Turmoil at Turrialba volcano (Costa Rica): Degassing and eruptive behavior inferred from high-frequency gas monitoring

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ABSTRACT

Eruptive activity at Turrialba volcano (Costa Rica) has escalated since 2014, causing airport and school closures in the capital city of San José. Whether or not new magma is involved in the current unrest remains a matter of debate. Here, we use high frequency gas monitoring to track the behavior of the volcano, and to decipher magmatic vs. hydrothermal contributions to the eruptions. Pulses of deeply-derived CO_2-rich gas ($CO_2/S_{total}>4.5$) precede explosive activity, providing a clear precursor to eruptive periods that occurs up to two weeks before eruptions, which are accompanied by sulfur-rich degassing from a shallow magmatic source. Degassing modeling suggests that the deep magmatic reservoir is ~8-10 km deep, whereas the shallow magmatic gas source is at ~3-5 km. Two cycles of degassing and eruption are observed, each attributed to pulses of ascending magma. The magmatic degassing signals were overprinted by a fluid contribution from the shallow hydrothermal system, modifying the gas compositions, contributing volatiles to the emissions, and reflecting complex processes of scrubbing, displacement, and volatilization. H_2S/SO_2 varies over two orders of magnitude through the monitoring period and demonstrates that the first eruptive episode involved hydrothermal gases whereas the second did not. Massive degassing (>3000T/day SO_2 and H_2S/SO_2 >1) followed, suggesting boiling off of the hydrothermal system. The gas emissions show a remarkable shift to purely magmatic composition ($H_2S/SO_2<0.05$) during the second eruptive period, reflecting the opening of new conduits, depletion of the hydrothermal system, and the transition from phreatic to phreatomagmatic eruptive activity.

1. INTRODUCTION

Magmatic eruptions at previously dormant volcanoes are often preceded by phreatic eruptions [e.g. *Barberi, et al.*, 1992]. Identifying the transition from phreatic to phreatomagmatic behavior is of paramount importance in hazard assessment during an evolving volcanic crisis as this change reflects the establishment of conduits directly connecting rising magma with the surface [e.g. *Nakada, et al.*, 1995; *Suzuki, et al.*, 2013]. The traditional method of defining this transition involves recognition of juvenile material in ash products. This approach involves detailed and time consuming compositional and textural analysis of complex mixed ash samples that is difficult to accomplish fast enough for monitoring purposes during rapidly evolving volcanic crises [e.g. *Suzuki, et al.*, 2013]. Moreover, distal ashes from phreatic and phreatomagmatic eruptions tend to be very fine grained, thus samples collected at safe distances are also challenging to work with for component analysis. Ultimately, it is exceedingly difficult to ascertain whether glassy clasts in multi-component ash represent fresh magma arriving at the surface or are derived from previously erupted (or shallowly intruded) material remobilized by explosive blasts, especially if the fresh material has similar composition to previous eruptive products [e.g. *Pardo, et al.*, 2014].

Given the remarkable compositional dissimilarity between magma-derived gas and hydrothermal gases (the latter being typically associated with phreatic activity), gas monitoring can potentially provide invaluable insights into the processes causing unrest [e.g. *Chiodini, et al.*, 2015; *de Moor, et al.*, 2016; *Giggenbach, et al.*, 1990]. However, continuous long-term instrumental records of gas compositional variations at the quiescence-to phreatic- to magmatic transition are essentially absent in the geological literature.

Here, we report on variations in gas composition measured in situ using a fixed Multi-component Gas Analyzer (Multi-GAS) at Turrialba volcano (Costa Rica; N 10.0183° W 83.7646°; 3340 m elevation) during an ongoing re-awakening process and volcanic crisis. Recent activity has involved frequent ash emission events that have opened new vents and represent the latest and most advanced manifestation of the transition from hydrothermal to magmatic activity. Turrialba volcano is located ~30 km upwind of San José (Fig. 1; the capital of Costa Rica) and ~50 km upwind of San José international airport (SJO). Thus, even small eruptions from this volcano threaten the quality of life for ~3 million people (~60% of the Costa Rican population lives in the central valley) and the economic heart of the country.

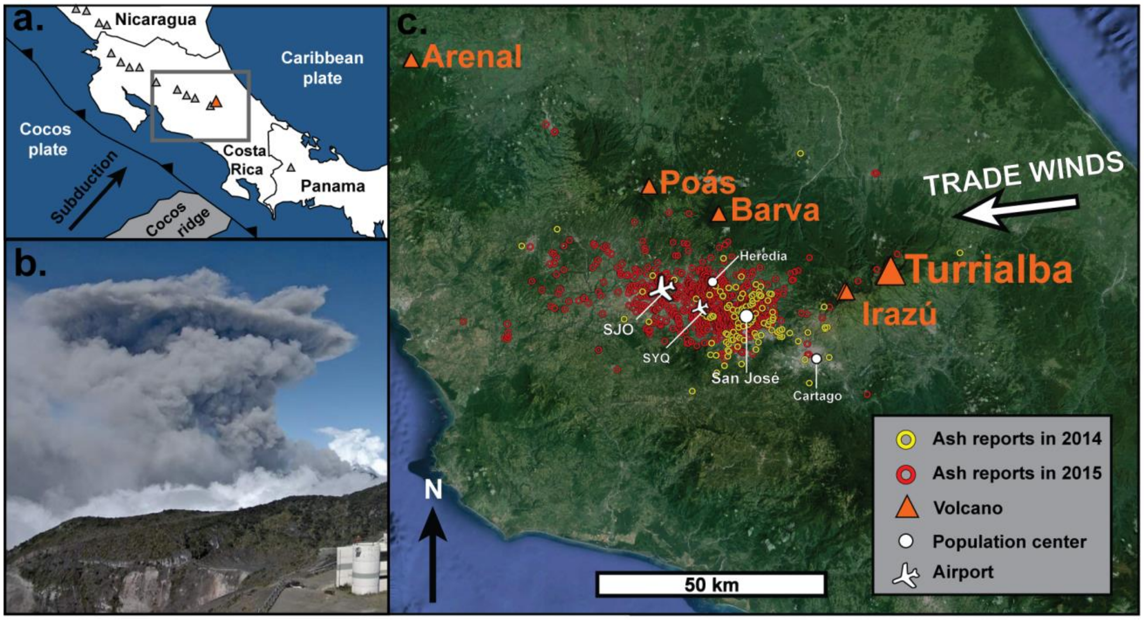

Figure 1. a. Tectonic setting of Turrialba volcano (orange triangle). Grey triangles indicate other volcanoes of the Central American Arc and the grey box indicates the area shown in panel c. b. Explosive eruption at Turrialba on 12 March 2015, as captured by an OVSICORI webcam located on the summit of Irazú volcano. c. Location map of Turrialba volcano in Costa Rica relative to the cities and airports (SJO: San José International Airport; SYQ: Tobias Bolaños International Airport) of the densely populated Central Valley, as well as volcanoes of the Cordillera Central. Hollow circles indicate reports received at OVSICORI of ash fall in 2014 (yellow) and in 2015 (red).

