Eruptive dynamics inferred from textural analysis of ash time series: the 2015 reawakening of Cotopaxi volcano

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Abstract

Forecasting future activity and performing hazard assessments during the reactivation of large andesitic volcanoes remain a great challenge for the volcanological community. On August 14, 2015 Cotopaxi volcano erupted for the first time in 73 years after approximately four months of precursory activity, which included an increase in seismicity, gas emissions, and minor ground deformation. Here we discuss the use of near real-time petrological monitoring of ash samples as a complementary aid to geophysical monitoring, in order to infer eruption dynamics and evaluate possible future eruptive activity at Cotopaxi. Twenty ash samples were collected between August 14 and November 23, 2015 from a monitoring site on the west flank of the volcano. These samples

contain a range of grain types that we classified as: hydrothermal/altered grains, lithic fragments, potentially juvenile material, and free crystals. The relative proportions of these grains evolved as the eruption progressed, with increasing amounts of potentially juvenile material and a decrease in hydrothermally altered material. In the initial explosion, potentially juvenile grains are microlite-poor and contain hydrothermal minerals (opal and alunite) in contact with fresh glass. The incorporation of hydrous minerals that are unstable at high temperature in melt would have liberated H₂O from the hydrothermal system, providing energy to trigger phreatomagmatic eruptions at Cotopaxi; only the initial eruptions preserve textural evidence for this process. Subsequent eruptions were also phreatomagmatic; none of the subsequent eruptions produced high proportions of highly vesicular, microlite-free ash grains, as are typical of high decompression rate magmatic eruptions. The combination of increasing crystallinity and proportion of potentially juvenile grains, and high measured SO₂ flux indicate decreasing integrated magma ascent rates and clearing of the hydrothermal system along transport pathways in a system open to gas loss. The near real-time monitoring of ash samples combined with traditional geophysical monitoring techniques during the reawakening of Cotopaxi allowed us to gain a much clearer understanding of events than when using traditional geophysical monitoring alone.

Key Words

Volcanic Ash

Volcano Monitoring

Cotopaxi volcano

Eruption dynamics

Hazard assessment

1. Introduction

The reactivation of andesitic volcanoes is commonly initiated by weeks to months of precursory activity such as increased seismicity, deformation and increased SO₂ emissions (e.g., Sparks 2003). This precursory activity can include small explosions and the emission of ash (e.g., Cashman and Hoblitt 2004). These explosions are often interpreted as phreatic or phreatomagmatic, where heat from the rising magma interacts with water in the sub-surface such as in a shallow hydrothermal system or in pore space (MacDonald 1972 and Sheridan and Wohletz 1981). Our ability to monitor the geophysical and geochemical signals from volcanoes has greatly improved our ability to forecast and interpret present and impending eruptive activity. Based on monitoring data, including seismic, geodetic, and gas geochemical data, scientists use both empirical pattern recognition and deterministic and probabilistic models to forecast eruptions (Sparks 2003). These forecasts can also be improved by the interpretation of the nature of material ejected during early, small volume explosive eruptions (e.g., Cashman and Hoblitt 2004).

Petrologic monitoring includes the characterization of erupted ash particles, providing a complement to remote monitoring methods. By classifying particles into lithologic and textural categories, and tracking their variations through time, information can be learned about the nature of the explosions, their source depths, the timing of formation of pathway from the magma reservoir to the surface, and the ability for (or rate at which) magma ascends through that pathway (e.g., Ersoy et al., 2006; Miwa et al., 2013; Wright et al., 2012). Quantitative characterization of ash includes measurement of grain size, phase composition, ash grain morphology, particle crystallinity and vesicularity, and componentry of constituents (e.g., Cioni et al. 2014; Eychenne et al., 2012).

The recognition of juvenile magma in ash from early explosions can be difficult, especially where remobilized rocks from the volcanic edifice are similar in composition through time, or where juvenile fragments are highly crystalline. Conventionally, juvenile ash was distinguished based on highly vesicular and/or glassy texture (Watanabe et al. 1999) making it easy to recognize through petrological analysis. However, studies of the ash from the precursory explosions of Mount

St. Helens before the climactic eruption on the 18 May 1980 have shown that juvenile material can be masked by decompression and degassing-driven crystallization (Cashman and Hoblitt 2004). Ash from Mount St. Helens was only recognized as juvenile material after its texture was found to be similar to the cryptodome fragments ejected on the 18 May 1980 and during subsequent eruptions. Indeed, highly crystalline, microlite-rich ash fragments have been recognized as juvenile magma at many volcanoes around the world. For example, at Sakurajima volcano, the distinction between juvenile fragments is not made based on crystallinity, but is distinguished based on the surface texture and luster (Miwa et al. 2009). Additionally, crystal textures can be widely variable within a single eruption (e.g., 1999-2006 Tungurahua eruptions, Wright et al. 2012). The crystal textures of volcanic materials are controlled by their integrated histories of decompression, degassing, and cooling. At relatively high degrees of undercooling (due to relatively rapid cooling, decompression and/or H₂O-loss), crystal nucleation dominates over growth and the resultant crystals are numerous and small in size (e.g., Hammer and Rutherford 2002). Small crystals or microlites (those crystals <40 µm in size) therefore provide important information about magmatic processes just prior to or during eruption. Changes in crystal textures, thereby, indicate changes in magma ascent history which has a major control on the explosivity of the system (Woods and Koyaguchi 1994). For example, crystallinity was found to decrease with: 1) increasing magma supply rate and therefore eruption style at Etna, Tungurahua and Eyjafjallajökull volcanoes (Taddeucci et al. 2004; Wright et al. 2012 and Cioni et al. 2014), 2) decreasing repose interval (and thus possible shallow residence time) at Pinatubo volcano prior to its climactic eruption (Hammer et al. 1999), and 3) with increasing lava effusion rate at Unzen volcano (Nakada and Motomura 1999).

