

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 significantly 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 seems probable but remains a matter of debate as ash deposits are dominated by hydrothermal material. Here, we use high frequency gas monitoring to track the behavior of the volcano between 2014 and 2015, and to decipher magmatic vs. hydrothermal contributions to the eruptions. Pulses of deeply-derived CO₂-rich gas (CO₂/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 shallowly derived sulfur-rich magmatic gas emissions. 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 magma ascending through the deep reservoir to shallow crustal levels. 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. H₂S/SO₂ 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 SO₂ and H₂S/SO₂>1) followed, suggesting boiling off of the hydrothermal system. The gas emissions show a remarkable shift to purely magmatic composition (H₂S/SO₂<0.05) during the second eruptive period, reflecting the depletion of the hydrothermal system or the establishment of high temperature conduits bypassing remnant hydrothermal reservoirs, 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. *Cashman and Hoblitt*, 2004; *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, 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; *Vaselli et al.*, 2010]. 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 ratios measured in situ using a fixed Multi-component Gas Analyzer (Multi-GAS) and gas fluxes measured by scanning Differential Optical Absorption Spectrometer (DOAS) 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.

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 active 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 recent 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].

Variations in volatile chemistry along the Central American Arc reflect along-arc changes in the influence of mantle versus slab-derived fluids. 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 $^3\text{He}/^4\text{He}$ value ($R_c/R_a = 8.1$) in the region [Di Piazza *et al.*, 2015], consistent with its slightly "back-of-the-arc" location and strong mantle signature. The chemical and isotopic compositions of C and He in fumarolic gas emissions from Turrialba and Irazú suggest that these volatiles have a greater mantle signature at these volcanoes in comparison with 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.* [2013a; see supplemental materials]) show a range of values between $+0.2$ ‰ and $+7.3$ ‰ with an average of $+3.4 \pm 0.5$ ‰ [de Moor *et al.*, 2013b], which falls closer to typical values measured in high temperature arc gases ($\sim +5$ ‰) than to values observed in purely mantle-derived gases [$\sim +0$ ‰; de Moor *et al.*, 2013a; 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; González *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 SO₂ 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.

A new and more vigorous 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. 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) until 18 May. The most energetic explosions during this period occurred on 12 March 2015 (Fig. 1; Fig. 2) 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. Small intracaldera pyroclastic flows have occurred

since 2015, and the first pyroclastic flow to leave the crater occurred in May 2016. 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 30 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 resulting in flight cancellations. The 12 March 2015 eruption in particular (Figure 1b) had significant impact, causing the closure of 12 schools, the evacuation of farms within 2 km of the crater, and causing 111 flights to be cancelled at SJO international airport, affecting ~7000 passengers.

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, capturing a significant change in activity from passive degassing with very sparse isolated ash emissions (~1 event per year) pre-2014 to much more frequent eruptive activity following the 29 October 2014 eruption. The Multi-GAS instrument measures gas concentrations of SO₂, H₂S, CO₂, and H₂O 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 (molar H₂S/SO₂, CO₂/SO₂, H₂O/SO₂) 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; de Moor *et al.*, 2016], 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 SO₂ 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 the sky continuously during daylight hours to measure the integrated absorption of UV light by SO₂ in the plume. Flux is estimated based on the integrated SO₂ 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 SO₂ emission rates with gas ratios (converted from molar ratios to mass based concentration ratios) expressed with SO₂ as the denominator result in estimations of the fluxes of CO₂, H₂S, and H₂O.

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. 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.