2. BACKGROUND AND GEOLOGIC SETTING

The name “Turrialba” may be derived from the Latin for “white tower”, probably referring to the condensed gas plume visible from ships bearing European settlers to the Caribbean coast [*Alvarado,* 2009]. Turrialba and Irazú (Figure 1) volcanoes share a common base covering an area of roughly 60 km by 45 km, with their summit craters just 10km apart. Together they form the largest and southernmost volcanic edifice on the Central American arc [*Carr and Stoiber,* 1990]. The subduction of the Cocos plate beneath the Caribbean plate is low angle (~40°) and high temperature in this region, due to the subduction of the buoyant and hot Cocos ridge [e.g. *Peacock, et al.*, 2005; Figure 1]. In southern Costa Rica and Panama, flat slab subduction (<30°) causes uplift of the Talamanca mountains (3800 m) without active volcanism. The magma source region feeding Turrialba and Irazú volcanoes is similar, in that the two show evidence of both arc-like and OIB-like (ocean island basalt) signatures in terms of trace elements and radiogenic isotopes [*Benjamin, et al.*, 2007; *Di Piazza, et al.*, 2015]. The enriched character of magmas in southern Costa Rica most likely originates from the subduction of seamounts formed by the Galapagos hotspot [*Gazel, et al.*, 2009].

Volatile chemistry of the volcanic gas emissions along the Central American Arc reflects geodynamic setting. In general, the volcanoes of Costa Rica show more mantle source and less sedimentary signature than the rest of the arc. Turrialba has the highest $^3He/^4He$ value (Rc/Ra = 8.1) in the region [*Di Piazza, et al.*, 2015], pointing to its slightly "back-of-the-arc" location and strong mantle signature. Carbon isotopes and C-He systematics for Turrialba and Irazú fumaroles suggest that carbon has less sedimentary component than the rest of the Arc [*Shaw, et al.*, 2003]. Along arc trends in CO_2 content of melt inclusions [*Wehrmann, et al.*, 2011] and CO_2/SO_2 in plume gas emissions [*Aiuppa, et al.*, 2014] both show that the southernmost volcanoes in Central America are also relatively carbon-poor. Interestingly, though Turrialba-Irazú volatile systematics are consistent with strong mantle and weak slab fluid signatures, water contents in basaltic Irazú melt inclusions show typical arc contents of ~3 wt% [*Benjamin, et al.*, 2007]. Similarly, new S isotope data for Turrialbas gas plume (samples collected and analyzed using the methods of de Moor et al. [2013b; see supplemental materials]) show a range of values between +0.2 ‰ and +7.3 ‰ with an average of +3.4 ± 0.5 ‰ [*de Moor, et al.*, 2013a], which falls closer to typical values measured in high temperature arc gases (~+ 5 ‰) than to values observed in purely mantle-derived gases [~+ 0 ‰; *de Moor, et al.*, 2013b; *Oppenheimer, et al.*, 2012].

3. **CURRENT ERUPTIVE ACTIVITY**

The re-activation of Turrialba has been a decades-long process. The last magmatic eruption occurred in 1864-1866, which was preceded by fumarolic degassing and phreatic activity [*Di Piazza, et al.*, 2015; *Reagan, et al.*, 2006]. Seismic swarms, increasing degassing intensity, and changes in fumarolic gas chemistry were the first indications of unrest in the late 20th century [*Martini, et al.*, 2010; *Vaselli, et al.*, 2010], heralding the end of ~120 years of repose. Seismicity peaked in 2009 and 2010 [*Martini, et al.*, 2010], and SO_2 flux reached a maximum of ~3500 T/day in mid 2009 [*Conde, et al.*, 2013]. The first phreatic eruption at Turrialba occurred on 5 January 2010, which formed a moderate to high temperature fumarolic vent (300°C to 600 °C) on the inner west crater rim that allowed open system degassing immediately after the vent-opening eruption [*Campion, et al.*, 2012]. Further phreatic eruptions in January 2012 opened a new high temperature vent (500°C to 800 °C) on the southeast rim of the west crater. On 21 May 2013, both vents (located about 300m apart) emitted ash simultaneously. Movie S1 provides a visual summary of the recent activity at Turrialba.

A new phase of eruptive activity began on 29 October 2014 with the most energetic blast to date and collapse of the eastern wall of the west crater (Movie S1). Ash emissions continued for two weeks and another more energetic explosion occurred on 9 December. This eruptive period was followed by 3 months of strong quiescent degassing and seismicity. Eruptive activity resumed on 8 March 2015 with at least 20 days of intermittent ash emissions (>32 events) up until 18 May. The most energetic explosions during this period occurred on 12 March 2015 (Fig. 1; Fig. 2; Movie S1) and 7 April 2015. Isolated ash emission events took place in June and August 2015. A period of frequent low energy ash emissions took place in October of 2015, with further passive ash emissions in early 2016. Frequent small explosive eruptions and persistent ash emissions resumed again on the 30th of April, 2016, and are ongoing at the time of writing. The ash emissions periods pertinent to this work (2014-2015) represent two distinct episodes of eruptive activity (Fig. 2; Degassing phases 3 and 6).

The 2014-present eruptions have blanketed the central valley in fine ash on at least 21 days since 29 October 2014, caused air traffic closures in five instances, closures of schools, and resulted in evacuations of the local farming communities. The ashes from the second eruptive episode (March-May 2015) had greater societal impact (Figure 1c), with reports of ash fall as far as 100km from the volcano, and 5 episodes of impact on aviation (flight cancellations). The 12 March 2015 eruption produced ash columns up to 2 km (Figure 1b), caused the closure of 12 schools, the evacuation of farms within 2 km of the crater, and caused 111 flights to be cancelled at SJO international airport, affecting ~7000 passengers. The ashes are dominated by hydrothermally altered material, but do contain a minor proportion of fresh-looking, glassy, vesicular clasts that are most likely juvenile [*Alvarado, et al.*, 2016; *Reagan, et al.*, 2011].

3. METHODS

We installed a fixed Multi-GAS station with data telemetry on the outer southwest rim of the active west crater of Turrialba in February 2014. This instrument measures gas concentrations of SO_2, H_2S, CO_2, and H_2O at a rate of 0.1 Hz for 30 minutes four times a day with data telemetered to OVSICORI in near real time. Gas ratios (H_2S/SO_2, CO_2/SO_2, H_2O/SO_2) are derived from linear regression through the concentration data and are independent of mixing with air [*Aiuppa, et al.*, 2009; *Aiuppa, et al.*, 2007; *Aiuppa, et al.*, 2014], allowing us to derive a time series of gas compositions (Figure 2). Errors in gas ratios as measured by Multi-GAS are <20% [*de Moor, et al.*, 2016] and are far less than the large (order of magnitude scale) variations observed in the data. The Multi-GAS instrument was calibrated in the lab periodically (on 30 May 2014, 14 September 2014, and 27 January 2015) and the slope and intercept of the calibration curves varied by less than 10% during the course of the study.