The reawakening of Cotopaxi Volcano provided an exceptional opportunity to study the temporal evolution of ash through the initial stages of renewed eruptive activity. The first ash samples were collected immediately after the first explosions and a high frequency sampling was realized through the three and a half months of eruptive activity. We use standard analysis and

characterization techniques to track changes in erupted material. Scanning electron microscope (SEM) analysis of both fresh and polished sections was combined with componentry analysis with a stereoscope to show the textural and compositional evolution of the ash. We use these data and textural observations to inform discussion regarding the eruption and potential fragmentation mechanisms, the shallow magmatic plumbing system, and the importance of continuously monitoring eruption products as a complementary aid to classical geophysical monitoring and eruption forecasting.

2. Cotopaxi volcano

Cotopaxi volcano is a 5987 m high ice-capped stratovolcano located in the eastern cordillera of the Ecuadorian Andes (Figure 1A). The volcano lies 50 km south of the capital city of Quito, Ecuador and has produced both andesitic and rhyolitic eruptive products over its ~560 kyr history (Hall and Mothes 2008). Andesitic volcanism has dominated the eruptive history of Cotopaxi over the past 4400 years, producing andesitic lava flows, lapilli and ash falls, pyroclastic flows, and triggering lahars with very long runout distances (e.g., Mothes and Vallance 2015). Cotopaxi has erupted several times within the historic record, producing Plinian eruptions and long-lived phases of variably explosive eruptive activity (Pistolesi et al. 2011). Based on historic accounts, several of these eruptive phases began with many months of precursory activity. However, unrest has not always led to eruption. In 2001-2, a period of seismic and geodetic unrest occurred at Cotopaxi, including an inferred intrusion of $20 \times 10^6 \text{ m}^3$ of magma (Molina et al., 2008; Hickey et al. 2015).

Cotopaxi's five eruptive cycles recorded during the historical period (since 1532) have been of andesitic composition with paroxysms ranging between VEI 3 to 4 (Pistolesi et al., 2011). The most intense periods were from 1532-1534, 1742-1744, 1766-1768, 1853-1854 and 1877. With the exception of the 1853 event, each of the other eruptive periods resulted in VEI=4 events, which

124 included regional ash and lapilli falls, pyroclastic flows and especially the generation of large
125 lahars. Typical tephra fallout volumes are 0.1 to 0.2 km³ (DRE) (Hall and Mothes, 2008). Based on
126 historical records and stratigraphy, eruptive activity at Cotopaxi follows repose periods that ranged
127 from 200 years to a mere 22 years. These eruptions commonly began with vent-clearing Vulcanian
128 style explosions in which abundant altered conduit-plugging rock were expelled. Subsequently,
129 after the initial conduit opening, sub-Plinian to Plinian style activity ensued, during which time
130 regional ash and lapilli falls were recorded, mostly directed to the W-NW of the cone and
131 depositing a mm-thick dusting of ash in Quito (Hall and Mothers, 2008). Before Cotopaxi's June
132 1877 eruption, the detonation sounds produced by ascending gas breaking through the conduit plug
133 were loud enough to have been heard in Pasto, Colombia and Guayaquil, Ecuador (both over 250
134 km away). These strong booms occurred a day before the onset of the main eruption (VEI=4) on 26
135 June 1877. Cotopaxi's historically erupted magmas generally are comprised of two pyroxene
136 andesites with 57-62% SiO₂, 1.2-1.7% K₂O, and a phenocryst assemblage that includes plagioclase,
137 hypersthene, augite, magnetite and olivine (Hall and Mothes, 2008).

138 Cotopaxi volcano is extremely well monitored by the Instituto Geofísico, who document
139 detailed temporal, observational and geophysical monitoring data at the volcano. The current period
140 of volcanic unrest began in April 2015. An increase in the number of seismic events per time and
141 size of seismic events (Figure 2) at the beginning of April, coupled with small but definite changes
142 in the deformation of the flanks of the volcano (tiltmeter data) signaled the start of this new eruptive
143 phase. In May, SO₂ flux from the summit crater began to increase as well, with values increasing
144 from background levels averaging around 28 tons/day to 3000 tons/day (Hidalgo et al. In Prep). On
145 June 4, seismic tremor appeared. Small fumarolic and water vapor plumes were visible beginning
146 June 10. Within vapor plumes, both BrO and HCl were detected and airborne Multi-GAS
147 measurements indicated that SO₂ formed >99% of total sulfur (H₂S +SO₂) (Hidalgo et al., In Prep).
148 Seismic activity generally decreased during the initial weeks of June and remained at a lower level

throughout July and the first 2 weeks of August. On August 14, a swarm of VT earthquakes preceded the first summit explosions by 12 hours. These initial explosions occurred at 04:02 and 04:07 (UTM-5) on 14 August, producing an ash and gas plume up to 8 km high. Relatively fine ash fell on local communities to the northwest of the volcano covering over 500 km² (Bernard et al., Submitted). On August 14, four subsequent ash emission events occurred, at 10:25, 13:45, 14:28 and 16:27. These emissions and coincident explosions coincided with the appearance of seismic tremor signals associated with gas and ash emissions and a 3 to 9-fold increase in the quantity of SO₂ release to between 12,000 and 24,000 tons/day over the following week (Hidalgo et al, In Prep). Almost four weeks of near continuous ash emissions occurred, producing ash continuously for between an hour and more than 24 hours at a time separated by hours of low level gas/ash emissions (Figure 1B). The amount of ash in the plume dramatically reduced during the week beginning September 11, 2015 which coincided with a decrease in the emission tremor signal and an increase in VT seismicity event rates to 220 events per day (Figure 2). SO₂ emission rates fluctuated significantly over this period, but remained relatively high, between 3000 and 10,000 t/d. Temperatures of up to 200 °C were measured with an IR camera on September 5. A third phase of lower intensity, intermittent ash emissions began on October 4, 2015 after a four week period of high VT seismicity rates. Intermittent, discrete explosions occurred over this period but were not associated with any significantly high volume ash emissions. A fourth phase of ash emissions occurred in November 2015, which produced a much smaller amount of ash. As of the start of 2016, surface activity was mostly limited to the emission of gas and water vapor, although VT seismicity rates remain high. The last ash emission was observed on January 24 but did not leave an observable ash deposit. The total volume of ash produced by this series of activity is 1.2x10⁹ kg (Bernard et al., Submitted).

