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Are the ashes from the latest eruptions (2010–2016) at Turrialba volcano (Costa Rica) related to phreatic or phreatomagmatic events?

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ABSTRACT

The initial eruptive episodes of explosive eruptions are classified as phreatic if the amount of juvenile material (scoria, glass, pumice) is null, and the amount of fresh accidental lithics, and hydrothermally altered lithics, is substantial. Phreatic eruptions have been in some cases recognized as precursory events preceding phreatomagmatic and magmatic eruptive phases. Usually, the lithological features of tephra deposits are investigated and sampled in the field. Investigation of ash samples under binocular microscope or by Back-Scattered Electron (BSE) microscope images of polished sections is usually considered sufficient to typify the fragmentation mechanism of the eruption. The opening eruptive phases at Turrialba volcano, together with the formation of new intracraters (i.e. 2010, 2012, 2014) and the enlargement of the Western Crater (29 October 2014 to present), were classified, in previous papers and internal reports as phreatic. We studied a series of ash samples erupted from 2010 to 2016, with the aim of understanding the fragmentation processes characterizing the vent opening phases. We used SEM + EDS analyses, in addition to field and microscopic investigation. Results showed a composition of accidental lithics of fresh to hydrothermally altered clasts and secondary minerals (82–98%), besides juvenile andesite fragments (2–18%), which leads us to revisit the classification of the initial eruptive phases of Turrialba as phreatomagmatic. Our method allowed the detection of a juvenile component directly involved in an effective magma-water interaction, which was possible only by a scrutinous examination of the glass surface textures by SEM in the range size between 3 and 3.5 phi. We recommend such a type of investigation when the identification of fresh magma in a new eruption is crucial for the preparedness and hazard evaluation at active volcanoes.

1. Introduction

In volcanoes that have been dormant for years or centuries, when dikes intruded at shallow levels of the volcanic edifice may encounter water-saturated rocks (aquifers/hydrothermal systems) near the surface, causing localized steam and phreatic explosions that form pathways for the eventual eruption of magma (Ollier, 1974; Barberi et al., 1992; Browne and Lawless, 2001; Francis and Oppenheimer, 2004). A study conducted at the beginning of the nineties in the last century, showed up that of the 132 reported phreatic eruptions, most (87%) were followed by magmatic or phreatomagmatic activity and only a few (13.6%) were preceded by premonitory signs (Barberi et al., 1992). Recent examples of phreatic eruptions that were followed by magma extrusion in the form of tephra or lava flow/dome, are Kirishima, Japan, 2011 (Suzuki et al., 2013) and Ubinas, Peru, 2013–2015 (Mariño et al., 2015; Del Carpio et al., 2015). Examples of recent phreatic eruptions that were not followed by magma extrusion include the 2012 eruption of Mt. Tongariro, New Zealand (Pardo et al., 2014) and the fatal 2014 eruption of Mt. Ontake, Japan (Sano et al., 2015). Thus, phreatic eruptions may or may not precede magmatic eruptions. About 5% of the eruptions listed in the Global Volcanism Database since 1900 are considered as phreatic in nature (Global Volcanism Program, 2013; de Moor et al., 2016a).

Phreatic deposits are often recognized on the basis of their macroscopic features in the field (brown, orange, whitish ash to block deposits), in particular, the lack of evidence for juvenile clasts is considered as a diagnostic feature, and generally no further detailed analysis is judged as necessary in order to better characterize the eruption mechanism. At most, morphological studies of pyroclasts are made in the laboratory under the binocular microscope and by means of Backscattered electron (BSE) image of thin sections (Suzuki et al., 2013; ERI, 2014; Sano et al., 2015). In fact, in several cases around the World, the initial events of stratovolcanoes are classified as phreatic

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eruptions simply judging from the appearance small (≤10%) amount of fresh material (scoria, glass, pumice), and the huge amount of hydrothermally altered lithics, compared to the substantial amount of juvenile large clasts that are found in the following magmatic (scoria deposits, bombs) or phreatomagmatic (i.e., breadcrusted blocks) stages. However, the detection of even a trivial amount of juvenile material at the onset of an eruption is crucial in order to understand if magma is rising to shallow depth and has a potential for further, larger, explosive eruptions, as pointed out by Cashman and Hoblitt (2004) and Pardo et al. (2014). The identification of a small quantity (1–10%) of juvenile component is particularly complex when it is dispersed within hydrothermally altered lithics and fine ash. It is usually not trivial to discern if this component corresponds to juvenile fragments or to previous volcanic components and/or unaltered accidental lithics recycled in the conduit system by reworking (Mastin, 1991; Cashman and Hoblitt, 2004; Suzuki et al., 2013; Pardo et al., 2014).

At Turrialba volcano, the vent opening phases and the successive cleaning phases were previously interpreted as phreatic eruptions (Reagan et al., 2011; Soto and Mora, 2013; Duarte, 2014; González et al., 2015; Lücke and Calderón, 2016; among internal reports of the local volcanological observatories). Thus, it was not clear whether the volcanic activity from 2010 to 2016 was purely phreatic and therefore not related to the intrusion of new magma (e.g., Martini et al., 2010), or related to the intrusion of a small volume of magma disrupting the pre-existing hydrothermal system (e.g., Campion et al., 2012). Both models had diametrically opposite implications with regards to the volcanic danger, with the second suggesting a more immediate volcanic hazard (Vaselli et al., 2010; Soto and Mora, 2013).

Therefore, the main goal of the present paper is to characterize the fragmentation process that triggered the Turrialba activity, and in addition to field and microscopic investigation, we emphasize the importance of micro-analytical techniques in the characterization of clast morphology in discriminating the different components of tephra deposit, using scanning electron microscope (SEM) combined with energy dispersive spectrometer (EDS) analyses.

2. Previous works of clast components at Turrialba current eruption

The main discussion surrounding the 2010 to 2016 eruptions at Turrialba is whether they were phreatic or if a juvenile component was involved. For several authors, the ashes of 2010 to at least 2013 were clearly phreatic from the macroscopic (binocular microscope) examination and field observation (i.e., Martini et al., 2010; Soto and Mora, 2013; Duarte, 2014; González et al., 2014, 2015). Others claimed that the ashes of 2010 (Reagan et al., 2011) contained ~1% of juvenile but persisted with the interpretation of the eruptions as phreatic. Avard et al. (2014) claimed to identify ~5–9% of juvenile component in the October 2014 eruptive products but did not propose an eruption classification.