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 $\text{H}_2\text{S}/\text{SO}_2 > 0.3$ to be a relatively unambiguous indicator of hydrothermal interaction; Figure 3). 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. $\text{SO}_2 + \text{H}_2\text{S}$), moderate $\text{H}_2\text{S}/\text{SO}_2$ of 0.2 to 0.7, and $\text{H}_2\text{O}/\text{SO}_2$ 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 $\text{H}_2\text{S}/\text{SO}_2$ 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 $\text{H}_2\text{S}/\text{SO}_2 \sim 0.2$ to ~ 0.7 . Significantly, the gas fluxes increase dramatically only after the 9 December eruption (Phase 4), coupled with further increase in $\text{H}_2\text{S}/\text{SO}_2$ 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 $\text{H}_2\text{S}/\text{SO}_2$ (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 $\text{H}_2\text{S}/\text{SO}_2$ (<0.1) with the transition to more energetic eruptions (Phase 6).

4.2 GLASS COMPOSITIONS: THE DEBATE OF NEW VERSUS OLD MAGMA

Table 1 and Figure 4a compare the composition of most pristine matrix glasses from the 29 October 2014 eruption with the 1864-1866 eruption, showing that the major element 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 (Figure 4a, See Supplementary Text, Table S2, and Figures S1 for petrologic results and discussion). We believe that at least some of these fresh-looking glassy and vesicular clasts represent true juvenile material, however it is difficult to ascertain with certainty whether these clasts were molten at the time of eruption represent the composition of the magma driving the current unrest.

Some of the fresh-looking glassy clasts in our ash sample from the 29 October 2014 eruption show anomalously high F contents (Fig. 4b; 2 wt.% to 5.5 wt.%), which cannot be a primary magmatic signature. Rather, the clasts with very high F content are interpreted to reflect “cryptic” alteration. This process probably occurs below the glass transition temperature, whereby HF-rich gas exsolved at shallow levels in the magmatic plumbing system interact with recently emplaced (though difficult to quantify when) quenched and degassed magma (Reagan et al., 2011). However, another possibility is that the alteration

occurs very rapidly during the eruption itself due to interaction with HF-rich gas in the sub-aerial environment [*Spadaro et al.*, 2002].

The crux of the argument as to whether the fresh-looking clasts are “juvenile” or not lies in quantifying when liquid melt quenched to glass and how fast alteration (cryptic or obvious) processes occur. Presently, not enough constraints on this timing are available to determine with confidence whether the fresh-looking clasts represent the eruption of new magma after rising rapidly from the mantle through the crust [e.g. *Ruprecht and Plank*, 2013], or remobilization of old (or even recently emplaced but not erupted) magmatic material entrained during hydrothermally driven eruptions [*Cashman and Hoblitt*, 2004; *Giggenbach et al.*, 1990; *Pardo et al.*, 2014; *Suzuki et al.*, 2013; *Williams et al.*, 1986]. Furthermore, newly intruded but unerupted magma can reactive overlying magma through the introduction of volatiles and heat, causing eruption of magma that may not be the direct parent of the associated emitted volatiles [e.g. *Claiborne et al.*, 2010; *Larsen et al.*, 2010].

Figure 5 compares magma chemistry 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 a large number of inclusions with higher K₂O than their respective matrix glasses, suggesting entrainment of a significant portion of old, previously degassed magma in past eruptive products.

The composition and morphology of the fresh-looking clasts from one ash sample (29 October 2014 eruption) alone cannot fully or adequately resolve the key question for monitoring of whether “new” magma is involved in the present eruptions or not. While magma petrology/geochemistry/texture all provide rather equivocal results, with terminology becoming problematic as the discussion evolves, the short-term variations in gas

compositions we observed at Turrialba (Fig. 2) require rapidly 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 $\text{CO}_2/\text{S}_{\text{total}}$ precedes both eruptive episodes, showing promise of a precursory signal useful in eruption forecasting.

High $\text{CO}_2/\text{S}_{\text{total}}$ (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.

Aiuppa et al. (2007) similarly observed high CO_2/SO_2 prior to eruptions at Etna, suggesting that precursory short-term pulses in CO_2 may be a common occurrence at many volcanoes.

