.%. The calculated volumes for volcanoes located in areas with irregular relief, such as Almas Santas and Corazón ( $\sigma_v > 7 \text{ km}^3$ ), show larger uncertainties compared to volcanoes located 428 429 in more regular or better-defined areas, such as Pasochoa or Cotopaxi ( $\sigma_{\nu} < 6 \text{ km}^3$ ). Likewise, basement 430 surface roughness in mountain areas may underestimate or overestimate the volumes of volcanoes such 431 as Corazón or Almas Santas, respectively, due to the possible presence of ridges or hills in these regions. 432 The present-day volume of eroded material is of at least 24% of the initial volume. Notably, the Almas 433 Santas, Corazón and Sincholagua volcanoes exhibit the highest erosion percentages, up to 74 vol.% of 434 the pre-erosion volume. Furthermore, the Santa Cruz volcano, partially covered by recent volcanic 435 structures and edifices, presents considerable difficulties in estimating the volume preserved nowadays, 436 thus preventing the calculation of the eroded volume.

437 Note that output and erosion rates have not been investigated here, given the multiplicity of 438 factors that control these processes, and which are beyond the scope of this research. For instance, 439 factors such as the heterogeneity of the constituent eruptive products in a volcanic edifice, their 440 distribution around the main vent, and their mechanical resistance to erosion could cause noticeable 441 discrepancies in the volume achieved at the end of the construction periods (e.g., Hora et al., 2007; 442 Zernack et al., 2009; Yamamoto et al., 2018). On the other hand, external factors may influence the rate 443 of syn-eruptive erosion, which in turn biases the output rates. Examples of such factors include the 444 elevation of the edifice and the geographic setting, which influence the precipitation range and/or the 445 extent of glacial cover to which volcanic edifices are exposed through (Brook et al., 2011; Conway et 446 al., 2016; Pure et al., 2020; O'Hara and Karlstrom, 2023). At the same time, tectonic activity can 447 influence both the geometry of the volcanic edifice cone and its degree of degradation (Lagmay et al., 448 2000; Mathieu et al., 2011; Mathieu and van Wyk de Vries, 2011). Additionally, output and erosion 449 rates are strongly influenced by the degree of knowledge of the eruptive history of each edifice, the 450 dispersion of geochronological information and the uncertainty in radiometric ages (e.g., Bablon et al., 451 2020a).

452

#### 453 4.4. Geochemical characterization

454 As shown in Figure 4a, most of the samples from this study are classified as medium-K basaltic 455 andesites to dacites, with SiO<sub>2</sub> contents ranging from 53 wt.% to 64 wt.%. The Cotopaxi-I obsidian 456 (20EQ77) is the only rhyolite in the group with 74 wt.% SiO<sub>2</sub>. The K<sub>2</sub>O contents vary between 0.7 wt.% 457 and 2.7 wt.%. Notably, samples 19EQ37 and 19EQ39, collected from Rumiñahui volcano, lie in the 458 boundary between the medium and high-K calc-alkaline series (Fig. 4a). Our data are consistent with 459 previous studies carried out on the central volcanic cluster. For instance, the sampled lavas from Almas 460 Santas volcano (19EQ36, 19EQ43) fall within the field defined by Chemin (2004) and Eissen et al. 461 (2005). Likewise, the lavas and breccias from the Corazón volcano form a more constrained lower silica 462 andesite field compared to the one provided by Schiano et al. (2010), which is defined by samples 463 collected around Cerro Bómboli. The andesitic lavas of Pasochoa are consistent with the field defined 464 by the same authors. Only two dacite lavas were found in both volcanoes: 19EQ14a and 19EQ33, 465 respectively. The samples collected from Rumiñahui volcano belong to the two sequences described by 466 Starr (1984), with samples 19EQ39 and the dated 19EQ27 belonging to the high-K series. Finally, the 467 Cotopaxi-I samples are consistent with available geochemical data (Bryant et al., 2006; Garrison et al., 468 2006, 2011). In particular, the obsidian 20EO77 shows silica and potassium contents similar to those

469 reported by Bellot-Gurlet et al. (2008), i.e., samples CTX45 and CTX 46 dated by Bigazzi et al. (1997). 470 Considering the analogous mineralogical composition described by these authors, we can argue that our 471 sample corresponds to the same obsidian flow. In addition, samples collected from the Cotopaxi-I 472 southern flank (20EQ76 and 20EQ78) are consistent with the Morurco andesitic series (Garrison et al., 473 2006). Although the Pita lava flow (19EQ29, 20EQ88) exhibits a lower silica content, plotting close to 474 the field described by the Pasochoa and Rumiñahui lavas, the Cotopaxi-I samples plot along a single 475 trend. Note that the geochemical data available for Cotopaxi-I are scarce, and thus its compositional 476 field is poorly defined.

477 Overall, the central volcanic cluster exhibits across-arc geochemical variations similar to those 478 described in other areas of the Ecuadorian arc (e.g., Barragan et al., 1998; Bourdon et al., 2003; Hidalgo 479 et al., 2012; Ancellin et al., 2017; Bablon et al., 2019, 2020a). Chondrite-normalized Rare-Earth 480 Elements (REE) plots (Fig. 4b; Sun and McDonough, 1989) show weak fractionation patterns between 481 Light REE (LREE; La, Ce, Nd) and Heavy REE (HREE; Dy, Er, Yb), with no significant Eu anomaly. 482 Trace elements normalized to primitive mantle diagrams (Fig. 4c) show an overall enrichment of Large-483 Ion Lithophile Elements (LILE; Rb, Ba, and K) and Sr, and depletion of Nb, P, and Ti. The Cotopaxi-I 484 obsidian (20EQ77) has the highest P and Ti negative anomalies. Samples from the volcanoes in the 485 Eastern Cordillera (e.g., Cotopaxi, Sincholagua) exhibit a slight REE enrichment compared to those 486 from the Inter-Andean Valley (e.g., Pasochoa, Rumiñahui), reaching stronger HREE depletions in the 487 Western Cordillera (e.g., Almas Santas, Corazón). Accordingly, most incompatible element contents 488 are higher (e.g., La, Ba, Rb, Sr, Nb) in the Eastern Cordillera volcanoes, i.e., with increasing distance 489 from the trench, while the ratios of fluid-mobile to fluid-immobile (e.g., Ba/Th, Ba/Nb) elements are 490 lower (e.g., Ba/Th vs La; Fig. 5). Variations in REE contents are also observed for each volcano. For 491 instance, the andesite lavas from Almas Santas (19EQ36, 19EQ43) show a slight HREE enrichment 492 compared to the rhyodacite-rhyolite series (Chemin, 2004; Eissen et al., 2005). Likewise, the high-K 493 andesites from Rumiñahui volcano (e.g., 19EQ27, 19EQ39) and the dacite sample 19EQ33 from 494 Pasochoa volcano show the highest LREE enrichments of the Inter-Andean Valley volcanoes. The Pita River lavas (Cotopaxi I - Morurco stage) are geochemically distinct from the Pasochoa lavas due totheir higher contents of incompatible elements and lower fluid-mobile to fluid-immobile ratios (Fig. 5).