González et al. (2014), on the other hand, conclude that the eruption of October 30, 2014 (3:46 a.m.) was strombolian given that observed the observation of projected incandescent material and measured temperatures from the viewpoint near 900 °C. However, the observation of incandescent ballistic missiles and its visual similarity with strombolian eruptions is not a conclusive criteria. Incandescence has a variable range, depending on the type of material, between 400 and >700 °C. High temperature fumaroles and gas vents (500–800 °C) were in fact incandescent before the eruption, thus entrainment of equally hot or hotter material heated by magmatic gas provides a more than adequate explanation for ejection of incandescent material without invoking the eruption of new magma. In addition, observation of incandescent projectiles are also presented in vulcanian eruptions (i.e., see Fig. 2 in Morrissey and Mastin, 2000), among others. The absence of a vesiculated tephra layer (scoriaceous bombs and lapilli, agglutinates) does not support strombolian eruption (cf., Cas and Wright, 1987; Francis and Oppenheimer, 2004), at least during the 2014 to 2015 eruption period.

In addition, the presence in the ash of fresh crystals of olivine, plagioclase as well as fresh glassy ash grains (Avard et al., 2014), is not a sufficient argument to assert the presence of juvenile component. Such material could be due to the reworking or erosion of tephra from the walls of the conduit and active crater, as has been observed in other ashes and similar cases (Mastin, 1991; Suzuki et al., 2013; and references cited therein).

Lücke and Calderón (2016) use scanning electron microscopy (SEM) and energy disperse X-ray spectroscopy for analyzing the ash from 2014 to 2015 under the fraction 2.7 phi fraction (fine ash), and they concluded that the 2014 eruption was phreatic because they concluded that the ashes were composed entirely of non-juvenile fragments, and only the 2015 eruption was phreatomagmatic. Alvarado et al. (2016) conclude that the 2014 eruption was instead phreatomagmatic based on the presence of hydratation cracks, and describe in Spanish the current eruption in detail, the tephra deposits, including granulometric and X-ray diffraction analyses, petrography and mineralogy, and applied the sequential fragmentation/transport theory.

In the present paper, we examine the deposits of the eruptive period of Turrialba from 2010 to 2015 by SEM + EDS in the range size between 3 and 3.5 phi (very fine ash), a classification diagram used to identify the fragmentation mechanism, and a comparison of the binocular microscopy results from ash samples from 2010 to 2016. Of the last 2016 events, no SEM analyzes is include, and only data from binocular investigation is reported.

3. Brief eruptive history of Turrialba volcano

Turrialba volcano, located at the eastern end of the Cordillera Central of Costa Rica (Fig. 1), began to show signs of reactivation since 1996, after more than a century of slumber (last major eruptive period: 1864–1866). The summit area of Turrialba consists of three craters (West, Central and East craters), and several others destroyed and eroded, into a volcanic graben modified by a sector collapse. Only the West and Central craters had active fumaroles until 2010. Signs of reactivation were more noticeable from mid-2001, although the strongest change began to occur in the chemical composition of the gases since mid-2007 (Martini et al., 2010; Vaselli et al., 2010).

Emission rates of SO_2 as measured by fixed scanning DOAS instruments showed that the peak gas emission (up to ~4000 tons of SO_2 per day) occurred in 2009 (Conde et al., 2013). Since that time, SO_2 fluxes decreased to background levels of 500 tons/day until October 2014; after which SO_2 flux has varied between back ground with peaks of up to ~5000 tons/day (de Moor et al., 2016b).

At the end of January 2010, Turrialba finished its dormant period of nearly 144 years. On 5–8 January 2010, a small eruption opened a new small vent (called Boca 2010), 120 m long and 30 m wide, on the southwestern side of the west crater, and resulted in ash fall reaching the suburbs of San José, about 40 km from the vent. On 14 January 2011, another small ash emission was recorded, which opened a new vent (Boca 2011). Another vent opened on the east-southeast flank of the active West crater on 12 January 2012 (Boca 2012), which was 15 m long by 10 m wide. This eruption was accompanied by minor ash emissions that also occurred on 18 January 2012 when the vent enlarged at 25 × 15 m, and ash fell 27 km SW from the vent. On 21 May 2013, an eruption from the 2010 and 2012 vents resulted in ash fall >40 km to the west. Small additional eruptions occurred on 4 June and 13 September 2013 (Duarte, 2014; González et al., 2015).

On 29 October 2014, Turrialba volcano entered a new more vigorous eruptive phase, with 3 main periods of major activity characterized by explosive events followed by ash venting, separated by weeks of relative quiescence. The first period started with the 29 October–1 November activity characterized by explosive events that enlarged the West crater and produced ballistic blocks and a substantial plume rich in fine ash and steam. Two or three vents were active inside the West crater. The activity faded after the 9 December 2014 explosion. The second