3. Sample Collection and Methodology

The transport of ash in volcanic plumes is dependent upon atmospheric conditions, especially wind speed and direction. Atmospheric transport of ash introduces a sorting effect (e.g., through density differences) therefore, sampling of distal ash can introduce large errors into the analysis due to the removal of different components (e.g., Eychenne et al. 2013). To ensure accurate analysis of ash samples, it is important to choose a sampling site close enough to the volcano and within the main deposition axis to reduce any sorting effects. BNAS is a seismic station from the Instituto Geofísico located on the western flank of the volcano, approximately six kilometers from the summit (Figure 3A). Between August and December, 18.8 kg/m^2 of ash fell at BNAS station (Figure 3C). By comparison, the sampling sites BREF, located only 3km from the crater on the north flank, and San Elisa, located 11.5km from the crater in the southwest flank have accumulated 0.2 kg/m^2 and $< 0.1 \text{ kg/m}^2$ respectively (Figure 3C). The proximity of BNAS to the summit and its position directly under the main axis of the ash plume makes it an ideal sampling site to minimize the effects of density sorting in the plume. Four emission episodes were identified in the 2015 eruption sequence. These episodes show typical wax and wane behavior where it was possible to identify periods of high emissions followed by periods of low emissions (Figure 2). The phases are: August 14 to August 15, August 15 to October 2, October 2 to November 4 and November 4 to November 30 (Phase 1, Phase 2, Phase 3 and Phase 4 respectively). The distinction between Phase 1 and Phase 2 was made due to the change from explosive emissions during the first phase to passive emissions in the second phase. Samples of ash were collected every two to four days throughout the first four weeks of activity and covering all of Phase 1 and Phase 2 (14/08/2015 – 11/09/2015) from a solar panel at BNAS monitoring station, for a total of 12 samples (Table 1). During these initial two phases of ash emissions (14/8/2015 to 15/8/2015 and 15/8/2015 to 2/10/2015), when significant amounts of ash were falling during the sample collection, the sampling methodology included collection of an initial sample representing multiple days of ash fall and subsequent collection of a second smaller sample, usually representing one to two hours' worth of fresh ash fall while scientists remained onsite. On the 26th of August, an ashmeter (cf., Bernard 2013) was installed at

BNAS seismic station to more accurately collect and monitor the quantity of ash emitted (Figure 3B). During the latter portion of Phase 2 there was a four-week period of low ash emissions (02/09/2015 – 02/10/2015), a total of two samples were collected from the ashmeter. Ash collected with the ashmeters is representative of approximately 1 week of ash fall. During the third phase of emissions (2/10/2015 to 4/11/2015) four samples were collected from the ashmeter, two samples during the first two weeks of high ash emissions and two during the following two weeks of low emissions. During the fourth phase of ash emissions (4/11/2015 – 30/11/2015), two samples were collected from the ashmeter. In total, 20 samples were collected from eruptions from August 14 to November 23, 2015.

Once collected, the ash samples were first dried in an oven over night at 40 °C and then half the amount of each of the samples was sieved manually up to 63 µm (in half-phi) in order to determine grain size distribution and to compare components among a consistent size fraction. The nominally sub-63 µm fraction was analyzed by laser diffraction at the Ludwig-Maximilians-Universität (LMU) Munich, Germany. 2 – 3 aliquots of approx. 0.1 g were measured for each sample in a Coulter LS230 to ensure reproducibility. In samples where there was less than 5 grams of ash, the whole sample was sieved and then analyzed. The grains between 350 and 500 µm in size were selected for componentry analysis. These grains were washed in water and cleaned in an ultrasonic cleaning bath to remove the fine ash coating. The cleaned grains were then dried in the oven at 40 °C for an additional day. Grains were then examined under a stereoscopic microscope and classified into one of four different petrographic classifications, as described and characterized below. Ideally, a minimum of 300 grains were classified to ensure a representative sample of the ash however, smaller ash samples did not contain the minimum number of 300 grains of this size; error is therefore larger and the results were omitted from the componentry analysis (SEM analysis was still performed on these samples) (Table 1). For SEM imaging, a small portion of each sample was sieved to the >125 µm size fraction, cleaned in water in an ultrasonic cleaning bath, and dried

again. A selection of these grains was mounted on carbon tape and sputter coated with gold to image surface textures using the SEM in the Departamento de Metalurgia Extractiva (DMEX) in the Escuela Politecnica Nacional in Quito; other grains were mounted in epoxy mounts and polished in order to document the textures of vesicles and crystals within ash grains. Electron microprobe analyses were performed using the JEOL 8900 electron microprobe at the USGS, Menlo Park, California. A 15-keV, 8-nA electron beam with a 3 μ m spot size was used to analyze glass compositions; Na and Si were analyzed first to minimize the effects of Na-loss.

4. Ash componentry classification

We analyzed 13 samples of ash (Table 1) using a stereoscopic optical microscope. Seven other samples were also analyzed but either did not contain enough grains of the correct size after sieving (e.g., extremely fine-grained ash from the 02/09/2015) or there was not enough sample to begin with (Table 1). We first classified the ash grains into four groups based on grain composition and morphology: hydrothermal/altered grains, lithic fragments, potentially juvenile material, and free crystals. Hydrothermal grains were classified based on their color (including metallic color to sulfide minerals, white color characteristic of gypsum and quartz, and red color of oxidized glass), and/or the presence of mineral deposits on the surface of the grains or within the vesicles of scoriaceous grains. Lithics fragments were classified according to their dull, opaque but unaltered appearance. Potential juvenile fragments were classified according to their black or dark grey color but more importantly, their glossy appearance and sometimes semi-vesicular nature. Free crystals consist of individual phenocrysts (here, phenocrysts is used to distinguish crystals based on size alone) or fragments of crystals of different minerals containing less than 10% adhering groundmass material.