497 Overall, the geochemical evolution of the magmas in the central volcanic cluster is strongly 498 influenced by crustal differentiation processes (cf. recharge, assimilation and fractional crystallization), 499 as suggested by the negative correlation between the compatible elements and the  $SiO_2$  contents (Fig. 500 D1 and D2, Appendix D), as well as by several petrogenetic models proposed for the volcanoes in the 501 area (Barragan et al., 1998; Bourdon et al., 2003; Bryant et al., 2006; Chiaradia et al., 2009; Hidalgo et 502 al., 2012; Ancellin et al., 2017). These models support fractionation of variable amounts of plagioclase, 503 pyroxene, amphibole, and olivine. However, the occurrence of certain lavas with strong Y and HREE 504 depletion reported for volcanoes such as Ilinizas, Almas Santas, and Cotopaxi, can be explained by 505 more complex petrogenetic processes leading to higher amphibole and/or garnet fractionation (cf. 506 Chemin, 2004; Garrison et al., 2006; Hidalgo et al., 2007). Furthermore, the higher fluid-mobile to 507 fluid-immobile ratios observed in volcanoes located closer to the trench (e.g., Almas Santas, Corazón, 508 Pasochoa) suggest a significant role of aqueous slab fluids or melts in the mantle wedge metasomatism 509 (Ancellin et al., 2017). In summary, the geochemical variation of the central volcanic cluster can be 510 explained both by changes in the subducting slab inputs that metasomatize the mantle wedge, and by 511 fractional crystallization, crustal assimilation and magma mixing (e.g., Garrison et al., 2006; Hidalgo 512 et al., 2007, 2012; Chiaradia et al., 2009, 2020; Schiano et al., 2010; Bellver-Baca et al., 2020).

513

#### 514 **5. DISCUSSION**

## 515 5.1. Comparison with previous geochronological data

516 Overall, the new radiometric ages obtained in this study are consistent with others reported in 517 the central volcanic cluster. An unpublished  ${}^{40}$ Ar/ ${}^{39}$ Ar age obtained at the Laboratoire Geoazur (Côte 518 d'Azur University, Nice, France) was obtained for the Corazón volcano (M. Fornari pers. com.). Hand-519 picked groundmass fragments from the sample BOM-5, collected north of the Bomboli cone (Fig. 2b), 520 yielded a plateau age of 190 ± 10 ka, and a consistent inverse isochron age of 188 ± 10 ka. These values 521 are significantly older than our K-Ar age of  $91 \pm 10$  ka obtained from a nearby lava flow (19EQ11). 522 Considering the lower stratigraphic position of the BOM-5 sampling site (Fig. 2b; Fig. D3, Appendix 523 D), the occurrence of two lava sequences of different ages is plausible. Indeed, the BOM-5 age falls 524 within the range obtained here for the early cone-building stage of Corazón volcano, dated at  $175 \pm 30$ 525 ka (20EQ84) and  $178 \pm 32$  ka (19EQ08), while the 19EQ11 age is consistent with the late stage, which 526 occurred between  $67 \pm 4$  ka (19EQ05) and  $95 \pm 3$  ka (19EQ07). Nevertheless, the groundmass 527 separation method used in BOM-5 does not prevent the occurrence of phenocrysts or weathered phases, 528 which could have biased the resulting age. Unfortunately, the lack of detailed data, such as age spectrum 529 and isochron age, makes this age difficult to interpret and prevents us from further investigation.

530 Opdyke et al. (2006) obtained a  ${}^{40}$ Ar/ ${}^{39}$ Ar plateau (three steps only) age of  $1.33 \pm 0.30$  Ma for 531 a normal polarity lava flow (EC-47) sampled on the eastern flank of Pasochoa. The corresponding isochron yielded an age of  $1.93 \pm 2.88$  Ma with an initial  ${}^{40}$ Ar/ ${}^{39}$ Ar ratio of  $271 \pm 116$ , indicating high 532 533 atmospheric contamination. The low precision of this age precludes comparison with the geomagnetic 534 polarity timescale; nevertheless, we note that the geomagnetic field was dominantly reverse during the 535 Matuyama Chron (i.e., 2.58 to 0.77 Ma; Cohen and Gibbard, 2019). Here we provide a K-Ar age of 450 536  $\pm$  7 ka obtained from a nearby lava flow (19EQ30) belonging to the same unit. Our age is in good 537 agreement not only with the normal polarity reported by Opdyke et al. (2006), but also with our new 538 ages for Pasochoa volcano, which range from  $423 \pm 10$  ka to  $472 \pm 8$  ka (Table 1).

Two obsidian blocks belonging to the Cotopaxi-I rhyolitic stage were previously dated at 540  $\pm$  50 ka (CTX 46) and 560  $\pm$  40 ka (CTX 45) using the obsidian fission-tracks (Bigazzi et al., 1997). By applying the K-Ar method for dating an obsidian flow (20EQ77), we obtained a consistent and welldefined age of 537  $\pm$  11 ka. The geochemical and petrographic similarities observed between our samples and those of Bigazzi et al. (1997), including the presence of biotite and scarce quartz, suggest that we have successfully dated obsidian samples from the same sequence using two different techniques. Note that biotite crystals were removed here during sample preparation process.

## 547 5.2. Comparison between K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar ages from this study

548 Two samples from Corazón volcano were dated here using two techniques, K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar, 549 showing contrasting results. This can be explained by the quality of the lava samples and their 550 atmospheric argon contamination. Sample 19EQ07 has a total-gas relatively high radiogenic <sup>40</sup>Ar 551 content (3.6-3.9%; Table 1), which allowed precise measurements. In fact, using K-Ar dating, which 552 has a detection limit of 0.1% (Quidelleur et al., 2001), we obtained an age of  $95 \pm 3$  ka. This value is in very good agreement with the  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  plateau age of 94.3 ± 4.9 ka obtained for this sample (Fig. 3). 553 554 On the other hand, sample 20EQ84 has a low total-gas radiogenic Ar content of only 0.6% (Table1), 555 resulting in a rather poorly constrained K-Ar age of  $175 \pm 30$  ka. This age is compatible at the onesigma level with the  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  inverse isochron age of  $148 \pm 48$  ka, and at the two-sigma level with the 556  $^{40}$ Ar/ $^{39}$ Ar plateau age of 115.1 ± 15.2 ka. This highlights the difficulty of dating groundmass separated 557 from andesitic lavas with high atmosphere contamination using the K-Ar or <sup>40</sup>Ar/<sup>39</sup>Ar techniques. Note 558 559 that the K-Ar age of  $178 \pm 32$  ka obtained for the nearby sample 19EQ08 (Fig. 2b), which is also highly contaminated (<sup>40</sup>Ar\* lower than 0.6%), is very close to the K-Ar age of  $175 \pm 30$  ka obtained for 560 20EQ84, and that the four individual analyses for these samples cluster between 175 and 181 ka despite 561 562 their large uncertainty (Table 1).

563 This comparison demonstrates that no systematic error has affected either of these dating 564 techniques, and that K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar ages are reliable when obtained for fresh rocks with relatively 565 high radiogenic yields, such as sample 19EQ07.

566

# 567 5.3. Eruptive history of the central segment

568 Based on our new K-Ar ages, stratigraphic and morphological data, and previous studies carried 569 out in the central segment volcanoes, we present the eruptive history for this area of the Ecuadorian arc 570 as follows (Fig. 6; Table 3).