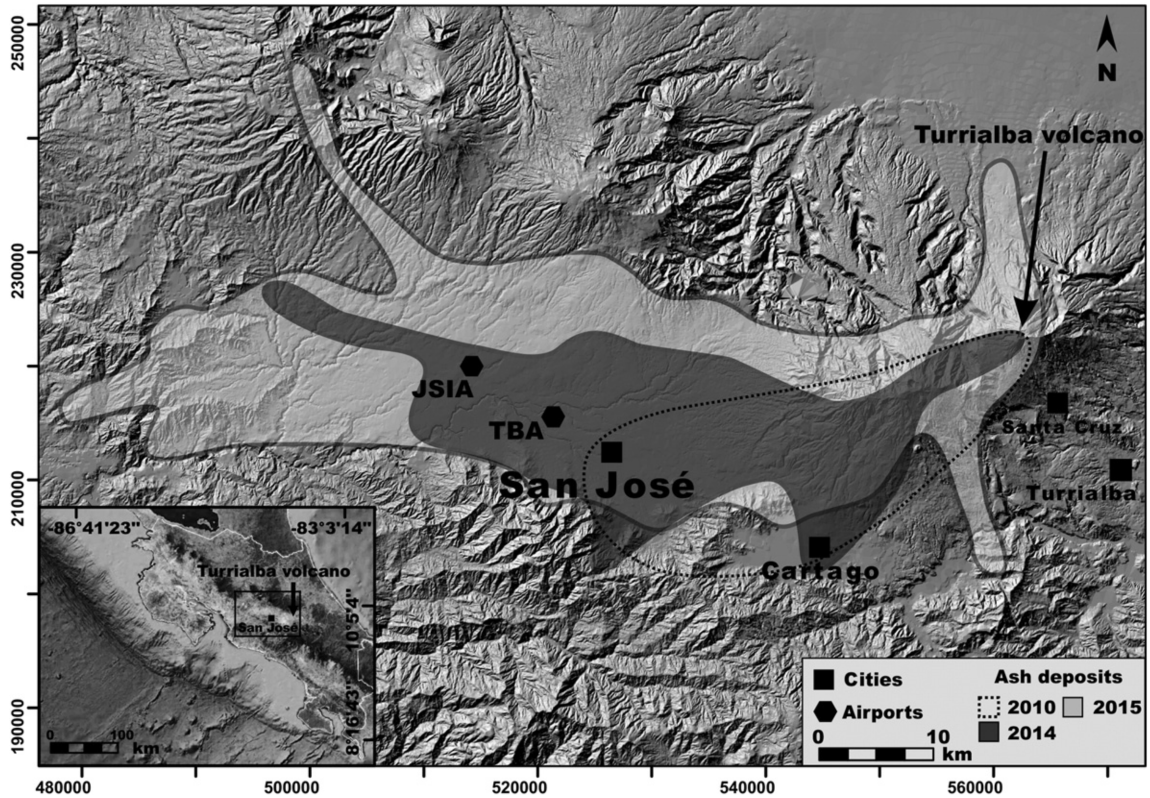

Fig. 1. Turrialba volcano and areas affected by fine ash deposits. JSIA: Juan Santamaría International Airport, TBA: Tobías Bolaños International Airport.

period started in March 2015 and was marked by various explosions on 12 March 2015. Fine ash from the plume (3 km high), blown by the WSW wind, was reported falling on Valle Central and the air traffic was closed at the Juan Santamaría international airport (located 49 km from Turrialba volcano). A similar situation repeated another 5 times, and twice the Tobías Bolaños airport was closed as well. In March and April eruptive activity was maintained with frequent small pulses of variable magnitude. As of 18 May 2015, the ash emission subsided, terminating the second period. On 15 August an isolated small eruption of ash occurred. On 16 October 2015, a new small explosion marked the beginning of the 3rd period of activity, which decreased after 1 November 2015. Sporadic small ash pulses repeated until the beginning of December 2015 and during January 3, 6 and 8, 2016 (Alvarado et al., 2016). A new major period of ash eruption initiated on 29 April 2016 and continues to present.

Most of the eruptions at Turrialba are discrete, relatively small explosions, generating plumes, which range from fine ash-rich to ash-poor, up to 4 km high, generally <1 km high. Most of them are not audible (shock waves are not frequent) and repeat with intervals of tens of minutes to hours or even days. Ash-laden clouds had, a light gray color during the early eruptions (2010–2014), but in 2015–2016 they changed to dark and dense in appearance. Large fragments in the column simply fell back around and into the vent, to be further fragmented and abraded. The vast majority – if not all – of the coarse ejected material (blocks and lapilli) is not juvenile. Small-volume pyroclastic density currents (mostly wet surge deposits) were also frequently generated both when large amounts of eject falls back around the vent and from column collapse, which traveled for short distances (<1000 m; mostly <250 m) from the vent area and surmounted small topographic obstacles. Clarke et al. (2002) called this type of vulcanian fountain collapse the 'overhang' style, without implying magmatic interaction with external water. Schmincke (1977) on the other hand suggested that vulcanian deposits from the 1880–1890 eruption of Vulcano, Italy, are similar to those typical of fluid dynamic interaction of water and magma, characteristic of phreatomagmatism, a conclusion supported by Frazzeta et al. (1983) for this eruption. Therefore vulcanian eruptions can be driven by purely magmatic process or involve external water, overlapping with phreatomagmatic eruption styles (Morrissey and Mastin, 2000). Thus, the previously describe characteristics of the Turrialba eruptions, generally support a classification as vulcanian style (cf., Cas and Wright, 1987; Francis and Oppenheimer, 2004; Clarke et al., 2002), with probable phreatomagmatic character, as we will discuss in the following sections.

Ash deposits (fallout, and surge deposits) are composed by accidental lithics dominated by hydrothermally altered clasts with a lesser proportion of fresh-looking clasts, and secondary hydrothermal minerals (anhydrite, gypsum, bassanite, alunite, hexahydrite, pyrite, heulandite, native sulfur), clay minerals (montmorillonite, halloysite, allophane), and a smaller quantity of fresh glassy ash grains (tachylite and sideromelane), primary and fresh/phenocrysts (plagioclase, pyroxene, olivine, opaques and cristobalite), and rare xenocrysts (riebeckite, biotite). The secondary minerals were sourced from the deeper to superficial hydrothermal systems (Alvarado et al., 2016).

4. Samples and methods

Ash was sampled in proximity of the active crater (between 80 and 700 m), on the flanks of the volcano (1–2 km) and the Central Valley (~ 40 km). For component analysis, the ash samples of all the eruptive phases between 2010 and 2016 (June) were analyzed under the binocular microscope at OVSICORI-UNA. We followed the methodology of Suzuki et al. (2013), who convincingly demonstrated successful forecasting of a magmatic eruption Shinmoe-dake volcano (Japan) by ash monitoring. Between 1000 and 1500 fragments per sample in the size range $1 \leq \text{phi} \leq 2$ after sieving, ultrasonic cleaning and sieving and rinsing again. Component analysis was conducted on each sample by visually inspecting grains under binocular microscope at 40× magnification and separating clasts into four categories: 1. Free crystals:

Minerals with no alteration or adhered glass, clear cleavage and crystal form, 2. Fresh glass: Glassy shards with vitreous conchoidal surfaces and no visible alteration, 3. Fresh to partially altered lithics and glass: Clasts with or without vesicles with evidence for weak alteration such as vesicle fillings or lacking vitreous lustre, 4. Strongly hydrothermally altered lithics: Clasts dominated by finely crystalline heterogeneous material containing sulfides, sulfates, and native sulfur, and clays.