The emission rate of SO_2 from Turrialba is monitored by scanning UV spectrometer systems installed through the Network for the Observation of Volcanic and Atmospheric Change project [*Conde, et al.*, 2013; *Galle, et al.*, 2010]. These instruments are located about 2 km from the summit downwind of the volcano and scan continuously during daylight hours to measure the integrated absorption of UV light by SO_2 in the plume. Flux is estimated based on the integrated SO_2 column amounts from 50 measurements taken at 3.6° steps to cover 180° plume width. Plume height is obtained from triangulation by the two stations or webcam images when triangulation cannot be made, and the wind speed and direction is measured by a weather station located at the summit of the volcano [*Conde, et al.*, 2013]. Multiplication of the SO_2 emission rates with gas ratios expressed with SO_2 as the denominator result in estimations of the fluxes of CO_2, H_2S, and H_2O.

We also conducted electron microprobe analyses of magmatic clasts erupted during the 1864-1866 eruption to compare their composition to fresh glassy clasts erupted in the recent eruptions. Melt inclusions and matrix glass from these deposits were analyzed. Our ash sample collected from the 29 October 2014 eruption contains fine hydrothermally altered material, lithics, and ~10% fresh glassy and vesicular material that is suspected to be juvenile [*Alvarado, et al.*, 2016; *Reagan, et al.*, 2011; *Rizzo, et al.*, in prep]. The latter component was analyzed via microprobe for major elements, S, Cl, and F. Full methods and sample details are reported in the supplementary materials.

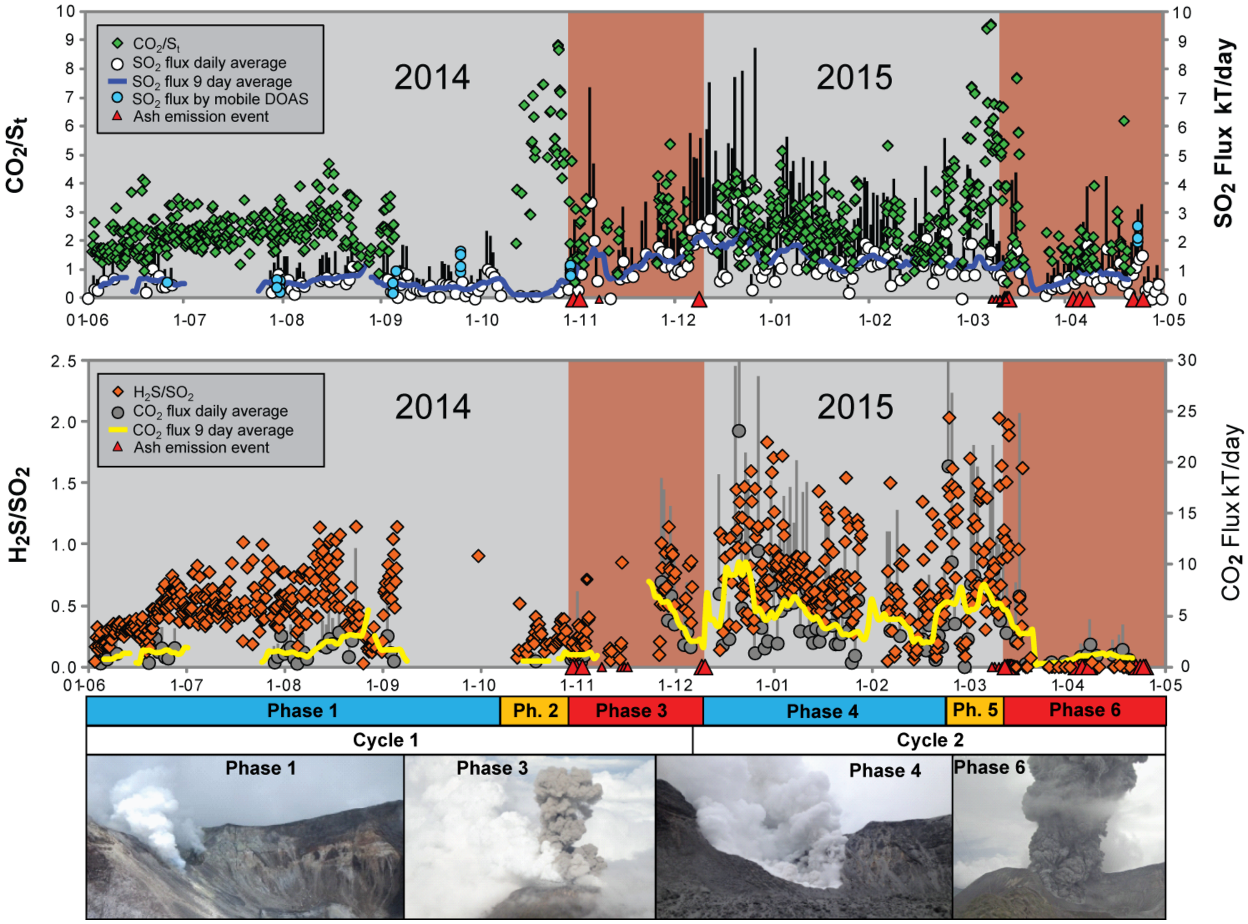

Figure 2. Time series of gas fluxes and gas compositions at Turrialba volcano since June 2014. Daily mean flux values are indicated by circles and associated bars indicate the 75th percentile of individual days. Blue and yellow lines indicate 9 day moving average of the gas flux. Diamonds show gas ratios as measured by permanent Multi-GAS station, and red triangles show the occurrence of explosions (larger triangles) or ash emissions (small triangles). Upper time series plot shows SO_2 flux measured by scanning DOAS and CO_2/S_{total} where S_{total} represents SO_2+H_2S. Importantly, two clear peaks occur in CO_2/S_{total} weeks prior to each eruptive period. The highest SO_2 fluxes occurred after the vent opening eruptions in 2014 followed by a relatively steady decrease. Lower time series plot shows CO_2 flux (calculated based on SO_2 flux and CO_2/SO_2) and H_2S/SO_2 as measured by Multi-GAS. Importantly, H_2S/SO_2 drops to purely magmatic values after the first series of eruption in 2015. H_2S unambiguously tracks the influence of hydrothermal fluids at Turrialba, and the time series shows that the peak in CO_2/S_t prior to the late 2014 eruptions has weak hydrothermal character. Six degassing phases are recognized based on variations in the gas fluxes and compositions (bottom axis). Phases 1 and 4 show stronger hydrothermal influence with relatively high H_2S/SO_2. Phases 2 and 5 precede the eruptive phases and display high CO_2/S_t with variable hydrothermal influence. Phases 3 and 6 are defined by eruptive activity and show low CO_2/S and low H_2S/SO_2 immediately after eruptions. Note that each individual phase shows unique combinations of gas flux and compositional characteristics. Photos from left to right displaying typical activity for the indicated phases: Quiescent degassing during phase 1 prior to the explosive eruption at 11:35pm on 29 October 2014. Ash emission event on 30 October 2014 (photo by Federico Chavarria). Intense degassing occurred in the months after the 29 October eruption during Phase 4. Ash eruption during Phase 6 on 4 May 2015 as captured by the OVSICORI webcam.