571 The oldest eruptive activity appears to have occurred in the north of the central segment. Several 572 geochronological studies suggest that volcanoes such as Pichincha (Robin et al., 2010), Chacana 573 (Opdyke et al., 2006; Bellot-Gurlet et al., 2008), Cayambe (Samaniego et al., 2005) and Mojanda-Fuya 574 Fuya (Bablon et al., 2020a) were active prior to  $\sim 1$  Ma. In the central volcanic cluster area, only the 575 Carcacha volcano (Atacazo-Ninahuilca complex; Western Cordillera), adjacent to the Pichincha 576 volcano, has lava flows dated at ~1.30 Ma (Hidalgo, 2006). After a period of apparent quiescence, 577 volcanic activity resumed southward, forming the Santa Cruz volcano in the Inter-Andean Valley at 578 about  $702 \pm 11$  ka (Santamaría et al., 2022). From ~550 ka, the volcanic activity seems to have increased 579 in the central volcanic cluster (Fig. 6). The Cotopaxi-I caldera (Eastern Cordillera) showed large, highly 580 explosive eruptions and effusive activity of rhyolitic affinity dated at  $537 \pm 11$  ka (20EQ77). Later, the 581 construction of the andesitic Pasochoa volcano occurred in the Inter-Andean Valley, which was already 582 active between  $472 \pm 8$  ka (19EQ34) and  $423 \pm 10$  ka (19EQ37). Massive dacite lava flows and PDC 583 deposits, corresponding to the pre-caldera Chalupas volcanic system, erupted in the Eastern Cordillera around  $459 \pm 9$  ka and  $418 \pm 10$  ka (plagioclase  ${}^{40}$ Ar/ ${}^{39}$ Ar plateau ages; Hammersley, 2003). 584

585 Eruptive activity throughout the central volcanic cluster occurred between  $\sim$ 400 and  $\sim$ 300 ka. 586 In the Western Cordillera, the onset of the Almas Santas volcano (dated at  $374 \pm 7$  and  $364 \pm 7$  ka) and 587 the extrusion of the Pilongo lava dome  $(353 \pm 6 \text{ ka}, \text{Iliniza volcano}; \text{Santamaría et al., 2022})$  took place. 588 We also note that the oldest dated activity of the Antisana (from  $378 \pm 38$  ka; Hall et al., 2017b), 589 Cotopaxi-I Morurco (around  $334 \pm 5$  ka), and Sincholagua (around  $312 \pm 6$  ka) volcanoes in the Eastern 590 Cordillera occurred during this period. Due to sampling bias, these ages may mostly correspond to the 591 intermediate or more recent eruptive stages of these volcanoes. We propose that the emplacement of an 592 older edifice of the Rumiñahui volcano occurred during this eruptive stage of the central volcanic 593 cluster, or earlier, as suggested by (1) the widespread exposure of the dyke network in the summit area, 594 which implies a much higher degree of erosion compared to other edifices in the area, and thus a longer-595 term erosional phase; (2) the upper bound provided by the  $207 \pm 9$  ka age (19EQ27), which belongs to 596 the high-K andesite series defined by Starr (1984); and (3) the required presence of a prominent edifice 597 at the site of Rumiñahui volcano to channel the Pita lava flows (295  $\pm$  10 ka) northward from the 598 Morurco cone (Cotopaxi-I volcano) to its terminus position east of Pasochoa volcano.

599 The apparent quiescence period in the Western Cordillera since ~300 ka ended when the 600 volcanic activity resumed south of Carcacha volcano, forming the basal edifice of Atacazo volcano. This early cone was dated at ~200 ka (groundmass  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  ages; Hidalgo, 2006). Further south, the 601 602 emplacement of the older Corazón series could have occurred at about  $178 \pm 32$  ka (19EQ08). The 603 block (20EQ50) collected from an avalanche deposit outcropping between Corazón and Atacazo 604 volcanoes yielded a K-Ar age of  $149 \pm 6$  ka. The Sr and Th contents compared to LILE (e.g., Ba) and 605 LREE (e.g., La) of this sample are consistent with those observed at Atacazo volcano (Fig. D4, 606 Appendix D), suggesting that this sample could be associated with Atacazo instead of Corazón. This 607 implies a possible extension of the Atacazo volcanic activity up to  $\sim 150$  ka, providing an older bound to its southwestern sector collapse. 608

609 In the Inter-Andean Valley, the activity resumed at Rumiñahui volcano around  $207 \pm 9$  ka 610 (19EQ27), as suggested by the plagioclase K-Ar age obtained from its terminal andesitic series. 611 Nonetheless, since this age could be biased toward too old values by inherited argon (e.g., Singer et al., 612 2008), it is possible that Rumiñahui volcano was active in more recent times. Synchronously in the 613 Eastern Cordillera, the voluminous Cuyuja lava flow (11 km<sup>3</sup>) was erupted from a fissure located to the southeast of Antisana volcano at  $210 \pm 30$  ka (groundmass  $^{40}$ Ar/ $^{39}$ Ar plateau age; Opdyke et al., 2006; 614 615 Hall et al., 2017b). Further south, the Chalupas ignimbrite eruption (VEI 7) occurred southeast of Cotopaxi-I volcano at 216 ± 5 ka (Bablon et al., 2020b), forming a ~17 km-wide caldera and a 616 617 widespread ignimbrite deposit that covered the Inter-Andean Valley (Mothes and Hall, 2008; Bablon 618 et al., 2020b). The early cone-building stages of Quilindaña volcano, an intra-caldera stratovolcano with activity dated at  $184 \pm 3$  ka (Buenavista dome; groundmass 40 Ar/39 Ar age; Córdova et al., 2020; Córdova 619 et al., 2020) and 169  $\pm$  1 ka (plagioclase <sup>40</sup>Ar/<sup>39</sup>Ar age; Hammersley, 2003), followed the Chalupas 620 621 eruption.

Finally, the volcanic activity appears to have been restricted to both cordilleras during the last ~100 kyr. In the Western Cordillera, the Atacazo (Hidalgo, 2006) and Corazón volcanoes were active until at least ~70 ka. Simultaneously, the construction of Iliniza volcano occurred to the south of the Pilongo dome, beginning with its northern edifice at ~123-116 ka. It was followed by the onset of its

southern edifice at ~46-25 ka (Santamaría et al., 2022). The growth of the Loma Saquigua cone (79-60 626 627 ka) in Santa Cruz volcano is the only eruptive activity documented in the Inter-Andean Valley during 628 this period (Santamaría et al., 2022). Despite the lack of radiometric dates, the stratigraphic and 629 morphological evidence suggests that the Antisana volcano was also active during this interval (Hall et 630 al., 2017b). During the Holocene, the explosive activity of the Ninahuilca dome complex followed the 631 sector collapse of Atacazo volcano (Hidalgo et al., 2008), while the activity of Iliniza volcano was 632 mainly effusive (Santamaría et al., 2022). In the Eastern Cordillera, several explosive rhyolitic eruptions 633 preceded the construction of the andesitic cone of Cotopaxi II (Hall and Mothes, 2008). The fallout 634 stratigraphic relationships observed in the Eastern Cordillera suggest that the activity of the Huañuna 635 and Rio Valle rhyolitic centers apparently occurred during the Holocene (Mothes and Hall, 2008; Hall 636 et al., 2017b), as well as that of Antisana volcano and the Buenavista dome (Quilindaña volcano; 637 Córdova et al., 2020).