Ash samples of the eruptive period 2010–2015 were also systematically investigated by the scanning electron microscopy (SEM; LEO EVO-50XVP Zeiss, Cambridge, Cambridge shire, UK) coupled with energy dispersive spectrometry (Oxford-Link Ge ISIS energy dispersive spectrometer (EDS) equipped with a super atmosphere thin window) at the Dipartimento di Scienzedella Terra e Geoambientali (University of Bari, Italy). The ash samples analyzed by SEM + EDS were collected between a few hours to days after the 5–8 January 2010 (J10-2010), 12 January 2012 (J18-2012), 21 May 2013 (M02-2013), 29 October 2014 (14-10-30), 9 December 2014 (14-12-09) and 12 March 2015 (12-03-15) eruptive events. Ash of the 2016 eruptive activity was not investigated at the SEM + EDS due to time constraints. The analysis of clast morphology at the SEM represents a powerful method to discriminate the fragmentation processes of pyroclastic deposits (e.g. Wohletz, 1983; Heiken and Wohletz, 1985; Marshall, 1987; Dellino and La Volpe, 1996; Büttner et al., 1999).

In the present paper, clast shape was also characterized quantitatively by image processing analysis that resulted in shape parameters useful for classifying the fragmentation processes by means of the diagram proposed by Büttner et al. (2002). For the SEM investigation we selected particles from a grain-size range between $3 \leq \phi \leq 3.5$ (i.e., a particle diameter d of 90 μm ≤ d ≤ 125 μm). This size fraction allows a better distinction between phreatomagmatic and magmatic processes (Dellino and La Volpe, 1996). Furthermore, as it was demonstrated in other papers, ash fragments of such grain size experience the highest fragmentation energies of magma-water interaction processes (Zimanowski et al., 1991, 2003, 2015; Dellino and La Volpe, 1996; Büttner et al., 2002).

The SEM investigation was carried out on ash particles that were gently cleaned by ultrasound as to eliminate fine adhesive dust that could obscure the clast surface features useful for the classification and interpretation of fragmentation processes. Observation was carried on mainly with Back Scattered Electrons (BSE) with a 15 kV accelerating potential, 500 pA probe current.

The energy dispersive spectrometer (EDS) was used as to evaluate the glass surface composition and to document whether particular surface features occurred on fresh or altered glass. EDS analyses allowed to document the presence of lithic material resulting from fragmentation of the crater walls (Dellino et al., 1995, Dellino and La Volpe, 1996; Sulpizio et al., 2008).

X-ray intensities obtained on clast surfaces by the EDS spectrometer were converted to wt% oxides by the ZAF4/FLS quantitative analysis software of Oxford-Link Analytical (UK). The accuracy of the analytical data was also checked by means of standard minerals manufactured by Micro-Analysis Consultants Ltd. (UK). Analytical precision was 0.5% for concentrations >15 wt%, 1% for concentrations of about 5 wt% and <20% for concentrations near the detection limit; the detection limit depends on the considered element, but never below 1000 ppm (Caggiani et al., 2015).