5. Textural characteristics

5.1 Surface textures and grain morphology

Hydrothermal/altered material

Surface textures of grains classified as hydrothermal material are characterized by surface alteration and oxidation, producing a red to rusty color and/or covered by secondary mineral precipitates white to metallic in color (Figure 4A, B and C). The grains have a wide range in particle morphology, including irregular angular to sub-angular shape and rounded varieties. Particles span a range of vesicularities. Vesicular scoriaceous particles commonly contain secondary precipitates on outer surfaces and within pore space (Figure 4B). Secondary precipitates include acicular gypsum needles (Figure 4D), abundant free or surface coating-sulfides (Figure 4A inset and C), and white or opaque hydrothermal quartz (vuggy quartz) (Figure 4C). Rounded aggregates of poorly consolidated grains can also be found.

Grey Lithics

Most commonly, the lithic fragments consist of grey to black andesitic rock fragments with dull, opaque, pitted surfaces (Figure 4D, E and F). These grains vary from blocky to very irregular in shape.

Potentially juvenile grains

Potentially juvenile grains are distinguished primarily based on their glossy surface texture and unaltered andesitic composition. These grains have been subdivided into two morphologic groups: blocky, and porous. The blocky grains have sub-planar faces and consist of dense, microlite rich clasts with large phenocrysts (Figure 4H and 5C) and sometimes contain large vesicles with thick interstitial groundmass septa (Figure 4G H). These dense grains often exhibited trans-granular and grain boundary micro-fractures with apertures of around 2 μm (Figure 5D). Blocky are usually light grey to black in color with a vitreous luster and contain variable amounts of microlites and fresh glass (Figure 4I). The porous grains consist of diktytaxitic lattices of microlite crystals with varying

amounts of interstitial glass and void space between crystal networks (Figure 4H and Figure 5A and B). The grains are highly porous, where pore space represents interstitial space between microlite crystals rather than individual pores surrounded by glass (Figure 5A and B). Energy dispersive spectroscopy (EDS) analysis of the crystals that formed these lattices show that the crystals are a mixture of pyroxene and plagioclase with a small proportion of Fe Ti oxides. The variation in groundmass glass contents is visible in SEM images of whole grains (Figure 4H), where microlite networks are present to varying degrees.

Free Crystals

Free crystals are generally large phenocrysts of plagioclase, with lesser amounts of pyroxene (Figure 4J, K and L). Crystals are generally intact and retain their crystal form. Fragments of free crystals are also present.

5.2 Microlite textures and glass compositions

Each particle type contains distinct textural and mineralogical associations between microlite and phenocryst phases, where crystal components common to most ash grains include a combination of plagioclase, pyroxene, and oxide phases, and sparse glass between microlites (crystals <40 µm in size). Hydrothermally altered and oxidized grains are the most petrologically diverse. Grains contain abundant opal, alunite, pyrite, and sparse cristobalite and primary magmatic phases that include plagioclase, pyroxene (clinopyroxene and orthopyroxene), and magnetite (Figure 6). In some cases, alunite fills pore space, in others it forms large portions of ash grains (Figure 6A) and pyrite coats grain surfaces (Figure 6B). In these sections, opal has replaced and pseudomorphs plagioclase (Figure 6C) and pyroxene. These grains contain completely or nearly completely devitrified, crystalline, or replaced groundmass (Figure 6C). Glass compositions were analyzed

from two ash grains in this category and contain 65.1 and 77 wt% SiO₂, with FeO and Na₂O contents distinct from analyses of glass in potentially juvenile grains (see below; Table 2).

Grey lithic fragments display a range of textures, but generally lack hydrothermal alteration phases. Many lithic grains contain abundant microlites with tabular pyroxene crystals most commonly measuring between 10 to 25 µm. Fresh glass is not visible between microlites in these grains.

Potentially juvenile grains contain the smallest microlite crystals and the greatest proportion of fresh glass. In the most crystalline clasts, pyroxene microlites are generally smaller than in clasts in the lithic category (Figure 6G), measuring between <1 and 20 µm, surrounding phenocrysts of plagioclase (Figure 6), but textures of the most crystalline grains in this class overlap with the finest microlite-rich lithic grains. Some grains further contain fresh glass interstitial between microlites; those microlites include plagioclase and pyroxene (Figure 6H), and also include opal (Figure 6I).

Glass compositions from five analyzed ash grains in this group have dacitic compositions (Table 2). The greatest abundance of glassy ash grains is contained in the earliest erupted sample, 15 August 2015. Glassy grains contain feldspar microlites surrounded by fresh glass, but also contain opalized feldspar that lacks reaction rims or alteration halos and can contain alunite domains. Glass is fresh, analytical totals range from 96.8-98.6 wt%; anhydrous glass compositions range from 63.4-66.4 wt% SiO₂ and 7.2-7.9 wt% FeO (Figure 7).

5.3 Grain size analysis

Globally, the ash emitted by Cotopaxi volcano is fine to extremely fine-grained with moderate to poor sorting, positive skewness and platikurtic to mesokurtic distribution. Most of the grain-size distributions are bimodal with a sharp coarse mode (0.0 to 3.7 Phi) and a flat fine mode (4.0 to 6.3 Phi) (Figure 8). It is interesting to note that the grain-size mean or median is mostly controlled by the proportion of coarse and fine mode rather than by their absolute value. The fraction of PM10

(breathable, range 2.5-20.1%) and PM2.5 (breathable and not settling, range 1.4-7.9%) is high, producing elevated air pollution in the affected area weeks after the heaviest ash falls. There is not a clear evolution through time, but the grain-size distribution is generally finer during the heaviest ash falls (14-15/08; 28/08-11/09; 13-20/10) whereas the finest ash deposits (21/08; 18-25/09; 23/11) have coarser distributions, potentially resulting from wind reworking of the fine-grained material.