4. RESULTS AND DISCUSSION

4.1 CHANGES IN DEGASSING DURING VOLCANO REACTIVATION

Our high frequency time series of gas compositions and fluxes (Fig 2) allows us to observe in unprecedented detail the degassing processes involved during reactivation of a previously dormant volcanic system. In this section, we highlight the most important observations of the changes in degassing during the reactivation of Turrialba. We recognize six phases (Fig. 2) within two cycles of degassing and eruption during the last year, which we group as such based on distinguishing features in the gas compositions.

During quiescent degassing Phase 1 the system was relatively stable, with low gas fluxes and hydrothermally-influenced gas composition, as demonstrated by the presence of H_2S (Fig. 3) (we here assume $H_2S/SO_2 > 0.3$ to be a relatively unambiguous indicator of hydrothermal interaction; Symonds et al., 2001). Daily mean SO_2 flux values were typically less than 1000 T/d with CO_2/S_t of 1 to 4 (S_t refers to total sulfur i.e. $SO_2 + H_2S$), moderate H_2S/SO_2 of 0.2 to 0.7, and H_2O/SO_2 of 10 to 40. In the weeks prior to the October 29 eruption (phase 2), CO_2/S_t increased dramatically, up to values of 7-9. Importantly, this precursory gas signal occurred in parallel with a decrease of H_2S/SO_2 down to 0.05-0.3, excluding a hydrothermal origin. Interestingly, both SO_2 and CO_2 flux are low during this period, suggesting that the conduits connecting the shallower magmatic system to the surface were less permeable to gas.

The CO_2/S_t values dropped in the hours prior to the 29 October eruption and remained low through the first eruptive period (Phase 3). The hydrothermal component (H_2S) increased through Phase 3, from H_2S/SO_2 ~0.2 to ~0.7. Significantly, the gas fluxes increase dramatically only after the 9 December eruption (Phase 4), coupled with further increase in H_2S/SO_2 to values > 1.5.

A second peak in CO_2/S_t (~5 to 9.5) occurred in the first two weeks of March 2015 (Phase 5), which heralded the onset of eruptive activity starting on 8 March. In comparison to Phase 2, Phase 5 displays much higher H_2S/SO_2 (0.8-2) and higher SO_2 and CO_2 fluxes. A series of low energy ash emissions on March 8-11 occurred prior to more energetic blasts starting on March 12. The gas composition changed dramatically to low CO_2/SO_2 (1-2) and very low H_2S/SO_2 (<0.1) with the transition to more energetic eruptions (Phase 6).

Table 1. Comparison between compositions of matrix glass erupted in 1864-1866 and that from the 29 October 2014 eruption. The compositions are essentially indistinguishable within the observed variability.

	1864-1866 Matrix Glass (n=15)		**2014 Matrix Glass (n=11)**	
	AVERAGE	**STD DEV**	**AVERAGE**	**STD DEV**
SiO_2	56.02	0.56	56.98	1.27
TiO_2	1.51	0.20	1.80	0.17
Al_2O_3	16.44	1.01	15.36	0.84
FeO	8.59	0.85	9.21	0.52
MnO	0.18	0.05	0.18	0.03
MgO	3.45	0.31	3.45	0.51
CaO	7.39	0.82	6.31	0.57
Na_2O	3.52	0.65	3.12	1.16
K_2O	2.31	0.41	2.55	0.48
P_2O_5	0.61	0.10	0.71	0.14
S ppm	93	104	175	98
Cl ppm	1108	208	1255	679
F ppm	887	421	1550	748
Total	100.2		100.0	