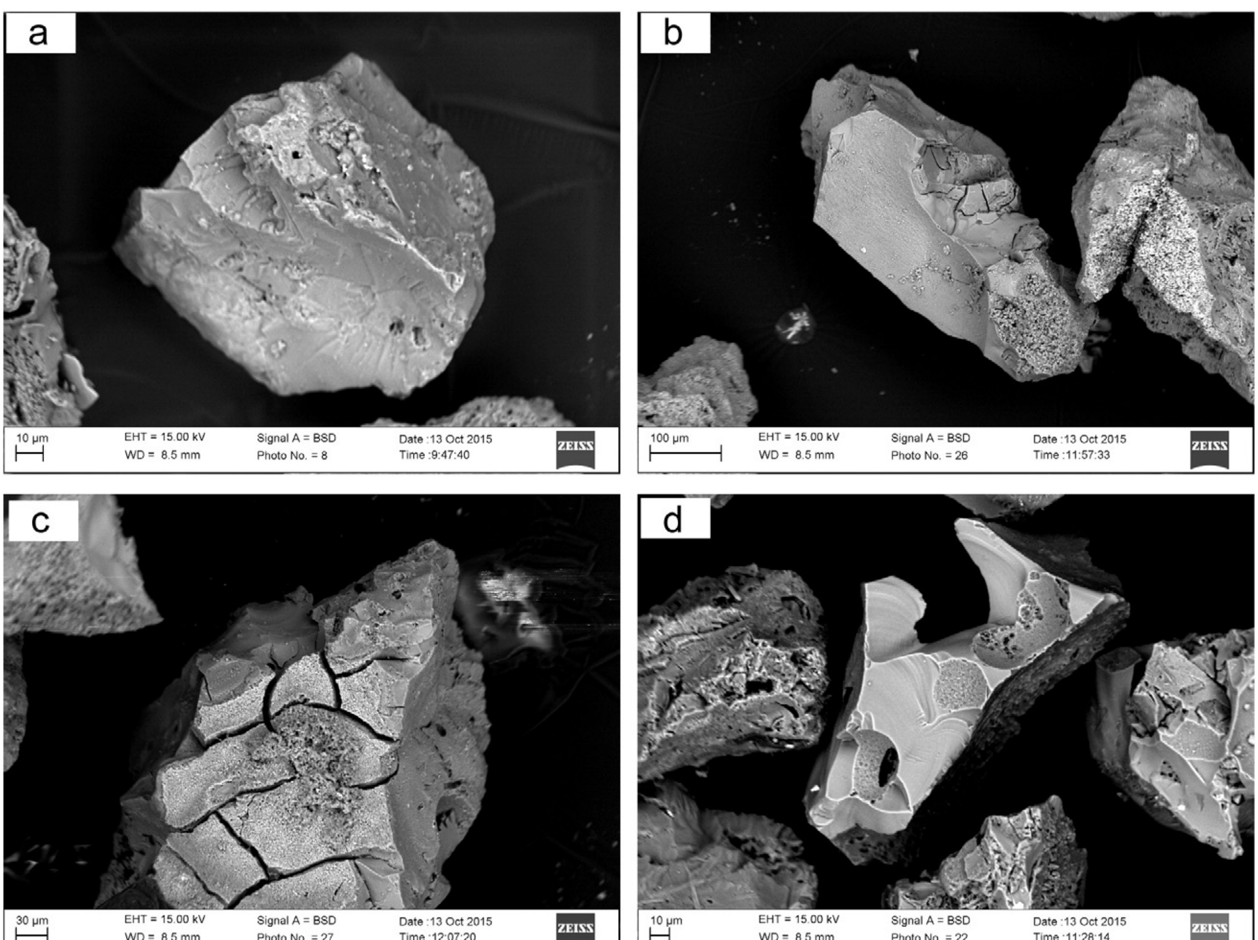

Fig. 2. A selection of SEM images of fine glassy ash clasts. a) Blocky shape clast with stepped features, b) an angular shape, blocky glass with quenching cracks, c) a blocky clast with quenching crack structures, d) a moderately vesicular clast.

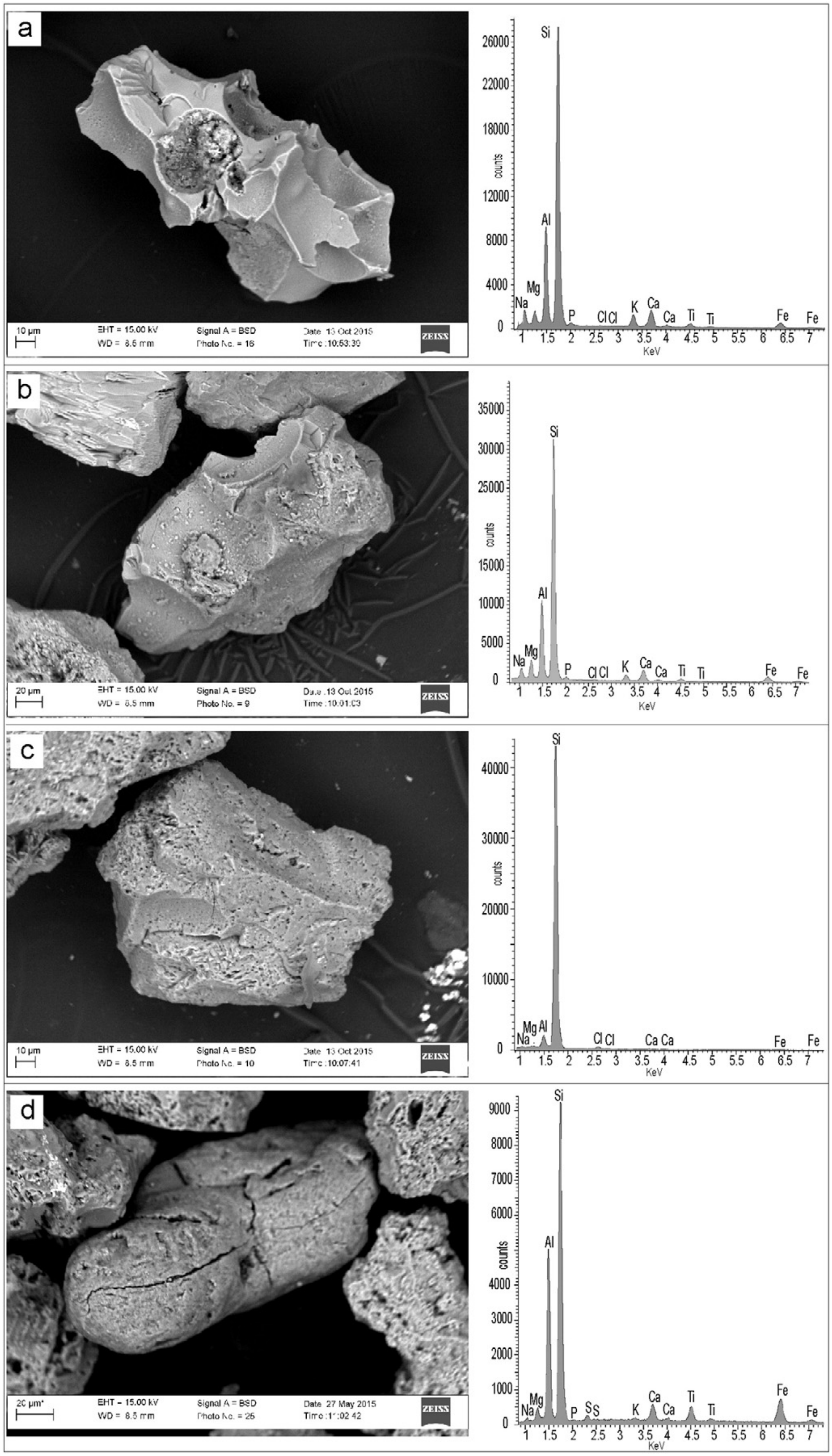

Fig. 3. Morphology and EDS analysis of two juvenile clasts (a, b) and two lithic clasts (c, d). a) A moderately vesicular juvenile clast (and EDS spectrum) with chemical pitting on few vesicle wall and adhering particles inside a vesicle, representative of fresh glass; b) a moderately vesicular juvenile clast (and its EDS spectrum) with blocky shape and adhering particles; c) a blocky shape, lithic clast with fractures, and its EDS spectrum, which shows the strongly hydrothermal alteration; d) a lightly altered, rounded lithic clast with fractures, and its EDS spectrum.