638

#### 639 5.4. Eruptive volumes

640 Volumetric calculations indicate that the volcanoes in the central cluster grew to roughly similar sizes (Table 2), reaching average bulk volumes of  $43 \pm 12$  km<sup>3</sup> (reconstructed volume). These volumes 641 642 provide a first-order estimate of the amount of erupted material, although factors such as the type, 643 distribution and bulk density of the volcanic deposits, as well as their syn-eruptive erosion, are not 644 accounted for. Tephra dispersion outside the volcanic edifice is an additional factor that is not 645 considered in our calculation. For instance, the bulk volume of fallout deposits of the Cotopaxi Holocene (< 4.5 ka) and esitic series is estimated to be between 4 and 9 km<sup>3</sup> (DRE volume  $\sim$ 1.5 to 3.5 646 647 km<sup>3</sup>; Hall and Mothes, 2008), whereas the calculated bulk volume of the Cotopaxi edifice is  $32 \pm 3$  km<sup>3</sup>. 648 We emphasize that all our calculated values should be considered as rough estimates, as more detailed 649 stratigraphic studies are required for each volcano. Figure 7b plots the accumulated bulk-volume of the 650 central volcanic cluster edifices over time. Due to its low density, the bulk volume of the Chalupas 651 ignimbrite of  $230 \pm 30$  km<sup>3</sup> (Bablon et al., 2020b) was replaced by its Dense Rock Equivalent (DRE) 652 of ~100 km<sup>3</sup> (Hall and Mothes, 2008; Crosweller et al., 2012) for comparison purposes only. Figure 7b

653 shows that the cumulative cone-building volume in the central volcanic cluster has been roughly stable 654 at a rate of  $1.2 \pm 0.2$  km<sup>3</sup>/kyr ( $R^2 = 0.958$ ) since ~550 ka. Thus, assuming that the cone-building 655 volumes are proportional to the erupted volumes, we suggest that the magmatic production has been 656 relatively constant for the central volcanic cluster during the last ~0.5 Ma. This observation also seems 657 to apply to the clusters located in the northern and southern segments, according to data from Bablon 658 et al. (2019, 2020a) and references therein. Significant variations in growth or magmatic production 659 rates could have occurred throughout the eruptive history of each volcano, and thus, we strongly suggest 660 that this value should be taken with caution due to the calculation assumptions made.

661

#### 662 5.5. Temporal and spatial arrangement of the central segment volcanoes

663 The most common volcanic landforms in the central segment are composite stratovolcanoes, lava domes, and calderas which are distributed in NE-SW alignments following the morpho-structural units 664 665 of the Ecuadorian arc (Fig. 1 and 2). The position of Almas Santas volcano, located 15 km west of the 666 Volcanic Front, makes the central segment one of the widest in the Northern Andes. This location, 667 geographically closer to the trench, is also shared by Quilotoa, a 3 km-wide caldera located 30 km to 668 the south of Almas Santas. Notwithstanding this arrangement, the overall correlation between the 669 temporal evolution and geographic location of these volcanoes is puzzling, especially in the central 670 volcanic cluster. Indeed, Figures 6 and 7a show that although volcanic activity has been continuous in 671 each alignment for the last ~550 ka, it was unevenly distributed. This observation contrasts with the 672 dynamics of the northern and southern segments, for which Bablon et al. (2019, 2020a) described a 673 relative migration to the northwest and south for the same period, respectively. Nevertheless, the 674 occurrence of edifices older than  $\sim 1$  Ma to the north of the central segment (e.g., Viejo Cayambe, 675 Samaniego et al., 2005; La Carcacha, Hidalgo, 2006; Chacana Caldera, Opdyke et al., 2006; Ruco 676 Pichincha, Robin et al., 2010; Pre-Mojanda lavas, Bablon et al., 2020a) suggests an overall southward 677 extension of Ecuadorian volcanism in this area between roughly 1 Ma and 600 ka (Bablon et al., 2019). 678 From the above considerations, the central segment appears as a key area to better understand the

679 formation of the Ecuadorian arc and the factors that controlled the emplacement of volcanoes in this680 area.

681 Evidence for the relationship between crustal architecture, and the position and timing of 682 volcanism is still scarce. Nevertheless, we offer a short discussion on this subject with possible issues 683 to be addressed in future research. As highlighted by Litherland and Aspden (1992), the distribution of 684 the Quaternary volcanoes in the Ecuadorian arc seems to be influenced by the major tectonic structures 685 of the continental crust (Fig. 8). In the central volcanic cluster, for instance, the Almas Santas volcano 686 and the Atacazo-Corazón-Iliniza volcanoes occur above ancient NE-SW oriented fault systems that 687 separate the Cretaceous oceanic units of the Western Cordillera (Hughes and Bermúdez, 1997; Hughes 688 and Pilatasig, 2002), e.g., the Pujilí fault. To the east, the tectonic structures of the Eastern Cordillera 689 are covered by thick Neogene volcanic sequences. Nevertheless, the position major structures such as 690 of the Peltetec fault, is inferred in our study area based on the change in slope of the western edge of 691 the Eastern Cordillera. This position coincides with the exposure of the Peltetec fault in the Chota 692 Valley to the north and in the Pisayambo area to the south (Litherland et al., 1994; Winkler et al., 2005). 693 The volcanoes of the Eastern Cordillera form NE-SW alignments that roughly coincide with the 694 orientation and position of these structures. The arrangement of the ancient structures of the Inter-695 Andean Valley remains unclear due to the scarce basement exposures.

696 Regarding Quaternary tectonics, the central volcanic cluster is located in the interaction zone 697 between the Quito and Latacunga reverse fault systems, which are expressed to the north and south of 698 this area as parallel strands of folds over large major west dipping, blind, en-echelon thrust faults (Fig. 699 9; Fiorini and Tibaldi, 2012; Alvarado et al., 2014, 2016). These structures, which mainly affect the 700 volcano-sedimentary deposits on the eastern margin of the Inter-Andean Valley, seem to converge 701 towards the ancient Pujilí fault at deep (Western Cordillera; Alvarado et al., 2016) beneath the Iliniza 702 and Corazón volcanoes. The relationship of this fault system to volcanism is not clear. Nevertheless, a 703 progressive southward migration of volcanic activity appears to have occurred at the Iliniza volcano, 704 following the NE-SW axis consistent with the projection of the Pujilí suture (Santamaría et al., 2022), 705 while the preserved areas of the western flank of the Corazón volcano show NE-SW faults that possibly

706 contributed to its destabilization and sector collapse. Accordingly, Figure 9 illustrates that shallow 707 seismicity is present in this area of the Western Cordillera along the volcanic and tectonic structures 708 described above. Northeast of Iliniza, the Machachi right-lateral strike-slip fault is hypothesized to run 709 across the Inter-Andean Valley, extending along the NW flank of Rumiñahui volcano toward the SE of 710 Pasochoa volcano (Soulas et al., 1991; Egüez and Yepes, 1994). Although, we found no clear 711 morphological evidence for the Machachi fault trace, its orientation is compatible with the strike-slip 712 focal mechanisms observed south of Iliniza volcano (Pastocalle seismic zone; Basualto and Troncoso, 713 2003) and south of Pasochoa volcano (Pita Valley seismic zone; Hernández et al., 2020). The 714 occurrence of intense historical earthquakes in these zones (Beauval et al., 2010) suggests a potentially 715 higher degree of fault coupling. Furthermore, north of the Cotopaxi volcano, Fiorini and Tibaldi (2012) 716 described several minor strike-slip faults with NNE-SSW orientation in the Pita Valley. For these 717 authors, the Cotopaxi volcano zone acts as a fault transfer zone that accommodates the higher shortening 718 observed in the Latacunga basin compared to the Guayllabamba basin. Therefore, based on these 719 statements, we hypothesize the existence of a NE-SW system of active tectonic structures (albeit 720 blinded) between the Iliniza, Rumiñahui, Pasochoa, and Sincholagua volcanoes, rather than a single 721 failure. We recognize that the identification of active faulting is not straightforward in the central segment due to the continuous cover of this area during the Holocene (mainly by tephra from the 722 723 Cotopaxi volcano). However, the above evidence suggests that Quaternary tectonics also played a 724 significant role in promoting magma ascent in this area.