6. Ash componentry

The componentry of ash samples from 2015 eruptions from Cotopaxi volcano shows a strong temporal evolution (Figure 9 and 10). Ash from the initial explosions on the 14th August produced samples dominated by lithic fragments and material from the hydrothermal system (27 and 47 % respectively; Figure 8). Free crystals and possible juvenile fragments make up only a relatively small percentage of that sample (26 % combined). In the following four days of the eruption the percentage of potential juvenile grains began to increase up to 60%, whereas the percentage of hydrothermal material and lithic grains significantly decreased (to 17 and 19%, respectively) (Figure 9). The relative abundance of hydrothermal material continued to decrease to below 16% where it remained throughout the rest of the eruption period, whereas the percentage of potentially juvenile material continued to increase (Figure 10) with some small fluctuations. The third phase of emissions began in the week of the October 4. Samples from the third phase of emissions contained predominantly potentially juvenile material at between 66 and 68 %, whereas the free crystal content remained below 6%, hydrothermal below 15% and lithics below 24%. This trend continued throughout the rest of the eruptive events, where the potentially juvenile content consistently stayed above 65%. The lithic content, hydrothermal material and free crystals remained relatively constant throughout emissions through the end of November 2015.

7. Discussion

7.1 Origin of the ash

The renewed eruption of Cotopaxi provided a unique opportunity to study the temporal evolution of ash through the reawakening of a large stratovolcano after a long period of quiescence. Samples of ash from the first week of the eruption were rich in lithics, hydrothermally or fumarolically altered grains and oxidized lithic material (Figure 4C and Figure 10A) (cf. red, altered components were classified ‘oxidized lithics’ by Pistolesi et al. 2011 in their analysis of Cotopaxi eruptive products over the past 800 years). These samples are representative of material that filled the conduit that was cleared out in the “vent clearing” phase (Figure 10A). Textural heterogeneity to conduit-lining material is expected based on the wide range in eruptive products that form any volcanic edifice. A variation in internal crystal textures to andesitic material belies a range of decompression and ascent histories forming eruptions of differing style and volume through time (e.g., Mothes and Hall 2008). During this initial eruption, the abundance of potentially juvenile material is low, however, the abundance of glass within this material is higher than in other ash samples. High analytical totals to electron microprobe analyses of glass are consistent with lack of alteration. Furthermore, glass compositions are consistent with that expected at Cotopaxi. Figure 7 shows glass compositions from a variety of previous tephra units from Cotopaxi; glass compositions of ash grains in this study have compositions overlapping with previous eruptive units. In contrast, glass compositions from hydrothermally altered components have distinct compositions (Figure 7). The most compositionally similar tephra unit of Pistolesi et al. (2011) is that erupted in small volume explosions that occurred post-1880. The presence of this unaltered glass with compositions not unexpected for Cotopaxi suggest that these grains are fresh, juvenile magma. Furthermore, the presence of fresh, juvenile magma that contains hydrothermal minerals fully coated in fresh melt preserves evidence for magma-hydrothermal system interaction, a potential cause for ensuing phreatomagmatic eruption.

After the first two weeks which saw the highest ash emission rates (Bernard et al. Submitted), a decrease in the relative proportion of hydrothermally-altered and oxidized fragments is interpreted to represent clearing of an eruptive pathway through the hydrothermal system and altered edifice gas escape network. Over the same interval, the proportion of microlite-rich, blocky fragments in the potentially juvenile component increased. The origin of these fragments includes two possibilities: (A) that the fragments represent unaltered past eruptive products from Cotopaxi, excavated from portions of the edifice that did not experience hydrothermal alteration, vapor-phase alteration from the extensive degassing prior to August 14, or oxidation; or (B) that the fragments represent juvenile magma that degassed and crystallized in response to slow ascent or shallow residence and shallow degassing prior to eruption. Distinction between the possibilities requires a holistic view of the system and comparison with past eruptive products from Cotopaxi.

Several different monitoring parameters support an interpretation of shallow magma intrusion and degassing at Cotopaxi in 2015. Magmatic degassing at Cotopaxi has been close to the detection limit for DOAS techniques over the past several years; background rates of SO₂ emission measure on average 28 tons/day since permanent DOAS instruments were installed in 2008. SO₂ emission increased in May, remaining high through eruptive/explosive events in August – November. Furthermore, chemical indicators of magmatic degassing were detected by August, where the presence of BrO was clearly detected in the plume after August 14 (Dinger et al., 2016), indicating magmatic degassing through a dry pathway (cf., Bobrowski et al., 2003). Moreover, measurements of high SO₂/H₂S ratios support interpretation of magmatic degassing rather than of a hydrothermal origin. Additionally, no broad deformation was detected via InSAR techniques, however minor deformation (≤ 1.5 cm) was detected with the GPS and tiltmeter network, consistent with possible minor inflation of the edifice. An observed orange glow within the crater for several days since October 02 also requires elevated (magmatic) temperatures to some phase at the surface. Finally, seismic patterns are consistent with shallow magma residence, including abundant low

frequency seismicity and coincident VT seismicity (Figure 2). LP and VT seismicity during this period were substantially elevated above previous levels of monitored unrest at Cotopaxi that were themselves interpreted to result from the intrusion and interaction of shallow hot material (e.g., magma) with water (e.g., in the hydrothermal system; Ruiz et al. 1998).

The circumstantial evidence for shallow magma ascent (to less than approx. 3 km) by August 2015 is abundant. This evidence combined with the appearance of fresh glass that contains few microlites in the earliest erupted ash and the more microlite-rich material erupted later in the sequence suggests the simplest explanation for compositional changes in ash produced from eruptions starting on 14 August 2015, is the ejection of juvenile magma. As inferred based on microlite textures, this magma ascended relatively rapidly before the first eruption, allowing excavation and incorporation of parts of the hydrothermal system, but prohibiting extensive microlite crystallization. This magma then continued to degas and crystallize as it formed a series of shallow conduit plugs that were erupted in the smaller volume eruptions through November 23. Fluctuations in the relative abundance of lithics and hydrothermal material after a magma-filled pathway reached the surface can be explained by variations in total eruptive volume during any single eruption. For small volume eruptions, the overprint of recycled material from previous eruptions is also likely (Taddeucci et al. 2002; Wright et al. 2012). The small amount of potentially juvenile material in the samples from 14 August explosions presents the strong possibility that new magma was involved and represents the trigger mechanism for the first explosions. The increasing percentage of potentially juvenile magma fragments in the ash as the eruption progressed and the decreasing content of “old” material is partly a function of erupted volume. This suggests a progressive increase in the relative involvement of the magmatic system, but a potential decrease in the integrated ascent rate that this magma experienced. This observation is coherent with the decrease of the seismic tremor associated to the ash emissions during the third and fourth phases (Bernard et al. Submitted) and allows a process explanation for it.