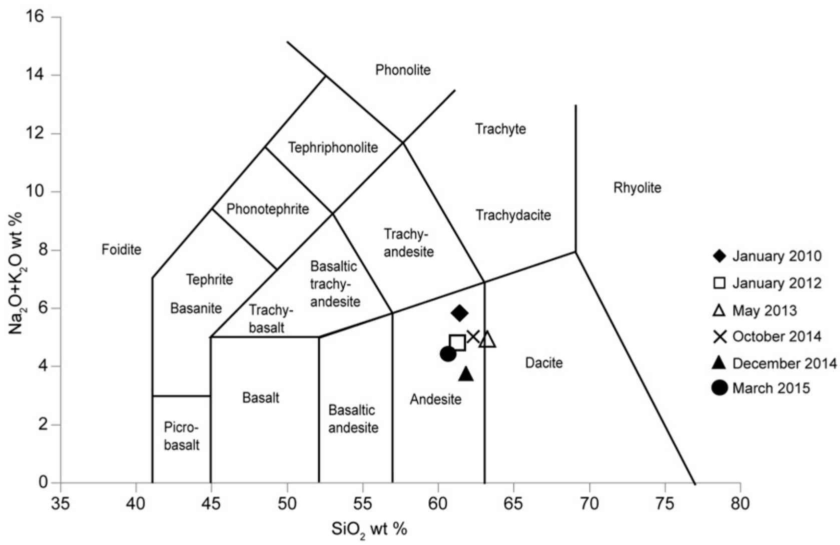

Fig. 4. TAS diagram of representative juvenile glass clasts from Table 1.

5. Results

The combined use of the SEM BSE observation and EDS analysis allowed the identification of both lithics and juvenile fragments. Juvenile glass fragments, which are the ones that better allow interpretation of fragmentation mechanisms (Dellino and La Volpe, 1996) were analyzed in detail with particular emphasis on the glass surface textures. The textural features identified on juvenile glass particles suggest that they were formed by both brittle and ductile fragmentation occurring during magma/water interaction, in all the eruptive phases of Turrialba eruption studied in this work. Blocky shaped (blocky-equant and blocky-angular) particles with stepped features (Fig. 2a) are quite common among juvenile glass particles of Turrialba eruptions and reflect an intense brittle magma fragmentation (Büttner et al., 1999, 2002; Dellino et al., 2001). Moss-like angular shapes and quench crack structures (Fig. 2b and c) are also present. They are typical of particles undergoing very fast cooling upon direct contact between fragmented particles and liquid water, as it is found in other pyroclastic deposits of ancient and recent eruptions and in clasts produced by experimental molten-fuel-coolant-interaction experiments (cf. Dellino and La Volpe, 1996; Büttner et al., 1999, 2002). Moderately vesicular particles are also present (Fig. 2d), suggesting that gas exsolution processes and gas bubble formation were active during the rise of magma, in which phreatomagmatic explosions favored fragmentation of a vesicle-poor magma into fine ash.

The high amount of accidental lithics (fresh and hydrothermally altered clasts and secondary minerals: 82–98%), suggests that fragmentation involved country rocks extensively, in the geothermal aquifer, which is typical of phreatomagmatism. This could possibly be due to the fact that the conduit was not well established and the fragmentation caused an additional significant breakup of the conduit. The magma ascent rate apparently was episodic and occurred in the form of a dike network, with each dike forming a small vent (locally called Bocas), inside or near the principal West crater.

The combined use of clast morphology and EDS data allowed relatively easy discrimination between different ash components. Fig. 3 shows an example in which two juvenile clasts (Fig. 3a, b) and two lithic fragments (Fig. 3c, d) are identified thanks to the combined use of clast surface textures and compositional data. The two juvenile particles have the same andesitic composition and represent: i) moderately vesicular juvenile clasts with chemical pitting occurring on vesicle walls and adhering particles inside a vesicle (Fig. 3a) and ii) clasts with blocky shape and cracks (Fig. 3b). The two lithic clasts show a different composition, both between them and in comparison with the juvenile particles (Fig. 3c, d). The severe depletion of chemical elements as Na, Ca, Fe, Mg (Fig. 3c), suggests that the first lithic clast (Fig. 3c) is strongly altered. The second lithic clast (Fig. 3d), instead, has been affected by a light hydrothermal process, because it has been leached only in the light alkaline elements Na and K, which are the first elements that are lost during the very early stage of the alteration process (Dellino et al., 2001).

The juvenile glass fragments have a composition (Fig. 4 and Table 1) that in the TAS diagram falls in the andesitic field at the border with the dacitic one. Although the EDS data cannot be used to derive detailed petrogenetic information, they suggest that the glass had a quite homogeneous andesitic composition during the eruptions, although the early eruptions appear to be a little more rich in alkalis than the later ones (December 2014–March 2015), and occur just when the amount of the juvenile component increases (Tables 1 and 2). The bulk-rock composition of the magma should have been a little more mafic, because of the presence of olivine, pyroxene, and opaque phenocrysts in the ash deposits together with vitric ash.

The EDS in our study are conducted on unpolished original clast surfaces. It is important to note that the compositions derived from these measurements show significantly lower alkali contents ($Na_2O + K_2O = 4.8$; average of all EDS analyses) compared to measurements conducted by electron microprobe on polished samples from similar fresh-looking clasts from the 2014 and 2015 eruptions ($Na_2O +$

Table 1
EDS analyses of representative juvenile clast.

	SiO_2	TiO2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
January 2010	61.29	2.09	15.65	6.34	3.33	4.35	2.58	3.48	0.81	99.92
January 2012	61.02	3.35	15.14	7.6	4.14	2.85	2.87	1.95	0.98	99.90
May 2013	63.56	2.32	15.52	5.4	1.78	5.57	2.08	2.88	0.82	99.93
October 2014	61.92	3.57	14.58	7.35	4.29	3.91	1.25	2.2	0.93	100.00
December 2014	62.34	2.48	13.48	8.3	2.49	5.02	1.64	3.37	0.88	100.00
March 2015	60.30	2.09	14.84	9.17	3.22	5.06	1.53	2.9	0.89	100.00

Table 2
Amount of fresh fragments as identified under the binocular microscope and juvenile ash clasts as identified at the SEM for ash samples of Turrialba representing activity between 2010 and 2016.