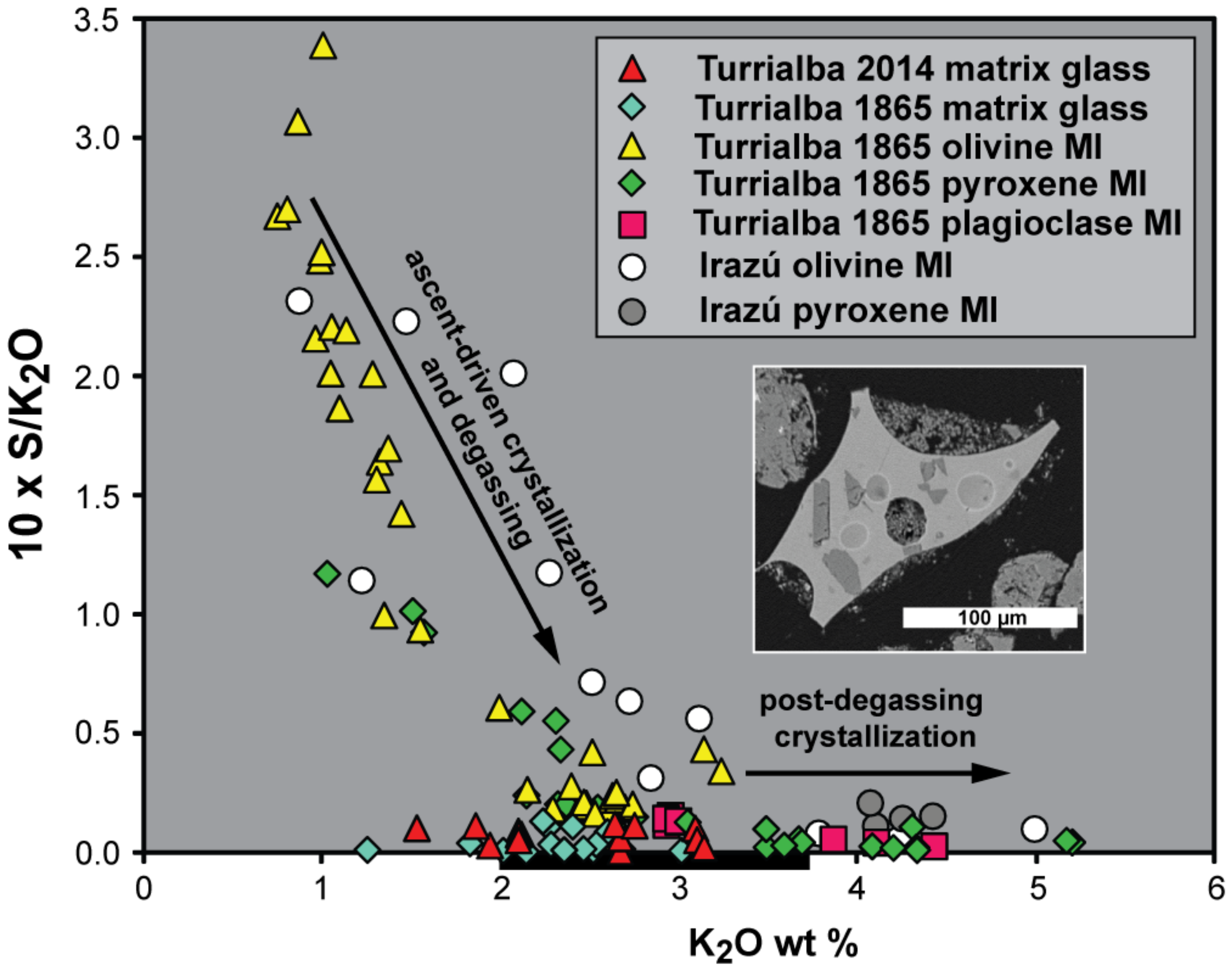

Figure 3. Plot of 10xS/K$_2$O versus K$_2$O with 2014 matrix glasses, 1865 melt inclusions and melt glasses, and melt inclusions from nearby Irazú volcano. Olivine-hosted melt inclusions (yellow triangles) from the 1865 eruption are sulfur-rich and K$_2$O-poor, representing primitive undegassed melt. Matrix glasses from both 1865 and 2014 eruptions have essentially the same composition and have degassed almost all of their sulfur. The inset BSE image shows a fresh-looking glassy shard (with adhered fine ash) erupted in October 2014 that is suspected to be juvenile. Interestingly, a significant group of pyroxene- and plagioclase-hosted melt inclusions from the 1865 eruption have higher K$_2$O than the Turrialba matrix glasses and are degassed. Irazú melt inclusions [data from *Benjamin, et al.*, 2007; *Wehrmann, et al.*, 2011] form a parallel trend to the Turrialba glasses. The black bar along the X axis shows the K$_2$O content of Irazú matrix glasses [*Alvarado*, 1993], again overlapping with Turrialba compositions but extending to higher K.

4.2 GLASS COMPOSITIONS: THE DEBATE OF NEW VERSUS OLD MAGMA

Table 1 compares the composition of most pristine matrix glasses from the 2014 eruption with the 1864-1866 eruption, showing that the compositions are indistinguishable within the variability observed in the samples. Both the 1864-1866 glasses and the allegedly juvenile clasts have compositions falling between basaltic andesite and trachyandesite (See Supplementary Text, Table S2, and Figures S1 for petrologic results and discussion). Thus, it is difficult to ascertain with certainty whether this material represents the eruption of new magma after rising through the crust, or remobilization of old magmatic material entrained during hydrothermally driven eruptions [*Giggenbach, et al.*, 1990; *Pardo, et al.*, 2014; *Suzuki, et al.*, 2013; *Williams, et al.*, 1986]. However, Alvarado et al. (submitted) and Reagan et al. [2011] argued that these glasses do represent true juvenile material (i.e. melt quenched to glass at the time of eruption).

Figure 3 shows the compositions of matrix glasses compared to melt inclusions from Turrialba (1864-1866 eruption) and Irazú (1963-1965 eruption). The two volcanoes show parallel degassing-crystallization trends, with Irazú falling at slightly more K-rich compositions. Interestingly, plagioclase- and pyroxene-hosted melt inclusions in both systems show higher K_2O than their respective matrix glasses, possibly suggesting entrainment of old, previously degassed magma (old magmatic phenocrysts at the very least i.e. antecrysts) in the eruptive products. This perhaps recalls the example of the 1985 Nevado del Ruiz (Colombia) eruption, which produced a large amount of gas but only a small amount of magma of which a lesser proportion was considered “new magma”, the majority being remobilized “old magma” [*Giggenbach, et al.*, 1990; *Williams, et al.*, 1986].

The composition and morphology of the fresh-looking clasts alone cannot fully or adequately resolve the vital question of whether fresh magma is involved in the present eruptions or not, as the fundamental problem relates to the timing of melt quenching to glass and time scales of alteration processes, neither of which can currently be constrained. Indeed, some of freshest-looking glass shards in the October 2014 ash have anomalously high F contents and low alkalis (Table S2), potentially indicating a cryptic alteration due to interaction with volatile-rich fluids. Thus, while magma petrology/geochemistry/texture all provide rather equivocal results, the short-term variations in gas compositions we observed at Turrialba (Fig. 2) require changing volatile sources and conditions of degassing (i.e. pressure of gas exsolution from melt) over monitoring time scales, and therefore shed light into the processes driving the volcano's current and evolving eruptive activity.

4.3 DEGASSING SOURCES AND PROCESSES

Each of the 6 phases of degassing (Figure 2) has unique characteristics in terms of gas composition and emission rate. Perhaps most importantly, high CO_2/S_{total} precedes both eruptive episodes, showing promise of a precursory signal useful in eruption forecasting. High CO_2/S_{total} (5-9) persisted for two weeks prior to the energetic eruption of 29 October 2014, and increased again five days prior to resumed onset of ash emissions in March 2015. Another striking feature of the gas composition time-series is the abrupt order of magnitude scale change in H_2S/SO_2 that coincided with the 12 March 2015 eruptions.

In order to explain the sources and processes responsible for the tumultuous variations in composition, we have conducted analysis of the CO_2-SO_2-H_2S-H_2O system (Figure 4), from which we propose three dominant sources or types of gas emissions: 1. Deep CO_2-rich magmatic gas; 2. SO_2-rich gas from shallow magmatic degassing; 3. H_2S-rich hydrothermal gas. We argue that the changes in gas compositions are driven by pulses of magma rising through the crust, and in this section we track the degassing pathways from deep to shallow levels (Fig. 4).