7.2 Ascent conditions

Changes in the crystallinity of the potentially juvenile material results from changing ascent and decompression conditions within the conduit (e.g., Hammer et al., 1999). By comparison with experiments and with ash studies of historic eruptions elsewhere, the presence of glassy ash grains, with low micro-crystallinities suggests relatively rapid ascent of juvenile magma, as was observed most abundantly (but still a minor portion of the eruptive material, Figure 6I, Figure 7) in the August 15 sample. As the eruption sequence continued, these potentially juvenile grains transitioned to higher micro-crystallinity material (Figure 6G and H). The presence of high micro-crystallinity eruptive products is likely the result of slow ascent and/or long residence times at shallow levels, as would be expected in a dome or a shallow conduit plug (e.g., Nakada and Motomura 1999; Hammer et al. 1999; Hammer and Rutherford 2002; Cashman and Hoblitt 2004). For example, coarsely vesicular clasts from 2010 Eyjafjallajökull eruptions reached 55% micro-crystallinity; blast deposits from Mount St. Helens in 1980 reached 62%; and eruptive products from Colima 1913 and May 2005 eruptions reached ~80% and ~90% micro-crystallinities, respectively (Savov et al. 2008). The increase in crystallinity of the juvenile fragments over the first week of the eruption alludes to a progressive rheological stiffening of the magma which would lead to increasingly lower ascent rates (e.g., Sparks et al 1997 and Cordonnier et al. 2012). Shallow, microlite-rich magma forms a plug in the shallow conduit that is repeatedly fragmented. Repetitive formation and destruction of a shallow magmatic plug in a system that has contained an extensive hydrothermal system, as at Cotopaxi, is also consistent with the ongoing shallow seismicity, including explosion-type signals that persist to the time of this writing even when no surface expression is seen.

After the first week of ash emissions, grains with a diktytaxitic textures (Figure 4A and B) and varying amounts of residual glass appeared and began to increase in abundance. Diktytaxitic textures in andesite magmas are commonly formed by two processes: filter-pressing and gas driven

filter-pressing (e.g., Sisson and Bacon 1999; Pistone et al., 2015). Filter-pressing is a process whereby a mass of crystals compacts under its own weight, expelling the melt phase. Whereas, gas filter-pressing results from the migration of the melt phase from regions of high pressure to regions of low gas pressure along a gas-pressure gradient. Gas-pressure gradients form as a result of varying degrees of crystallization (e.g., Sparks 1997). Regions of melt in between crystals are driven out through flow down the pressure gradient from regions of high to low pressure (Sisson and Bacon 1999), leaving behind a crystal lattice with void space where there was once melt. This process has occurred to varying degrees within the conduit of Cotopaxi, resulting in grains with varying amounts of residual glass/melt coating the lattices of microlite crystals. Here both processes are possible however, high measured SO₂ fluxes suggest that at least transiently high gas pressures are present in the conduit, we therefore suggest that gas filter-pressing is the most likely process. Although diktytaxitic textures to microlite-rich, potentially juvenile grains imply the presence of transient high gas over-pressures within the shallow conduit, the creation of porosity as interstitial space between crystals has been shown to maintain if not increase permeability in the magma, allowing the escape of gas from the shallow environment (Kushnir et al., 2016). High SO₂ fluxes recorded by the surface gas monitoring system support this hypothesis. Coupled with other observations such as the abundance of dense, microlite-rich, micro-fractured ash grains and high measured SO₂ emissions, this suggests integrated slow magma ascent rates and residence times sufficient to allow degassing, crystallization of the magma.

7.3 Fragmentation mechanisms and eruption dynamics

The fragmentation mechanisms for dense, microlite-rich pyroclasts emitted during continuous ash emissions has been somewhat enigmatic. The initial explosions and emission phase over the first two days are interpreted as phreatomagmatic due to the high lithic content, the presence of hydrothermally altered material (including hydrous opal and alunite) encased in fresh melt (Figure

6I); the fine grain size distribution of erupted ash; and the relatively low juvenile component of ash samples (Figure 8). For these explosions, the interaction of magma with fluids in the hydrothermal system and fluids liberated by heating of hydrous minerals in hydrothermally altered rocks may have triggered magma fragmentation and explosion. In contrast, the second, third and fourth eruptive phases were semi-continuous, low-energy ash venting and lacked thermal plumes (max. recorded temperature of 200 °C). Heat from rising magma in the conduit will likely have dried out the environment and remove external water sources required for phreatic or phreatomagmatic fragmentation. Likewise, the absence of highly vesiculated pumice or scoria in the ash samples indicates that fragmentation was not the result of bubble wall breakage as expected for the rapid decompression of gas-rich magma (e.g., Alidibirov and Dingwell 1996 and Gardner et al. 1996). Furthermore, magma interactions with water derived from the large summit glacier are more likely to cause discrete explosions or ash emissions than continuous ash emissions. Due to the increase in amount of highly microcrystalline juvenile material, we believe that the fragmentation involves an interplay between gas pressure and magma strength (Ono et al. 1995; Taddeucci et al. 2002). Microfractures that were identified in the ash grains most likely formed due to the anisotropic contraction of minerals during cooling (Fredrich and Wong 1986), which can significantly reduce the rock strength. High gas over-pressures can exceed the tensile strength of the rock, forcing fractures apart, causing the magma to shatter in a brittle fashion (Ono et al 1995; Taddeucci et al 2002; Spieler et al., 2004). The fragments of ash are then passively carried out of the vent by the emission of gases. This mode of fragmentation has been shown to generate blocky grains with planar edges representative of the plug/cap rock (Miwa et al., 2013; Taddeucci et al., 2002), as seen in Cotopaxi ash samples. Fine grain size distributions to ash samples suggest that the fragmentation mechanism was very efficient and its constancy may reflect self-similar fragmentation mechanisms throughout the ensuing period of continuous ash emissions. Therefore the decrease of seismic tremor associated to the ash emission during the third and fourth phases (Bernard et al. Submitted) is probably due to

a cleaner path between the fragmentation source and the surface rather than a change in the eruptive dynamics. This is supported by the deep clean vertical crater observed since September 29.