Year	2010	2011	2012	2013	2014	2015	2016
% Fresh fragments (1–2 Φ)	5–6	–	6–7	11–12	5–9	7–20	8–10
% Juvenile content (3–5 Φ)	1–2	–	5–7	15–18	12–15	12–15	ND

$K_2O = 6.1$; average of 149 analyses; de Moor et al., 2016b; Rizzo et al., submitted). Similarly, the silica concentration as measured on raw clast surfaces is significantly higher (61.7% SiO_2) than that measured on polished surfaces (58.5% SiO_2; average of 149 analyses; de Moor et al., 2016b; Rizzo et al., submitted). These observations are consistent with loss of alkalis during interaction with hydrothermal fluids (Dellino et al., 2001). Higher silica contents have also been reported during rapid alteration by plume gases during eruption at Etna volcano (Spadaro et al., 2002). As our samples were collected very soon after eruption and generally upwind of the volcano, we do not believe that "cryptic" geochemical alteration observed on clast surfaces is due to post-depositional exposure to gas. Rather, we propose that alkali loss and silicification of the clast surfaces occur during eruption due to direct contact between acidic hydrothermal fluids and hot juvenile material. Similarly, Lücke and Calderón (2016) reported analyses from recent Turrialba ash surfaces with high silica and low alkali content, which probably do not reflect true magmatic compositions. Rather, our analyses provide strong geochemical evidence indicating juvenile magma interaction with hydrothermal fluids, supporting a phreatomagmatic eruption mechanisms.

It is important to note that the small amount of juvenile clasts supports a phreatomagmatic classification for even the very first phases of the Turrialba eruptions. A small fraction of juvenile material has also been noted in other eruptions that were initially categorized as phreatic and that preceded magmatic eruptions (e.g. Cashman and Hoblitt, 2004). In order to better define the fragmentation processes during the eruption, the shape of juvenile glass fragments were investigated by image processing analysis (Dellino and La Volpe, 1996). The circularity, rectangularity, compactness and elongation parameters were quantitatively determined. These were used to classify the fragmentation processes by means of the shape-parameters diagram introduced by Büttner et al. (2002). Fig. 5 shows how clasts from the Turrialba eruptions studied in this paper plot on such a diagram. Most of the particles fall in the brittle fragmentation field indicating that they represent so-called "active particles" (cf. Büttner et al., 1999, 2002). These clasts represent the fine fragmentation of magma directly in contact with liquid water during the melt-fuel-coolant-interaction of phreatomagmatic eruptions. Other particles fall in the ductile field and represent the "passive particles" that form during the expansion phase of the phreatomagmatic explosion (cf. Büttner et al., 1999, 2002). Classification of particles by means of the shape-parameters diagram therefore confirms that juvenile glass fragments are compatible with typical phreatomagmatic fragmentation processes, even in the very small quantities observed in the early phases of the Turrialba eruptions.

Ash was also analyzed under the binocular microscope. Gray altered fragments were described as partly altered, and glassy fragments presented an altered "coating" described as glassy altered. Glassy fragments with or without altered "coating", and all free crystals including olivine and translucent are considered together as juvenile material as the observed trace of alteration could be due to incomplete cleaning or alteration that occurred during eruption. All of the samples contain fresh-looking glassy fragments (negligibly altered pyroclasts), some of which are considered true juvenile clasts from SEM analysis but in different percentages (Table 2, Fig. 6). In particular, by Table 2, it is possible to compare the percentage of juvenile clasts, identified at the SEM for the different eruptive phases of Turrialba, with the percentage of the fresh fragments identified by the binocular microscope. It appears that the amount of juvenile glass at the SEM tends to broadly follow the trend as the fresh material at the binocular microscope. Here, it is

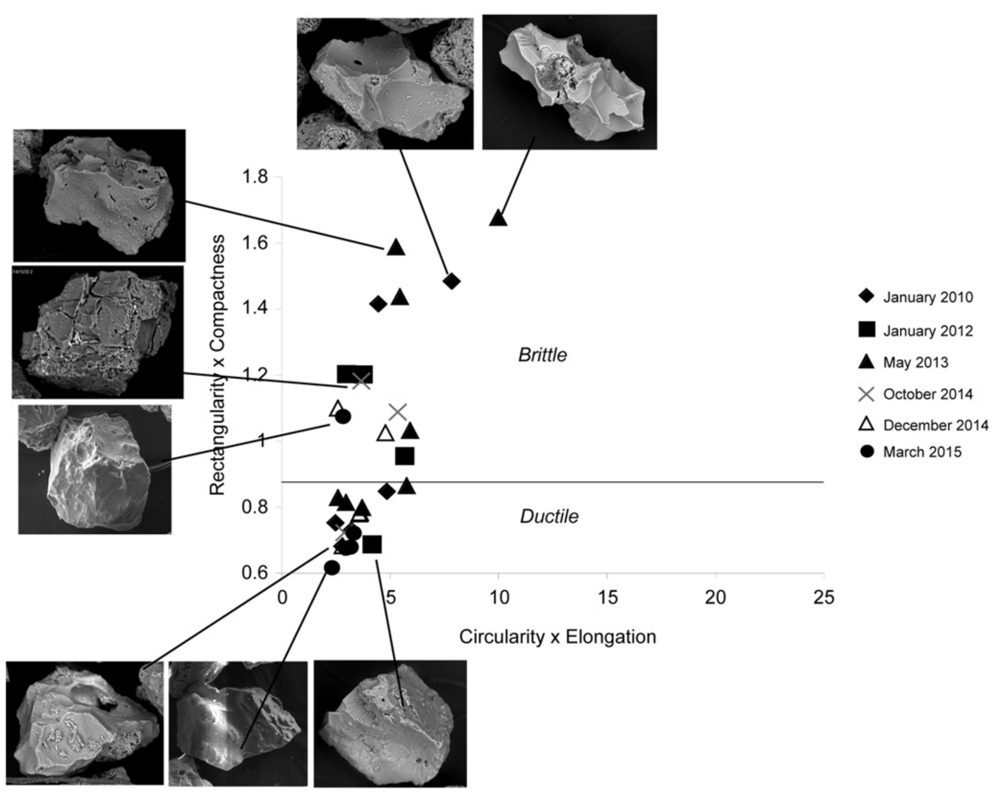

Fig. 5. Classification diagram of fragmentation processes. Data points represent typical clasts of the eruptive phases of Turrialba recent eruptions. Miniature photos of clasts are added for a visual comparison. The boundary between the brittle and ductile fields is drawn as it was in the original paper by Büttner et al. (2002) where the diagram was introduced.