725

### 726 6. CONCLUSIONS

The 22 new radiometric ages presented in this article provide the first geochronological data for several edifices of the central volcanic cluster of the Ecuadorian Arc. Despite the significant erosion experienced by some edifices, suggesting long-term exposures, most of them were constructed during the Late Pleistocene. The earliest volcanic activity occurred between ~1.3 Ma and ~700 ka with the onset of La Carcacha and Santa Cruz volcanoes (Hidalgo, 2006; Santamaría et al., 2022). From ~550 ka onwards, the volcanic activity in the region increased with the gradual formation of a "volcanic 733 cluster" composed of at least a dozen of stratovolcanoes and some smaller volcanic cones and lava 734 domes, spread over an area 70 km wide (E-W) and 40 km long (N-S). These volcanic features seem to 735 have been constructed probably over or near basement-inherited fault systems and sutures. Although 736 several Quaternary NE-SW fault systems have been described in this area (e.g., Soulas et al., 1991; 737 Egüez and Yepes, 1994; Alvarado, 2012; Fiorini and Tibaldi, 2012), the low deformation associated 738 with these systems suggests that they probably played a secondary, albeit important, role in the 739 development of the volcanoes arrangement, however, more research is needed on this topic. Although 740 the spatial development of volcanism in the central segment appears to be random in time, the 741 occurrence of older volcanoes in the north of this area is suggestive of a southward extension of 742 volcanism between ~1 Ma and ~550 ka. Numerical reconstructions show that the volcanic edifices from 743 the central cluster reached typical volumes on the order of  $43 \pm 12$  km<sup>3</sup>. Based on the proposed 744 evolutionary history and our volumetric calculations, we infer that the overall volcanic output rate in 745 the region (and presumably the magmatic production rate) has been roughly stable at  $1.2 \pm 0.2$  km<sup>3</sup>/kyr 746 during the last ~550 ka. However, we do not exclude the occurrence of sporadic magmatic pulses and 747 short periods of quiescence that could affect this rate over at shorter timescales.

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## 1179 Figure captions



Figure 1. a) Regional geodynamic setting of the Ecuadorian margin. The white arrow indicates the 1182 1183 direction of motion of the Nazca plate relative to South America (DeMets et al., 2010). Topography 1184 and bathymetry from the GEBCO 2020 program. b) Major geomorphologic provinces of Ecuador 1185 (modified from Litherland and Aspden, 1992). c) Schematic map of the Ecuadorian volcanic arc 1186 (modified from Bernard and Andrade, 2011). Volcanoes are colored according to their distance from 1187 the trench, which includes the N-S alignments of the Volcanic Front (Western Cordillera), Inter-Andean 1188 Valley, Main Arc (Eastern Cordillera), and Back-Arc. Variability in the number of volcanoes along-arc 1189 is represented by the northern, central, and southern across-arc segments. Active fault systems are 1190 represented by red lines according to Alvarado et al. (2016). CCPP: Chingual-Cosanga-Pallatanga-Puná 1191 Fault System; Q-fs: Quito Fault System; L-fs: Latacunga Fault System. Suture zones are shown by grey 1192 segmented lines. Major cities are shown in black.





Figure 2. a) Hill-shaded digital surface model (from the Sigtierras program) of the central volcanic
cluster of the Ecuadorian Arc showing the sampling locations and geochronological results. Numbers
correspond to the last two digits of the sample's names (19EQxx or 20EQxx, depending on the year of
recollection). K-Ar dated samples are shown as solid black dots. Volcanoes labelled in black. Satellite
lava domes and cones are denoted by dashed lines and are labeled with red letters. Rivers and valleys
names are labeled with blue letters. Coordinates are in Universal Transverse Mercator (UTM) zone 17.
b) Extended view of the Corazón summit area. <sup>40</sup>Ar/<sup>39</sup>Ar plateau ages are shown in italic letters.



Figure 3. Results of <sup>40</sup>Ar/<sup>39</sup>Ar analyses for samples 19EQ07 (left) and 20EQ84 (right). K/Ca ratio and
 apparent age spectra (in ka) are shown below as a function of the cumulative <sup>39</sup>Ar content (in %), inverse
 isochrons are shown below. Details are given in Appendix B.



Figure 4. a) K<sub>2</sub>O vs. SiO<sub>2</sub> diagram (Peccerillo and Taylor, 1976) for eruptive products of the central volcanic cluster. HK: high-K, MK: medium-K, and LK: low-K calc-alkaline series. Data from this study represented as point symbols. Shaded areas represent the compositional fields of volcanoes sampled in

- 1211 this study while dashed areas are for other volcanoes, both areas with data taken from the Georoc 1212 database and other studies (Starr, 1984; Chemin, 2004; Garrison et al., 2006; Bellot-Gurlet et al., 2008; 1213 Schiano et al., 2010; Ancellin et al., 2017; Hall et al., 2017b; Bablon et al., 2020b; Chiaradia et al., 1214 2020; Córdova et al., 2020; Santamaría et al., 2022). b) Rare Earth Elements normalized to chondrites, 1215 and c) Incompatible trace elements normalized to the primitive mantle diagrams (Sun and McDonough, 1216 1989) for the same arrangements. The sampled volcanoes were organized according to their location in 1217 the Western Cordillera (yellow and orange lines), the Inter-Andean Valley (red and purple lines), and 1218 the Eastern Cordillera (blue and turquoise lines). The shaded areas represent the compositional fields 1219 from bibliographic data; volcanoes with insufficient data are denoted as ND fields.
- 1220



1221

Figure 5. Ba/Th vs La diagram for eruptive products of the central volcanic cluster. Same data as Fig.
4a. Data from this study represented as point symbols. Shaded areas represent the compositional fields
of volcanoes sampled in this study while dashed areas are for other volcanoes, both areas with data
taken from the Georoc database and other studies (Starr, 1984; Chemin, 2004; Garrison et al., 2006;
Bellot-Gurlet et al., 2008; Schiano et al., 2010; Ancellin et al., 2017; Hall et al., 2017b; Bablon et al.,
2020b; Chiaradia et al., 2020; Córdova et al., 2020; Santamaría et al., 2022)



1228

1229 Figure 6. Synthesis cartoons of the eruptive history of the Ecuadorian central arc segment. a) Early 1230 stage of the Quaternary volcanic arc. Formation of the volcanoes Carcacha (1.3 Ma) and Santa Cruz 1231 (700 ka), as well as other contemporaneous edifices outside the study area: El Cinto (16), Ilaló (17), 1232 Chacana (18). b) Early construction of the volcanic cluster. Cotopaxi-I (Barrancas stage) at 550 ka. c) 1233 Pasochoa; Chalupas (pre-caldera deposits). d) Antisana-I; Almas Santas; Cotopaxi-I (Morurco stage); 1234 Pilongo lava dome of Iliniza; early stage of Rumiñahui; and Sincholagua. The distal flows of the 1235 Morurco cone are represented as a purple field north of Cotopaxi-I. e) Antisana; Atacazo; Chalupas 1236 caldera-forming eruption ( $216 \pm 5$  ka; Bablon et al., 2020b), and construction of the Quilindaña post-

- 1237 caldera edifice; Corazón; North Iliniza edifice; late stage of Rumiñahui. f) Modern stage of the volcanic
- 1238 cluster (dark green) and its Holocene activity (light green). Antisana II and III; Atacazo satellite lava
- 1239 domes, and Ninahuilca lava dome complex; Corazón; Cotopaxi-II edifice; Bellavista lava dome;
- 1240 Huañuna lava dome; South Iliniza edifice, and its satellite lavas; Rio Valle lava dome; and Quilotoa
- 1241 caldera (19). Active fault systems are shown as red lines for all charts, according to Alvarado et al.
- 1242 (2016) and this study. Note that the maps are rotated slightly counterclockwise to match with the E-W
- 1243 orientation of the volcanic cluster. See text for full references.