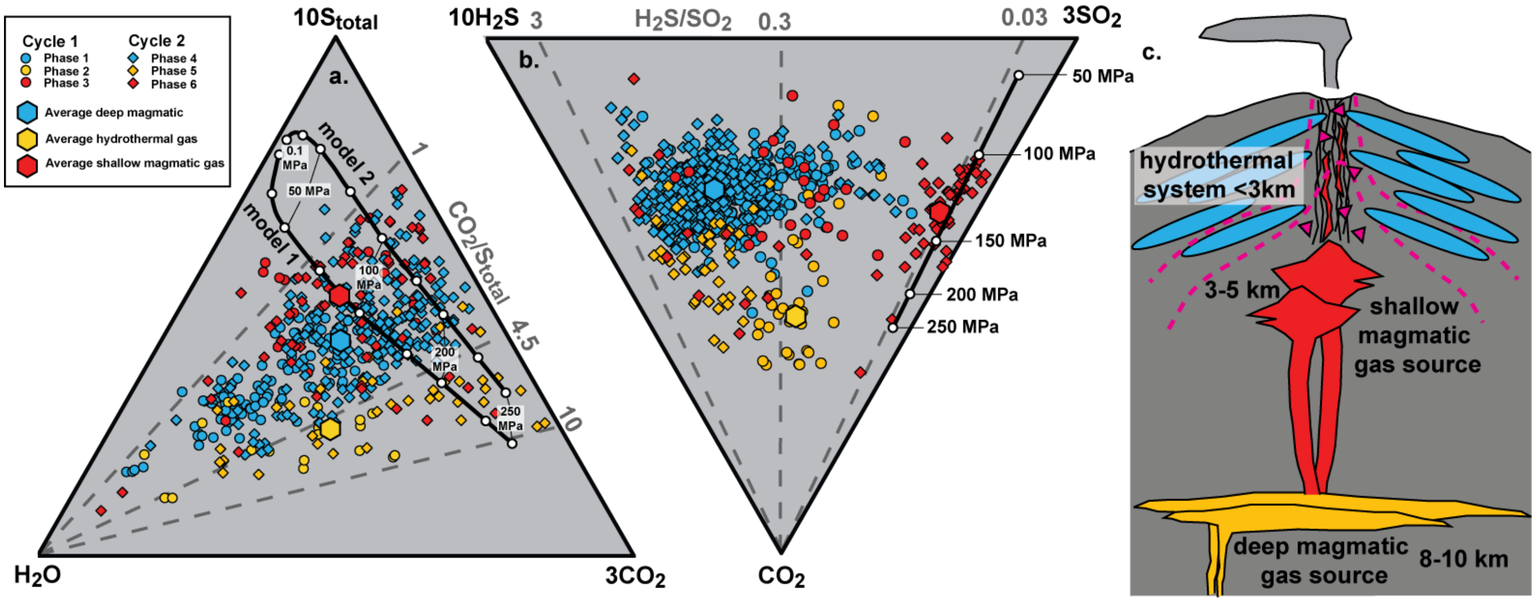

Figure 4. Triangular plots distinguishing gas sources and degassing trends. The left plot shows S_{total} - H_2O - CO_2 relationships. The only periods that show CO_2/S_{total} compositions greater than 4.5 are the precursory periods (orange symbols; phases 2 and 5) to eruptive periods (phases 3 and 6), and emissions during the initial part of the phase 6 eruptive period (Fig. 2). Decompression degassing models [Moretti, et al., 2003] are shown as solid black lines with pressure varied from 250 MPa to 0.1 MPa with melt composition based on melt inclusion data (see supplementary material for details). Models as initialised using melt inclusion compositions from the 1864-1866 eruption at Turrialba (for major elements and S; supplemental materials; Table S2) and nearby Irazú volcano (for CO_2 and H_2O contents; Benjamin, et al., 2007; Wehrmann, et al., 2011]). Model 1 with starting composition of 3 wt% H_2O and QFM +1, model 2 with 2.5 wt% H_2O and QFM +0.5. In plot a, high H_2O compositions are mostly associated gases from hydrothermal and precursory phases probably indicating meteoric water input. Apart from the high H_2O compositions, the gases are consistent with magmatic degassing between >250 MPa and ~100 MPa. In plot b, only model 1 is shown as exsolved gas compositions are recalculated to surface conditions (QFM +3, 0.1 MPa, 650°C). At these conditions the H_2S/SO_2 ratio is fixed at 0.02 independent of original H_2S/SO_2 composition, which is a function of T, P, H_2O, and fO_2. Importantly, the H_2S/SO_2 clearly distinguishes hydrothermal phases 1 and 4 and magmatic degassing, which is characterized by $H_2S/SO_2 < 0.3$. Cartoon on the right shows the magma plumbing system as envisioned from gas compositions and modeling. Pink dashed lines indicate rising vapor-liquid transition and triangles symbolize hydrothermal mineral deposition and breccias.

4.3.1 Deep Magmatic Gas

Pulses of CO_2-rich gas are observed before both the October-December 2014 and the March-May 2015 eruptive episodes (Fig. 2, 4a). The high CO_2/S_t ratio signature of this gas precursor only occurs in the weeks to days prior to energetic explosive eruptions and is not associated with other periods (Fig. 4), implying a distinct gas source. Based on results of decompression degassing models (Fig. 4), we interpret the pulses of CO_2-rich gas as due to degassing of intruding magma batches arriving at deep-mid crustal levels, where CO_2 is preferentially exsolved from the melt over higher solubility S [e.g. *Aiuppa, et al.*, 2007; *Baker and Moretti*, 2011; *Giggenbach*, 1996; *Holloway and Blank*, 1994; *Lesne, et al.*, 2011]. Results of decompression degassing modeling, in particular, suggest that CO_2-rich gases correspond to the magmatic gas exsolved at equilibrium conditions from melt at 200-250 MPa or depths of 8-10 km (Fig. 4)[*Moretti, et al.*, 2003]. An additional key piece of evidence leading to this interpretation is the fact that edifice inflation is an ongoing process at Turrialba (Figure S5), supporting the scenario of magma intrusion.

4.3.2 Shallow Magmatic Degassing during Eruptions

Gases released in phases 3 and 6 follow the pulses of deep magmatic gases (phases 2 and 5) and are closely associated with eruptive activity (Fig. 2). These emissions are characterized by low CO_2/S_t, in the range of 1-2 on average (Fig. 3), which is in agreement with regional trends in magmatic gas ratios [*Aiuppa, et al.*, 2014; *Moussallam, et al.*, 2014]. Comparison with degassing model outputs (Fig. 4) indicate that these syn-eruptive CO_2-poor gases probably originate from magmatic degassing at far shallower conditions (150-75 MPa; 3-5 km) than during phases 2 and 5.

Importantly, the gases released during the first eruptive episode initiated by the 29 October 2014 eruption (phase 3) show a distinct gas composition in terms of H_2S/SO_2 from phase 6. The first eruptive episode shows average H_2S/SO_2 of 0.3, which is about an order of magnitude higher than the average H_2S/SO_2 measured after mid-March 2015 (phase 6). Following the modeling methods of de Moor et al. (2013), we calculate that at expected magmatic conditions (QFM +0.5 to +1.5 and 900 to 1100ºC) the magmatic H_2S/SO_2 ratio at outlet pressure should be in the range of 0.0002 (high T, high fO_2) to 0.25 (low T, low fO_2). Thus, the first eruptive episode may have involved a minor hydrothermal component. Alternatively, gas released during the first eruptive episode may have been magmatic gas equilibrated at lower temperature than the magmatic gas released during the second eruptive episode. Assuming an fO_2 of QFM +1, the average H_2S/SO_2 of 0.3 measured during the first phase would indicate gas equilibration temperature of ~800 ºC, whereas the H_2S/SO_2 of <0.03 during the second period of eruptions implies gas equilibration temperatures of >950 ºC.

The gas emission rates from the two eruptive episodes were also very different. The phase 3 eruptions were preceded by a period of low gas flux, suggesting that degassing pathways were blocked. This concept is supported by field evidence, as the 29 October explosion erupted blocks of highly indurated hydrothermal breccia (Figure S3), which have not been observed in deposits from the latter eruptions. The matrix of these breccias consists of fine rock clasts with intense hydrothermal mineralization, which causes decreased permeability and self sealing that can inhibit the release of hydrothermal vapor and magmatic gas [e.g. *Christenson, et al.*, 2010; *Sillitoe*, 2010]. These types of breccias are common in porphyry deposits, often form diatremes that cross-cut large volumes of intense hydrothermal alteration and mineralization, and can transport hydrothermally altered clasts for > 1km vertically [*Sillitoe*, 2010]. The expulsion of the hydrothermal seal by the 29 October 2014 eruption was followed by the highest gas fluxes observed at Turrialba to date (Fig. 2).