Another striking feature of our gas composition time-series is the abrupt order of magnitude scale change in $\text{H}_2\text{S}/\text{SO}_2$ that coincided with the 12 March 2015 eruptions. To our knowledge, this is first report of dramatic short term changes in $\text{H}_2\text{S}/\text{SO}_2$ correlated with eruptive activity.

In order to explain the sources and processes responsible for the tumultuous variations in composition, we have conducted analysis of the $\text{CO}_2\text{-SO}_2\text{-H}_2\text{S-H}_2\text{O}$ system (Figure 6), 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)

4.3.1 Deep Magmatic Gas

Pulses of CO₂-rich gas are observed before both the October-December 2014 and the March-May 2015 eruptive episodes (Fig. 2, 6a). The high CO₂/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. 6), implying a distinct gas source. Based on results of decompression degassing models (Fig. 6), we interpret the pulses of CO₂-rich gas as due to degassing of intruding magma batches arriving at deep-mid crustal levels (Figure 7), where CO₂ 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 CO₂-rich gases correspond to the magmatic gas exsolved at equilibrium conditions from melt at 200-250 MPa or depths of 8-10 km (Fig. 6)[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 CO₂/S_t, in the range of 1-2 on average (Fig. 6), 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. 6) indicate that these syn-eruptive CO₂-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 $\text{H}_2\text{S}/\text{SO}_2$ from phase 6. The first eruptive episode shows average $\text{H}_2\text{S}/\text{SO}_2$ of 0.3, which is about an order of magnitude higher than the average $\text{H}_2\text{S}/\text{SO}_2$ 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 1100°C) the magmatic $\text{H}_2\text{S}/\text{SO}_2$ ratio at outlet pressure should be in the range of 0.0002 (high T, high $f\text{O}_2$) to 0.25 (low T, low $f\text{O}_2$). 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 $f\text{O}_2$ of QFM +1, the average $\text{H}_2\text{S}/\text{SO}_2$ of 0.3 measured during the first phase would indicate gas equilibration temperature of ~800 °C, whereas the $\text{H}_2\text{S}/\text{SO}_2$ of <0.03 during the second period of eruptions implies gas equilibration temperatures of >950 °C.

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 H₂S in the gas emissions during phases 1 and 4. The dominance of H₂S over SO₂ 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 H₂S/SO₂ ratio greater than 0.3 is hydrothermally influenced (section 4.3.2), pointing to reactions involving magmatic SO₂ and hydrothermal fluids.

One mechanism to produce H₂S is by disproportionation of SO₂ [e.g. *Kusakabe et al.*, 2000]:



This reaction is commonly called upon to explain scrubbing of SO₂ by hydrothermal systems, which would be expected to lower SO₂ flux, increase H₂S/SO₂, and also increase CO₂/S_t through bulk removal of S from the gas phase. At Turrialba, this reaction was probably significant during phase 1 passive degassing, where SO₂ fluxes were relatively low and H₂S/SO₂ and CO₂/S_t were slowly increasing. However, in general, the CO₂/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).

Alternatively, stored hydrothermal sulfur can be released during volcano reactivation, either as H₂S or SO₂ [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]:



Heating of the hydrothermal system and previously deposited native S drives this reaction to the left, resulting in 2 moles of H₂S and 1 mole of SO₂ for every 3 moles of elemental S consumed, with an expected H₂S/SO₂ ratio of 2, or similar to the maximum H₂S/SO₂ observed in the intense degassing period following phase 3 eruptions. Combustion of native S has also been directly observed in the field (burning native sulfur in the west crater), presenting evidence that a further hydrothermal contribution to the gas emissions is derived from:



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:



as H₂ is a significant component of hydrothermal and magmatic gases at Turrialba [Vaselli *et al.*, 2010].