1245

1246 Figure 7. Temporal evolution of volcanism in the central segment of the Ecuadorian Arc. a) Schematic 1247 representation of the individual cone-building stages through time. See text for details. b) Cumulative 1248 bulk volume (km<sup>3</sup>) for the central volcanic cluster over time. Uncertainty bars indicate the extent of the 1249 considered construction periods in ka according to Table 2. The bulk volumes of Antisana, Rumiñahui, 1250 Corazón and Atacazo volcanoes do not distinguish the different cone-building stages due to the lack of 1251 detailed stratigraphic data. The dashed line symbolizes the cumulative volume rate over the last  $\sim$ 550 1252 ka, while the shaded area represents the cumulative volumetric uncertainty range. Volcano numbers as 1253 in Figure 1.



1254

1255 Figure 8. Geologic map of the central segment basement (modified from Litherland et al., 1994; Hughes

1256 and Bermúdez, 1997; Egüez et al., 2017; Vallejo et al., 2020). Dashed lines show tectonic structures

1257 inherited from the basement. The Pujilí suture is drawn as a continuous line, and the inferred location

1258 of the Peltetec suture as a dotted line.



Figure 9. Schematic map of the Quaternary fault systems of the central segment focused in the Inter-Andean Valley (Egüez and Yepes, 1994; Alvarado, 2012; Alvarado et al., 2014; Fiorini and Tibaldi, 2012; and this study). Q-fs: Quito fault-system; L-fs: Latacunga fault-system; M-fs: Machachi faultsystem. Locations of the historical earthquakes according to the "Catalogo Homogenizado 1587 – 2011" of the IG-EPN, with hypocenter depths less than 40 km. The location of the AD 2020 earthquake according to Hernández et al. (2020). Moment tensor solutions from Basualto and Troncoso (2003) and Hernández et al. (2020).

# 1268 Tables

**Table 1.** K-Ar ages obtained in this study for central segment volcanoes. Column headings indicate sample name, outcrop nature and relative location, sample coordinates projected using the Universal Transverse Mercator (UTM) coordinate system (Zone 17), potassium (K) content in percent, radiogenic argon ( $^{40}$ Ar\*) content 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. All measurements were performed on groundmass, except for one sample measured on plagioclase phenocrysts (<sup>P</sup>) and one sample measured on volcanic glass (<sup>G</sup>).

| Sample               | Location and Unit         | UTM<br>Easting | UTM<br>Northing | K<br>(%) | <sup>40</sup> Ar*<br>(%) | <sup>40</sup> Ar*<br>(10 <sup>11</sup><br>at/g) | Age±1<br>σ(ka) | Mean age<br>(ka) |  |
|----------------------|---------------------------|----------------|-----------------|----------|--------------------------|---|----------------|------------------|--|
| Almas Santas volcano |                           |                |                 |          |                          |   |                |                  |  |
| 19EQ43               | Lava flow, Cerro Azul     | 740786         | 9934033         | 0.992    | 8.4%                     | 3.8562  | $372\pm7$      | $374\pm7$        |  |
|                      |                           |                |                 |          | 8.1%                     | 3.8998  | $377\pm7$      |                  |  |
| 19EQ36               | Lava flow, Tangan         | 734605         | 9929768         | 0.756    | 8.2%                     | 2.8759  | $364\pm7$      | $364\pm7$        |  |
|                      |                           |                |                 |          | 7.4%                     | 2.8822  | $365\pm7$      |                  |  |
|                      |                           |                |                 |          |                          |   |                |                  |  |
| Corazón v            | volcano                   |                |                 |          |                          |   |                |                  |  |
| 19EQ08               | Lava flow, pyramidal peak | 759536         | 9940634         | 1.579    | 0.6%                     | 2.9028  | $176\pm28$     | $178\pm32$       |  |
|                      |                           |                |                 |          | 0.5%                     | 2.9836  | $181\pm38$     |                  |  |
| 20EQ84               | Lava flow, pyramidal peak | 759883         | 9940775         | 0.972    | 0.6%                     | 1.7824  | $176\pm30$     | $175\pm30$       |  |
|                      |                           |                |                 |          | 0.6%                     | 1.7798  | $175\pm29$     |                  |  |
| 19EQ07               | Lava flow, S flank        | 759112         | 9938136         | 1.334    | 3.9%                     | 1.3350  | $96\pm3$       | $95 \pm 3$       |  |
|                      |                           |                |                 |          | 3.6%                     | 1.2996  | $93\pm3$       |                  |  |
| 19EQ11               | Lava flow, Cerro Bómboli  | 759847         | 9950892         | 1.323    | 0.9%                     | 1.2223  | $88\pm10$      | 91 ± 10          |  |
|                      |                           |                |                 |          | 1.0%                     | 1.3013  | $94\pm10$      |                  |  |
| 19EQ10               | Lava flow, S flank        | 759148         | 9940026         | 1.057    | 2.8%                     | 0.9700  | $88\pm3$       | $86 \pm 3$       |  |
|                      |                           |                |                 |          | 2.7%                     | 0.9196  | $83\pm3$       |                  |  |
| 19EQ13               | Lava flow, N flank        | 761280         | 9946424         | 1.279    | 1.1%                     | 1.0225  | $77\pm7$       | $75 \pm 7$       |  |
|                      |                           |                |                 |          | 1.1%                     | 0.9799  | $73\pm 6$      |                  |  |
| 19EQ05               | Lava flow, SW flank       | 756746         | 9939943         | 0.966    | 2.0%                     | 0.7031  | $70\pm4$       | $67 \pm 4$       |  |
|                      |                           |                |                 |          | 1.9%                     | 0.6539  | $65\pm4$       |                  |  |
|                      |                           |                |                 |          |                          |   |                |                  |  |
| Atacazo volcano      |                           |                |                 |          |                          |   |                |                  |  |
| 20EQ50               | Dacite block, S avalanche | 762881         | 9950592         | 1.279    | 2.5%                     | 1.9833  | $148\pm 6$     | $149 \pm 6$      |  |
|                      |                           |                |                 |          | 2.8%                     | 2.0019  | $150\pm 6$     |                  |  |