7.4 Eruption scenarios and hazard assessment and future activity

Completely aphyric, glassy fragments are absent, indicating that no single eruption has tapped all the way down to the gas rich magma source region, as has happened in Cotopaxi's past. Large volume past eruptions produced pyroclasts with glassy textures, as are common in the eruptive products from the VEI=4 eruption of 1877 (reference Pistolesi pers. comm). The presence of ash grains that we now recognize as juvenile, with low micro-crystallinities of very finely micro-crystalline textures suggests that there is at least a semi-open pathway existed from the magma source to the surface. Pre-eruptive gas emissions indicate that magma was able to freely and effectively degas under "open-system" conditions, reducing the potential for a buildup of large, hazardous gas-overpressures (Woods and Koyaguchi, 1994). Instead, the juxtaposition of glassy groundmass with few growth microlites and hydrothermal minerals/fragments may indicate that initial eruptions were triggered by the interaction of magma with the hydrothermal system. Furthermore, gas emissions have continued, suggesting that significant gas overpressures are not accumulating in the conduit, potentially decreasing the *short term* likelihood for a large explosive event (e.g., Eichelberger et al., 1986; Woods and Koyaguchi, 1994; Jaupart 1998). However, an open pathway to the surface may also allow a new batch of magma to ascend easily in the future (e.g., Scandone et al. 2007) and equally, the dynamics of the magmatic system can rapidly change with little warning, resulting in a sudden large explosive eruption as happened at Reventador volcano in 2002 (e.g., Hall et al. 2004 and Samaniego et al., 2008). It is also feasible that not all the intruded magma was expelled during the emission phases and that the semi-open conduit that existed during the ash emission phases now contains a highly crystalline plug of degassed magma. Any future eruptive activity would require a vent-clearing phase to allow the ascent or eruption of a new magmatic pulse. However, only through continued monitoring of the volcano (e.g.,

deformation, seismicity and gas) can we detect changes in the magmatic system that would change potential forecasts for future activity.

8. Ash analysis for volcanic monitoring at Cotopaxi

The near real-time analysis of ash samples from precursory explosive activity at Cotopaxi volcano during the months of August, September, October and November 2015 was used as a complementary aid to assist with the interpretation of the geophysical monitoring signals. Compositional and textural analysis provided invaluable information about the degree of involvement and the ascent conditions of the newly intruded magma body. Ash analysis in itself cannot and should not be used to inform forecasts about future activity, but can provide perspective about the ascent conditions and dynamics of erupted material. Accurate knowledge of past eruptions helps to constrain possible future eruption scenarios, especially for well-preserved large eruptions. At Cotopaxi in 2015, petrologic monitoring of ash grains was used to complement geophysical monitoring techniques. Based on these studies we conclude that there was new magma involved in ash emissions but that the ascent rate was slow and the system was open to continued gas outgassing and escape, which lowered the *short term* probability of a large explosive eruption. While ash analysis can help provide crucial information regarding the eruptive dynamics, real time ash analysis also allows ash inhalation hazard assessment. Certain types of ash are extremely hazardous to people's health. For example, eruptive episodes that emit a high proportion of respirable ash, with elevated crystalline silica content or angular glass fragments can cause significant respiratory health problems (Horwell and Baxter 2006). Quick identification of the emission of ash can allow authorities and the population to respond quickly and take action to alleviate the effects of such ashes.

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Figure Captions

Figure 1. Location map of Cotopaxi volcano and photo taken on 03/09/2015 during an overflight mission by the Instituto Geofísico to measure thermal anomalies and perform Multi-gas measurements.

Figure 2. Time line of events. Daily LP and VT seismicity event rates recorded by the seismic monitoring network of the Instituto Geofísico on Cotopaxi. Grey shaded areas show the 4 phases of ash emissions after the initial explosion on the morning of August 14 (the dark grey represents the period of high emissions and the light grey the period of low emissions within the phase) and the yellow arrow indicates the maximum SO₂ emission during this period of unrest. Red dashed lines indicate important changes in geophysical monitoring parameters and are indicated in the text. The green stars denote the sample collection dates.

Figure 3. (A) Location map of Cotopaxi with the seismic and ashmeter networks. BNAS (west), BREF (north) and San Elisa (south) are labeled on the image. The dashed line represents the extent of Cotopaxi Volcano. (B) Photograph of the ashmeter at BNAS taken on 26/08/15 after its

installation. (C) Cumulative ash fall collected at each sample site between August 14 and the end of November 2015.

Figure 4. SEM backscatter photomicrographs and stereoscope images of the different classified components of the Cotopaxi ash samples: Hydrothermal material (A, B and C), lithics (D, E and F), potentially juvenile (G, H and I) and free crystals (J, K and L). Altered surfaces (A), pyrite crystals (A inset top and C), cubic quartz (A inset bottom) and infilled vesicles (B) are apparent in the majority of grains along with red and orange oxidation of the grains (C). Pitted and worn surface of lithic fragments are apparent (D) as are fresh fractures in highly microcrystalline grains (G) and residual glass between microlite grains of the juvenile grains (H) with black vitreous fresh surfaces (I). Free crystals retain their euhedral shapes (J and K).

Figure 5. SEM backscatter photomicrographs of ash grains of important ash textures. (A and B) Ash grains showing diktytaxitic textures (disorganized lattices of plagioclase, pyroxene and Fe-Ti oxide crystals with varying amounts of interstitial glass). (C) Blocky planar-edged grain containing a large plagioclase phenocryst surrounded by microlite. (D) Dense microlite-rich grain containing a thermal fracture.