4.3.3 The influence of the hydrothermal system

The influence of the hydrothermal system potentially manifests in various ways: 1. Modification of the composition of gases passing through the hydrothermal system after gas separation from magma, 2. Scrubbing of reactive gases by interaction with meteoric/hydrothermal water, 3. Addition of volatiles through boiling off of hydrothermal liquids and sublimation/combustion of hydrothermal minerals 4. Changes to the permeability of the upper volcanic system.

The influence of the hydrothermal system at Turrialba is clearly demonstrated through the abundance of H_2S in the gas emissions during phases 1 and 4. The dominance of H_2S over SO_2 cannot be explained by magmatic degassing conditions at reasonable redox and temperature conditions for an arc-like magma [e.g. *de Moor, et al.*, 2013b], and any H_2S/SO_2 ratio greater than 0.3 is hydrothermally influenced (section 4.3.2), pointing to reactions involving magmatic SO_2 and hydrothermal fluids.

One mechanism to produce H_2S is by disproportionation of SO_2 [e.g. *Symonds, et al.*, 2001]:

$$4SO_{2(g)} + 4H_2O_{(l)} \rightarrow H_2S_{(g)} + 3H_2SO_{4(aq)} \qquad \text{eq. 1}$$

This reaction is commonly called upon to explain scrubbing of SO_2 by hydrothermal systems, which would be expected to lower SO_2 flux, increase H_2S/SO_2, and also increase CO_2/S_t through bulk removal of S from the gas phase. At Turrialba, this reaction was probably significant during phase 1 passive degassing, where SO_2 fluxes were relatively low and H_2S/SO_2 and CO_2/S_t were slowly increasing. However, in general, the CO_2/S_t during hydrothermal phases 1 and 4 is only slightly higher than that of the shallow magmatic gases, suggesting that scrubbing by the hydrothermal system was not very efficient, most likely due to the strong gas flux and availability of relatively dry degassing pathways (i.e. 2010 and 2012 vents; Movie S1).

Alternatively, stored hydrothermal sulfur can be released during volcano reactivation, either as H_2S or SO_2 [*de Moor, et al.*, 2005; *Giggenbach*, 1987; *Oppenheimer*, 1996]. Gases in moderate to high temperature hydrothermal systems are usually saturated with respect to elemental sulfur [e.g. *Delmelle, et al.*, 2000]:

$$SO_2 + 2H_2S \rightarrow 3S_0 + 2H_2O \qquad \text{eq. 2}$$

Heating of the hydrothermal system and previously deposited native S drives this reaction to the left, resulting in 2 moles of H_2S and 1 mole of SO_2 for every 3 moles of elemental S consumed, with an expected H_2S/SO_2 ratio of 2, or similar to the maximum H_2S/SO_2 observed in the intense degassing period following phase 3 eruptions. Combustion of native S has also been directly observed in the field (Movie S1), presenting evidence that a further hydrothermal contribution to the gas emissions is derived from:

$$S_{0(s,l)} + O_{2(g,\, aq)} \rightarrow SO_{2(g)} \qquad \text{eq. 3}$$

under shallow to surficial oxidizing conditions. In this case, oxygen can either be supplied from air or from air saturated meteoric water. Alternatively, under deeper reducing conditions a potential reaction would be:

$$S_0 + H_2 \rightarrow H_2S \qquad \text{eq. 4}$$

as H_2 is a significant component of hydrothermal and magmatic gases at Turrialba [*Vaselli, et al.*, 2010].

Importantly, the total gas flux was highest during period 4, which was also a period of high H_2S/SO_2 values. The coincidence of very high gas flux and high H_2S/SO_2 probably reflects large scale S expulsion from the hydrothermal system after shallow magma intrusion, degassing, and heat transfer during phase 3. Interestingly, the expulsion of the hydrothermal system is also accompanied by high CO_2 fluxes (Fig 2.). Recently, Malowany et al. [2014] have found that C isotope composition of all but the highest temperature gas emissions at Turrialba are affected by hydrothermal fractionation. The large CO_2 fluxes observed during phase 4 could thus partially represent remobilization of CO_2 stored chemically or physically in the hydrothermal system [*Chiodini, et al.*, 2015; *Dawson, et al.*, 2016].

Volatiles can be trapped in volcanic edifices chemically in hydrothermal fluids (dissolved S or C species) or as hydrothermal minerals (e.g. native sulfur, sulfides, sulfates, carbonates). Additionally, gases can be physically trapped below low permeability hydrothermal seals [e.g. *Christenson, et al.*, 2010]. Blocked conduits can lead to pressurization below hydrothermal seals and explosive eruption. Phase 2 demonstrates low gas fluxes suggesting sealing of the shallow conduits prior to the 29 October eruption (Figure S6), providing a reasonable explanation for the explosivity of that blast. After this eruption and intense volcano tectonic seismicity and fracturing, the permeability of the volcanic edifice increased significantly, allowing the expulsion of hydrothermally stored volatiles during phase 4. A second deep magmatic pulse was superimposed on this ongoing process during phase 5 and hydrothermal volatiles were still involved in the first eruptions of phase 6. These eruptions were most likely associated with the rise of a magma pulse into the shallow plumbing system and opening of new conduits that allowed high temperature magmatic gas ($H_2S/SO_2 << 0.3$) to reach the surface without hydrothermal interaction.

5. EVOLUTION OF THE ERUPTIVE ACTIVITY AND IMPLICATIONS

Since the first ash eruption at Turrialba in 2010, the key questions have been whether a new magma body is rising to the surface, whether and how a magmatic eruption will occur, and for how long the eruptive activity will continue. By summing averaged daily gas flux measurements, we estimate that Turrialba has released ~2.04 Mt of SO_2 through persistent degassing since 2008, which requires a magma source of ~0.3 km^3 (Table 2). In comparison, Reagan et al. [2006] estimated a volume of <0.03 km^3 for the 1864-1866 eruptive products. However, the amount of gas emitted *per se* gives no indication of the timing of gas separation from the magma, and as such there remains the possibility that gas has been accumulated in the crust over tens to thousands of years during slow magma crystallization [*Christopher, et al.*, 2015]. Indeed, our data do suggest that large volumes of volatiles were stored in the hydrothermal system and released in phase 4 following the 29 October 2014 eruption. Degassed melt inclusions with more evolved compositions than matrix glass further point to the possibility that old, previously degassed magma is involved (either passively or actively) in eruptions at Turrialba, suggesting that some of the emitted gas could also be old. Instability in a system of accumulated magmatic gas beneath a well-sealed hydrothermal system could conceivably cause small phreatic eruptions that do not lead to large and explosive magmatic eruption. However, gas compositional changes consistent with decreasing pressure of melt degassing, the observations of edifice inflation, and the presence of fresh glassy clasts in the eruptive products taken together provide strong support for a model involving magma rising from the deep to shallow crust. Our data do suggest that a significant portion of the total emitted sulfur is remobilized from the hydrothermal system, which could potentially store volatiles for considerable periods of time between eruption episodes. Therefore, the estimation of magma volume based on sulfur emissions should be considered a maximum, as a significant but unquantifiable proportion may not be directly degassed by the rising magma bodies but rather be stored hydrothermal sulfur.