| Sample              | Location and Unit                  | UTM<br>Easting | UTM<br>Northing | K<br>(%) | <sup>40</sup> Ar*<br>(%) | <sup>40</sup> Ar*<br>(10 <sup>11</sup><br>at/g) | Age±1<br>σ(ka) | Mean age<br>(ka) |  |  |
|---------------------|------------------------------------|----------------|-----------------|----------|--------------------------|---|----------------|------------------|--|--|
| Pasochoa            | volcano                            |                |                 |          |                          |   |                |                  |  |  |
| 19EQ34              | Lava flow, N flank                 | 780987         | 9953901         | 0.856    | 12.0%                    | 4.1969  | $469\pm8$      | $472\pm8$        |  |  |
|                     |                                    |                |                 |          | 12.4%                    | 4.2349  | $474\pm8$      |                  |  |  |
| 19EQ33              | Lava flow, N flank                 | 781758         | 9952313         | 1.807    | 26.5%                    | 8.6492  | $458\pm7$      | $459\pm7$        |  |  |
|                     |                                    |                |                 |          | 28.9%                    | 8.6627  | $459\pm7$      |                  |  |  |
| 19EQ30              | Lava flow, E flank                 | 786494         | 9948763         | 1.080    | 11.5%                    | 5.1295  | $455\pm8$      | $450\pm7$        |  |  |
|                     |                                    |                |                 |          | 13.3%                    | 5.0254  | $446\pm7$      |                  |  |  |
| 19EQ32              | Lava flow, NW flank                | 783362         | 9951701         | 1.093    | 6.9%                     | 5.0002  | $438\pm9$      | $441\pm9$        |  |  |
|                     |                                    |                |                 |          | 7.1%                     | 5.0665  | $444\pm9$      |                  |  |  |
| 19EQ37              | Lava flow, S flank                 | 781599         | 9945191         | 1.086    | 5.2%                     | 4.7482  | $419\pm10$     | $423\pm10$       |  |  |
|                     |                                    |                |                 |          | 5.1%                     | 4.8376  | $427\pm10$     |                  |  |  |
| Rumiñahı            | Rumiñahui volcano                  |                |                 |          |                          |   |                |                  |  |  |
| 19EQ27 <sup>P</sup> | Lava flow, E flank                 | 779336         | 9933840         | 0.523    | 47.7%                    | 1.0812  | $198\pm8$      | $202 \pm 8$      |  |  |
|                     |                                    |                |                 |          | 43.4%                    | 1.1254  | $206\pm8$      |                  |  |  |
| Sincholag           | Sincholagua volcano                |                |                 |          |                          |   |                |                  |  |  |
| 19EQ41              | Lava now, summit area              | /90298         | 9939301         | 1./39    | 9.0%                     | 5.0975  | $314 \pm 0$    | $312\pm0$        |  |  |
|                     |                                    |                |                 |          | 9.2%                     | 5.6261  | $310\pm 6$     |                  |  |  |
|                     |                                    |                |                 |          |                          |   |                |                  |  |  |
| Согорахі            | Obsidian flow Morurco              |                |                 |          |                          |   |                |                  |  |  |
| 20EQ77 <sup>G</sup> | peak base                          | 783660         | 9920417         | 2.430    | 6.2%                     | 13.5144   | $532 \pm 11$   | 537 ± 11         |  |  |
|                     |                                    |                |                 |          | 6.4%                     | 13.7703   | $542\pm11$     |                  |  |  |
| 20EQ78              | Lava flow, Morurco peak            | 782119         | 9919377         | 1.743    | 13.0%                    | 6.1003  | $335\pm5$      | $334\pm5$        |  |  |
|                     |                                    |                |                 |          | 12.7%                    | 6.0550  | $333\pm5$      |                  |  |  |
| 20EQ88              | Lava flow, Tanipamba (Pita valley) | 786939         | 9949596         | 1.746    | 3.0%                     | 5.3977  | $296\pm11$     | 295 ± 10         |  |  |
|                     |                                    |                |                 |          | 3.9%                     | 5.3573  | $294\pm9$      |                  |  |  |

**Table 2.** Construction and erosion volumes calculated from numerical reconstructions. Results

| Volcano                         | Construction<br>Volume (km <sup>3</sup> ) | Uncertainty<br>percentage | Present-day<br>Volume<br>(km³) | Erosion<br>Volume<br>(km³) | Erosion<br>percentage | Reference  |
|---------------------------------|---|---------------------------|--------------------------------|----------------------------|-----------------------|--|
| Almas Santas                    | $90\pm14$                                 | 15%                       | $25\pm10$                      | $67\pm3$                   | 74%                   | This study   |
| Atacazo                         | $61\pm7$                                  | 12%                       | $25\pm 6$                      | $36\pm1$                   | 60%                   | This study   |
| Carcacha                        | $8\pm1$                                   | 12%                       | $5\pm1$                        | $3\pm0$                    | 41%                   | This study   |
| Corazón                         | $31\pm7$                                  | 21%                       | $9\pm7$                        | $22\pm0$                   | 71%                   | This study   |
| Pasochoa                        | $63\pm 6$                                 | 10%                       | $44\pm5$                       | $19\pm1$                   | 30%                   | This study   |
| Rumiñahui                       | $43\pm10$                                 | 24%                       | $22\pm10$                      | $21\pm1$                   | 49%                   | This study   |
| Santa Cruz                      | $21\pm3$                                  | 15%                       | ~16                            | ~5                         | 24%                   | This study   |
| Sincholagua                     | $42\pm7$                                  | 16%                       | $11\pm5$                       | $31\pm2$                   | 74%                   | This study   |
| Cotopaxi II                     | $32\pm3$                                  | 9%                        | $29\pm3$                       |                            |                       | This study   |
| Quilindaña                      | $25\pm3$                                  | 18%                       | $9\pm1$                        | $16\pm1$                   | 63%                   | This study   |
| North Iliniza                   | $28\pm9$                                  | 32%                       | ~22                            | $6\pm 2$                   | 21%                   | Santamaría et al. (2022)                           |
| South Iliniza                   | $18\pm 6$                                 | 33%                       | ~12                            | $6\pm 2$                   | 33%                   | Santamaría et al. (2022)                           |
| Iliniza (whole)                 | $46\pm15$                                 | 32%                       | $34\pm14$                      | $12\pm4$                   | 26%                   | Santamaría et al. (2022)                           |
| Cotopaxi I –<br>Barrancas stage | ~32                                       |                           |                                |                            |                       | Hall and Mothes (2008)                             |
| Cotopaxi I –<br>Morurco stage   | ~4  |                           |                                |                            |                       | Hall and Mothes (2008)                             |
| Cotopaxi II                     | ~51                                       |                           |                                |                            |                       | Hall and Mothes (2008)                             |
| Antisana<br>(whole)             | ~50                                       |                           |                                |                            |                       | Hall et al. (2017b)                                |
| Chalupas (bulk)                 | $230\pm30$                                | 8%                        |                                |                            |                       | Bablon et al. (2020b)                              |
| Chalupas (DRE)                  | ~100                                      |                           |                                |                            |                       | Hall and Mothes (2008)<br>Crosweller et al. (2012) |

1278 are given with a 1- $\sigma$  uncertainty (see text for details).