Figure 6. Backscattered electron images of (A-C) hydrothermally altered grains. (A) Alunite (dark gray) covers the bottom half of this grain, opal has replaced plagioclase microlites; (B) pyrite crystals (white) coat the surface of this grain that surrounds opal (dark gray), plagioclase (light gray) and crystalline groundmass; (C) opal replaced plagioclase microlites (see original plagioclase core at image bottom); (D-F) lithic grains: note the abundance of microlites in the groundmass and the lack of visible fresh glass (E) mafic microlites are concentrated along plagioclase crystal margins; (G-I) potentially juvenile grains including: (G) highly microcrystalline grain containing fresh glass interstitial between tabular microlites <30 μm in length; (H) moderately microcrystalline grain containing plagioclase and orthopyroxene in a glassy groundmass; (I) low micro-crystallinity

ash grain containing opal xenocrysts (dark gray), and pyroxene and plagioclase microlites (white and light gray).

Figure 7. Glass compositions of potentially juvenile grains and hydrothermally altered grains in 2015 ash samples superimposed on glass compositions of Holocene pyroclasts from Cotopaxi of Pistolesi et al. (2011).

Figure 8. Grain-size distribution of five ash samples from the Cotopaxi eruption (in half-Phi interval). Note that most samples show bimodal distribution with a sharp coarse mode ($\sim 3 \Phi$) and a flat fine mode. Distributions are positively skewed and platikurtic to mesokurtic.

Figure 9. Ash componentry histogram. Percentage of hydrothermal, lithics, free crystal and potentially juvenile grains in 13 samples of ash. 7 other samples were analyzed but there was not a sufficient number of grains for representative analysis and so these results have been omitted.

Figure 10. Time series of SEM backscatter photomicrographs of ash samples from (A) 15/08/2015, (B) 19/08/2015, (C) 31/08/2015, (D) 08/09/2015, (E) 25/09/2015, (F) 20/10/2015 and (G) 23/11/2015. The sequence of photomicrographs shows the evolution of the ash grains throughout the eruptive sequence.

Table 1. Ash sample details. The date corresponds to the date the sample was collected (except where indicated with a * where a fresh sample was collected while scientists were on site). The sample weight refers to the amount of ash collected (from the solar panel, the ashmeter or a combination of both). ** Incomplete grain-size data with minimum analyzed grain size bin of 63 μm .

Table 2 Anydrous glass compositions of erupted ash grains from Cotopaxi, 2015.

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Representative Juvenile ash grains from 15 August 2015 sample:

Representative Juvenile ash grains from post-15 August 2015 samples:

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Sampling Data							Component classification				
Emission Phase Number	Sample Number	Sample Date	Sampling condition	Ash load (g/m ²)	Mean Grain Size Mz (Phi)	Sorting Sigm a-I (Phi)	Hydrothermal (%)	Lithics (%)	Free Crystals (%)	Juvenile (%)	Glassy with hydrothermal (%)
Phase 1	NASA -1	15/08/15	Solar panel	176	4.62	1.99	47	27	2	24	4
Phase 2 High emissions	NASA -2	19/08/15*	Solar panel	87	5.32	1.82	39	17	18	26	3
	NASA -3	21/08/15	Solar panel	205	2.95	1.89	30	21	18	31	4
	NASA -4	24/08/15	Solar panel	1710	-	-	17	19	4	60	0
	NASA -5	26/08/15*	Solar panel	3255	-	-	11	12	4	73	0
	NASA -6	28/08/15	Ashmeter	2110	3.98	1.92	16	23	3	57	0
	NASA -7	30/08/15	Solar panel	238	-	-	10	14	3	72	0
	NASA -8	31/08/15	Solar panel	564	4.73	2.05	17	15	3	65	0
	NASA -9	02/09/15	Solar panel	1129	4.82	2.10	-	-	-	-	0
	NASA -10	04/09/15	Solar panel	71	4.37	1.97	-	-	-	-	0
	NASA -11	08/09/15	Solar panel	627	4.58	2.00	12	23	3	62	0
	NASA -12	11/09/15	Ashmeter	1838	4.57	2.09	4	10	2	84	0
	NASA -13	18/09/15	Ashmeter	229	2.90	0.98	-	-	-	-	0
Phase 2 Low emissions	NASA -14	25/09/15	Ashmeter	351	3.63	1.47	-	-	-	-	0
Phase 3 High emissions	NASA -15	13/10/15	Ashmeter	807	4.13	1.94	11	15	6	68	0
	NASA -16	20/10/15	Ashmeter	3497	4.70	2.18	8	21	5	66	0
Phase 3 Low emissions	NASA -17	27/10/15	Ashmeter	121	-	-	-	-	-	-	0
	NASA -18	04/11/15	Ashmeter	31	-	-	-	-	-	-	0
Phase 4	NASA -19	16/11/15	Ashmeter	94	-	-	-	-	-	-	0
	NASA -20	23/11/15	Ashmeter	202	3.15	1.26	15	15	4	66	0

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Sample Details		Glass Chemistry (wt.%)											
Sample Date and Grain designation	# of analyses	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	P ₂ O ₅	Unnormalized total
Juvenile													
15August 2015 B1	9	63.6	1.3	14.3	7.4	0.2	1.6	4.3	3.2	3.5	0.09	0.6	98.65
15August 2015 B3	5	66.4	1.2	13.5	7.6	0.1	1.1	2.5	3.9	3.0	0.08	0.6	96.82
15August 2015 XL	3	63.4	1.3	14.1	7.9	0.1	1.6	4.3	3.5	3.1	0.16	0.6	97.00
15August 2015 BW2	9	64.2	1.3	14.5	6.7	0.0	1.9	4.4	3.8	2.6			97.52
15August 2015 BW3	6	64.2	1.2	14.3	7.2	0.2	1.9	4.9	3.3	2.1	0.04	0.6	96.88
15August 2015 BW4	9	64.7	1.2	14.5	7.6	0.1	1.6	4.0	3.3	2.3	0.10	0.6	97.12
15August 2015 BW6	10	65.8	1.3	13.7	6.2	0.0	1.6	3.5	2.5	4.9			97.70
Hydrothermal													
15August 2015 W1	3	77.0	1.0	13.7	3.4	0.0	0.1	0.6	0.4	3.5	0.2	0.2	93.48
15August 2015 P2	5	65.1	0.0	23.9	0.9	0.0	0.0	6.4	6.9	0.9			97.70

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