Table 2. Sulfur budget and magma volume calculations for Turrialba, calculated based on flux monitoring data since 2008.

SO_2 emitted Tons	H_2S emitted* Tons	Total S emitted Tons	Melt S content wt%	Mass melt degassed kg	Magma vol km^3
2.04×10^6	6.12×10^5	1.60×10^6	0.2	7.99×10^{11}	0.296

* The average H_2S/SO_2 ratio of 0.6 from Multi-GAS data (Figure 2) is assumed in order to estimate total H_2S emissions

Monitoring of multiple gas components allows us to see through the hydrothermal overprint in the gas signatures and recognize two cycles of magmatic degassing (phases 1-3 and phases 4-6), progressing from deep magmatic CO_2-rich gas to shallow magmatic SO_2-rich gas, which is accompanied by eruptive activity. High frequency monitoring of volcanic gas compositions allowed by technological advances in the last decade are repeatedly showing the value of these measurements in forecasting and understanding volcanic eruptions [*Aiuppa, et al.*, 2007; *Burton, et al.*, 2007; *de Moor, et al.*, 2016; *Oppenheimer, et al.*, 2011]. Modeling of the compositional trends strongly suggests decompression degassing of pulses of magma arriving from deep to shallow crustal levels. The variations are not consistent with a single volatile source of old stored magmatic gas, as this would be expected to be compositionally homogenous without variations controlled by pressure dependent gas solubility in melt.

Ashes erupted over the measurement period are all dominated by hydrothermally altered material, however there has been discussion on whether there is juvenile material present in the ashes or not since the first eruption in Turrialba in 2010 [*Reagan, et al.*, 2011], a discussion which entered the public forum (http://www.ticotimes.net/2015/03/13/costa-ricas-turrialba-volcano-appears-to-erupt-lava; http://www.ticotimes.net/2015/04/11/possible-lava-rocks-indicate-turrialba-volcano-may-have-entered-more-dangerous-phase) and has even reached high levels of Costa Rican government. The composition of the fresh glassy component in these complex ash samples is similar to that of magmatic clasts derived from the 1864-1866 eruption (Figure 3) leaving us with the seemingly irreconcilable conundrum of whether this material represents erosion of old magmatic (or phreatomagmatic) deposits or newly quenched magma reaching the surface.

Our high frequency gas composition data, the first reported for vent-opening eruptions, demonstrate that the transition from phreatic to phreatomagmatic activity can be monitored using in situ Multi-GAS, providing a more reliable, near-real time, and safer indication of the transition from hydrothermally influenced to magmatically dominated eruptive conditions than examination of ash samples. The gas compositions as measured by Multi-GAS demonstrate a first order change from hydrothermal (presence of H_2S) to magmatic (H_2S/SO_2 close to zero) over the period of unrest. The unambiguous change in gas chemistry combined with deformation monitoring convincingly argue for rising magma that has established open vents to the surface. Using the abrupt change in H_2S/SO_2, we propose that the transition from "phreatic" to "phreatomagmatic" dominated conditions occurred between the 17th and 20th March. Based on the combined gas and deformation data, it seems likely that the fresh clasts in the recent ashes do in fact represent new magma arriving at the surface.

The general similarity in the progression of the activity and the observation that the composition of the fresh component in the ash is similar to that of the 1864-1866 eruption suggests that it is reasonable to use the previous eruption as a model for preparation plans for the current crisis. If so, the current eruptions are probably reflecting a similar transition from phreatic to phreatomagmatic as that recorded in geological record (Figure S 4). If the progression of eruptive activity continues in a similar fashion to the 1864-1866 eruption, continued eruptive activity would be expected in the future, perhaps terminating with magmatic eruptions. The volume of gas released from Turrialba suggests the intrusion of a volume (0.3 km^3) of the same order of magnitude to that driving the1864-1866 eruption (<0.03 km^3 erupted), because arc magmas typically release about an order of magnitude more gas than can be supplied by the amount of erupted magma [e.g. *Wallace and Edmonds*, 2011]. However, we cannot exclude the possibility that the magma body stalls and fails to erupt, or that a more silicic and voluminous eruption [such as the 2000 ka subplinian eruption; *Reagan, et al.*, 2006] takes place. Furthermore, a significant portion of the sulfur emitted from Turrialba from 2008-present could have been remobilized from an extensive hydrothermal system, as is exemplified by high SO_2 flux and H_2S/SO_2 during phase 4 degassing (Figure 2).

Recent studies have also shown that large reservoirs of carbon can be stored in and released from hydrothermal systems [*Chiodini, et al.*, 2015; *Dawson, et al.*, 2016]. During the period of study (June 2014 – April 2015) we estimate that a total of ~0.86 Mt of CO_2 has been released from Turrialba based on daily calculated CO_2 fluxes. Of this total, ~0.52 Mt of CO_2 was released during phase 4 degassing, which followed breaking of the hydrothermal seal by the 29 October eruption, and is associated with hydrothermal values of H_2S/SO_2. Thus, a significant proportion of volcanic CO_2 may be accumulated beneath hydrothermally sealed carapaces and released after relatively small vent-opening eruptions at volcanoes with extensive and long-lived hydrothermal systems.

6. CONCLUSION

Turrialba volcano continues to represent a significant and growing threat to the society and economy of Costa Rica. Here, we show that periods of activity are the due to the arrival of distinct magma batches from the deep crust to a shallow crustal magma reservoir. CO_2-rich gas pulses derived from deep degassing occur before eruptive episodes, and ash emissions are accompanied by shallow magmatic degassing. The hydrothermal system has continued to play a significant role in voluminous volcanic degassing at Turrialba over decades of unrest.

The transition from phreatic to phreatomagmatic eruptive behavior is a fundamental change in any evolving volcanic crisis. Phreatomagmatic eruptions tend be more violent, prolonged, and emit fine ash that can travel long distances [*Morrissey, et al.*, 2000; *Nakada, et al.*, 1995]. Here, we have shown that volcanic gas monitoring can be used to identify this transition, which is quicker, safer, and less ambiguous than ash component analyses. Specifically, high frequency monitoring of H_2S/SO_2 is a valuable parameter for assessing the relative contributions of hydrothermal and magmatic sources during eruptive crises. Variations in these contributions can be large and occur rapidly. At Turrialba, the transition from hydrothermal to purely magmatic degassing took place between the 17th and 20th March, which coincided with numerous disruptions to air traffic at San Jose international airport (12, 21, and 23 March, 4 and 18 May). If phreatomagmatic eruptions continue at Turrialba, the tourism-based economy of Costa Rica will suffer. Numerous examples from the past decade show that high frequency monitoring of volcanic gases is consistently revealing important new insights into eruptive behavior with clear implications for volcanic hazard assessment.

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