**Table 3.** Generalized chronostratigraphy of the central volcanic cluster of the Ecuadorian arc

1282 showing the main cone-building stages of its volcanoes

| Volcano                   | NW-SE<br>Aligment          | Location                                    | Cone-building stage   | Magma Composition   | Age (ka)                     | References  |         |  |
|---------------------------|----------------------------|---|---|---|------------------------------|---|---------|--|
| Ancient<br>volcanism      | All                        | North of lat.<br>0°20'S                     | E.g., Pichincha (El<br>Cinto), Chacana (old<br>lavas), Cayambe<br>(Viejo Cayambe) |   | >1 Ma                        | Samaniego et al., (2005);<br>Opdyke et al., (2006);<br>Robin et al., (2010);<br>Bablon et al. (2020a) |         |  |
| Almas Santas              | Volcanic                   | lat. 0°35'S                                 | Early stage (andesite lavas)  | 53-57 wt.% SiO <sub>2</sub><br>medium-K series                                | ~375 to ~365                 | Chemin, (2004); This<br>study   |         |  |
| Annas Santas              | Front                      | long. 78°51'W                               | Late stage and Cerro<br>Azul satelite lavas                                       | SiO <sub>2</sub><br>medium-K series   | < 365 ka                     | Chemin, (2004); This study  |         |  |
|                           |                            | lat. 0°19'S<br>long. 78°36'W                | La Carcacha edifice   | 60-61 wt.% SiO <sub>2</sub><br>medium-K series                                | ~1.3 Ma                      | Hidalgo, (2006)   |         |  |
| Atacazo-<br>Ninahuilca    | Volcanic<br>Front          | lat. 0°21'S<br>long. 78°37'W                | Atacazo edifice and satellite lava domes  | 57-63 and 66-67 wt.%<br>SiO <sub>2</sub><br>medium-K series                   | ~200 to ~71 ka               | Hidalgo, (2006); This study   |         |  |
|                           |                            | lat. 0°23'S<br>long. 78°39'W                | Ninahuilca dome<br>complex  | 61-66 wt.% SiO <sub>2</sub><br>medium-K series                                | <8 ka                        | Hidalgo, (2006)   |         |  |
| Corazón                   | Volcanic<br>Front          | lat. 0°32'S<br>long. 78°40'W                | Main Edifice  | 53-64 wt.% S1O <sub>2</sub><br>medium-K series                                | ~115 to ~70 ka               | Chiaradia et al., (2009);<br>This study   |         |  |
|                           |                            | lat. 0°37'S<br>long. 78°41'W<br>lat. 0°39'S | Pilonga lava dome   | 68-69 wt.% SiO <sub>2</sub><br>medium-K series<br>62-65 wt % SiO <sub>2</sub> | 353 ± 6 ka                   | Hidalgo et al., (2007);<br>Santamaría et al., (2022)<br>Hidalgo et al. (2007):                        |         |  |
| Iliniza                   | Volcanic<br>Front          | long. 78°43'W                               | North Iliniza edifice   | medium-K series   | ~125 to ~115 ka              | Santamaría et al., (2022)   |         |  |
|                           |                            | lat. 0°40'S<br>long. 78°43'W                | and late satellite<br>lavas   | SiO <sub>2</sub><br>medium-K series   | ~45 to ~6 ka                 | Hidalgo et al., (2007);<br>Santamaría et al., (2022)  |         |  |
| Pasochoa                  | Inter-<br>Andean<br>Valley | lat. 0°28'S<br>long. 78°29'W                | Main Edifice  | 55-61 wt.% SiO <sub>2</sub><br>medium-K series                                | ~470 to ~425 ka              | Schiano et al., (2010); This<br>study   |         |  |
| D                         | Inter-<br>Andean<br>Valley | lat. 0°35'S<br>long. 78°30'W                | Early stage   | 53-58 wt.% SiO <sub>2</sub><br>medium-K series                                | >300 ka                      | Starr, (1984); This study   |         |  |
| Kuminanui                 |                            |   | Late stage  | 61-63 wt.% SiO <sub>2</sub><br>high-K series                                  | ~210 ka                      | Starr, (1984); This study   |         |  |
| Santa Cruz                | Inter-<br>Andean<br>Valley | lat. 0°39'S<br>long. 78°38'W                | Main Edifice  | 56-66 wt.% SiO <sub>2</sub><br>medium-K series                                | ~700 ka                      | Santamaría et al., (2022)   |         |  |
|                           |                            |   | Loma Saquigua cone  | 58-64 wt.% SiO <sub>2</sub><br>medium-K series                                | ~80 to ~60 ka                | Santamaría et al., (2022)   |         |  |
| Sincholagua               | Main arc                   | lat. 0°32'S<br>long. 78°22'W                | Main Edifice  | 59-61 wt.% SiO <sub>2</sub><br>medium-K series                                | ~310 ka                      | This study  |         |  |
|                           | Main arc                   |   |   | lat. 0°43'S   | Barrancas stage              | 74-77 wt.% SiO <sub>2</sub><br>medium- to high-K series   | ~540 ka | Hall and Mothes, (2008);<br>Garrison et al., (2011);<br>This study |
| Cotopaxi                  |                            | long. 78°27'W<br>Iain arc                   | Morurco stage   | 57-63 wt.% SiO <sub>2</sub><br>medium-K series                                | ~335 to ~295 ka              | Hall and Mothes, (2008);<br>Garrison et al., (2011);<br>This study                                    |         |  |
|                           |                            | lat. 0°41'S<br>long. 78°26'W                | Cotopaxi II   | 56-66 and 70-76 wt.%<br>SiO <sub>2</sub><br>medium- to high-K series          | <13 ka                       | Hall and Mothes, (2008);<br>Garrison et al., (2011)   |         |  |
| Antisana                  | Main arc                   | arc lat. 0°29'S<br>long. 78°08'W            | Main Edifice  | 54-68 wt.% SiO <sub>2</sub><br>medium- to high-K series                       | ~400 to <0.8 ka              | Hall et al., (2017b)  |         |  |
|                           |                            |   | Cuyuja lava flow  | 55-58 wt.% SiO <sub>2</sub><br>high-K andesite series                         | $210\pm30\ ka$               | Hall et al., (2017b)  |         |  |
| Huañuna                   | Main arc                   | lat. 0°37'S<br>long. 78°14'W                | Lava dome   | Rhyolitic lavas<br>high-K series  | ${\sim}12$ and ${\sim}10$ ka | Mothes and Hall, (2008);<br>Hall et al., (2017b)  |         |  |
| Chaupiloma<br>(Rio Valle) | Main arc                   | lat. 0°40'S<br>long. 78°16'W                | Lava dome   | Rhyolitic lavas<br>high-K series  | ~15 to 6 ka                  | Mothes and Hall, (2008);<br>Hall et al., (2017b)  |         |  |
| Chalupas-<br>Quilindaña   | Main arc                   | lat. 0°48'S<br>long. 78°23'W                | Pre-caldera lavas   | 55-71 wt.% SiO <sub>2</sub><br>high-K series                                  | ~460 to ~420 ka              | Hammersley, (2003);<br>Córdova et al., (2020)   |         |  |

| lat. 0°47'S         Quilindaña         57-70 wt.% SiO <sub>2</sub> ~185 to ~45 ka         Hammersley, (2003);           long. 78°20'W         Quilindaña         57-70 wt.% SiO <sub>2</sub> ~185 to ~45 ka         Hammersley, (2003); | lat. 0°47'S<br>long. 78°20'W     | Caldera-forming ignimbrite eruption | 73-76 wt.% SiO <sub>2</sub><br>high-K series | $216\pm5\ ka$  | Hammersley, (2003);<br>Bablón et al., (2020b);<br>Córdova et al., (2020) |
|---|----------------------------------|-------------------------------------|--|----------------|--|
|   | <br>lat. 0°47'S<br>long. 78°20'W | Quilindaña                          | 57-70 wt.% SiO <sub>2</sub><br>high-K series | ~185 to ~45 ka | Hammersley, (2003);<br>Córdova et al., (2020)                            |