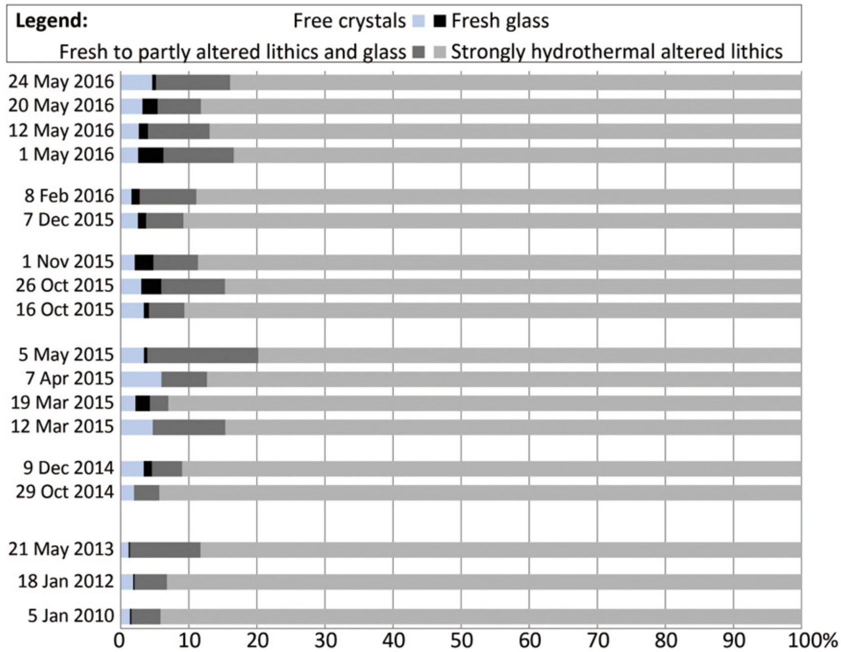

Fig. 6. Modal analysis, obtained under the binocular microscope, of the phi 1–2 fraction of the main ash emission of Turrialba since January 2010 to May 2016. Free crystals are represented by plagioclase, olivine and others.

important to note that far fewer clasts were assessed by SEM and thus this method may not be as representative of the bulk ash sample. On the other hand, component analysis by binocular microscope does not allow observation of microtextures or composition, therefore resulting in more error in determining whether clasts should be considered juvenile or not. Finally, both methods of component analysis are semi-quantitative and the distinction between "partially altered" and "unaltered" is rather subjective, especially when considering that cryptic alteration occurs on even the surfaces of the most pristine-looking clasts (i.e. alkali loss and silicification). It is therefore surprising that the two methods do not agree on the percentage of juvenile material, especially when one considers that two different clast sizes were assessed by each method. Nevertheless, what is consistent between the methods is that the proportion of juvenile material is increasing with time at Turrialba volcano, which has a clear significance the evolution of the eruptive activity and hazard assessment.

6. Discussion and conclusive remarks

Our study documents that the recent Turrialba events involved phreatomagmatic fragmentation of magma, even in the early eruptive phases that previous papers and internal reports defined as phreatic. The present study shows also that Turrialba had an increase in the proportion of juvenile material with time during the recent eruptive period, while the amplitude of eruptions was decreasing or at least at the same size. Our research demonstrates the general importance of a detail ash characterization for the definition of the first phase of an eruption, and for monitoring ongoing eruptive activity and forecasting activity changes.

The method used in this study for Turrialba has implications for the interpretation of explosive processes of other active volcanoes. In fact, many past and recent eruptions, which were considered to be phreatic in nature, could in fact contain a small amount of juvenile clasts that (i.e. precursory ash events of the 18 May 1980 eruption of Mt. St. Helens, USA, Cashman and Hoblitt, 2004), if identified by means of the methodology we used in this research would change their classification from phreatic to phreatomagmatic. The previously unrecognized presence of juvenile material would more importantly change the interpretation of the fragmentation mechanisms involved in these eruptions.

For example, it is well documented that phreatic precursory events have been described in a large number of eruptive phases in historic and prehistoric eruptions, which have been frequently followed by larger phreatomagmatic or magmatic events. Many vulcanian eruptions are thought to involve a plug of solidified material in the throat of a vent, and the early eruptive phases are interpreted as phreatic (Ollier, 1974; Cas and Wright, 1987; Barberi et al., 1992; Browne and Lawless, 2001). In many of these phreatic-like eruptions, including several recent examples, the tephra deposit consists of ash and ballistic blocks without any obvious macroscopic evidence of a juvenile component. In such examples, detailed SEM + EDS investigation, of the kind that was performed in the present paper, could help interpreting the true juvenile origin of fine ash (phreatic or phreatomagmatic?), which would indicate whether there is the involvement of fresh magma, even in the early eruptive events in very small quantity (<10%).

It is notable that in some of these opening phases, the premonitory geochemical and geophysical signals suggest the ascent of new magma, which is revealed by an increase of magmatic gases in fumaroles (SO_2, HCl, HF, etc.), and of seismic signals (*tornillo* earthquakes, volcanic tremor, volcano-tectonic events (Morrissey and Mastin, 2000; Francis and Oppenheimer, 2004; Cashman and Hoblitt, 2004). All of these are compatible with the presence of shallow juvenile material in the early eruptive phases and, therefore, one of the first targets to be investigated is the first appearance of juvenile material.

In order to unravel the origin of the opening phases of such eruptions, ash should be continuously sampled (at safe places) and analyzed, allowing rapid characterization of eruptive activity. The presence of juvenile material indicates that magma is rising to shallow depth, which is a crucial concept in civil preparedness as volcanic unrest evolves (Suzuki et al., 2013; Pardo et al., 2014). Thus, in addition to field studies and rapid characterization by binocular microscope, it is strongly recommended to assess complex ash samples by SEM + EDS analysis, in particular in the range between 3 and 3.5 phi, in order to robustly evaluate the presence of juvenile glass. Analysis of clast surface ash compositions can also provide an estimation of the magma type involved. However, care should be taken in interpretation of compositions attained from unpolished surfaces as these could be affected by interaction with hydrothermal fluids during phreatomagmatic eruptions.

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