Acidification of hydrothermal aquifers is yet another mechanism that could liberate stored volatiles. Hyper-acid hydrothermal fluids (such as pH<1 volcanic lakes) can be almost transparent to volcanic gases [Capaccioni *et al.*, 2016; de Moor *et al.*, 2016; Tamburello *et al.*, 2015] whereas less extreme hydrothermal conditions significantly scrub acidic volcanic gases [e.g. Symonds *et al.*, 2001]. Thus, as a hydrothermal reservoir experiences more acidic magmatic gas input, it may release dissolved volatiles such as sulfur and chlorine.

Importantly, at Turrialba the total gas flux was highest during period 4, which was also a period of high H₂S/SO₂ values. The coincidence of very high gas flux and high H₂S/SO₂ 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 CO₂ fluxes (Fig 2.). The large CO₂ fluxes observed during phase 4 could thus partially represent remobilization of CO₂ 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 ($H_2S/SO_2 \ll 0.3$) 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 suggests emplacement of new magmatic intrusions of ~ 0.3 km³ in total (Table 2). A negligible volume of this magma has been erupted, as the new ashes are still dominated by altered material and the ash volumes erupted are too small to accurately constrain in a meaningful sense. In comparison, Reagan et al. [2006] estimated an eruptive volume of < 0.03 km³ for the 1864-1866 eruption products.

In conjunction with continuous inflation since 2010 and increasing component of fresh-looking magmatic clasts, voluminous degassing strongly suggests intrusion of new magma. However, the amount of gas emitted *per se* gives no indication of the timing of gas separation from the magma, and as such (without strong independent evidence such as inflation) 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 (but still mobile) magma is involved (either passively or actively) in

eruptions at Turrialba, perhaps suggesting that some of the emitted gas could also be remnant from previous intrusions (pre 1866). 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 repetitive magma decompression events provides strong support for a model involving magma batches rising from the deep to shallow crust (Figure 7). Our data do suggest that a significant (but unquantifiable) portion of the total emitted sulfur is remobilized from the hydrothermal system, which could potentially store volatiles for considerable periods of time between eruptive episodes. Therefore, the estimation of new intruded magma volume based on sulfur emissions should be considered a maximum, as a proportion of the emitted sulfur may not be directly degassed by the rising magma bodies but rather be stored hydrothermal sulfur remobilized during reactivation of the volcano.

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 CO₂-rich gas to shallow magmatic SO₂-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 logically this would be expected to be compositionally homogenous without major variations related to pressure dependent gas solubility in melt.

Ash deposits 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 ash 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 (Figures 4,5) leaving us with the seemingly irreconcilable conundrum (at least geochemically speaking) 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 reliable, near-real time, and safe indication of the transition from hydrothermally influenced to magmatically dominated eruptive conditions. The gas compositions as measured by Multi-GAS demonstrate a first order change from hydrothermal (presence of H₂S) to magmatic (H₂S/SO₂ 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 H₂S/SO₂, 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 (Figure S2), 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 [González *et al.*, 2015], continued eruptive activity would be expected in the future, perhaps terminating with magmatic eruptions producing material similar in composition to the 1864-1866 eruption (this work). 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 the 1864-1866 eruption ($<0.03 \text{ km}^3$ 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 [Moran *et al.*, 2011], 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 $\text{H}_2\text{S}/\text{SO}_2$ 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 $\sim 0.86 \text{ Mt}$ of CO_2 has been released from Turrialba based on daily calculated CO_2 fluxes. Of this total, $\sim 0.52 \text{ Mt}$ 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 $\text{H}_2\text{S}/\text{SO}_2$. 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 due to the arrival of distinct magma batches from the deep crust to a shallow crustal magma reservoir. CO₂-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 a more than a decade of unrest.

The transition from phreatic to phreatomagmatic eruptive behavior is a fundamental change in any evolving volcanic crisis. The reactivation of Turrialba has been an extraordinarily slow progression, allowing detailed study of the evolution towards magmatic conditions at a volcano with an extensive hydrothermal system. Phreatomagmatic eruptions tend to 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 H₂S/SO₂ 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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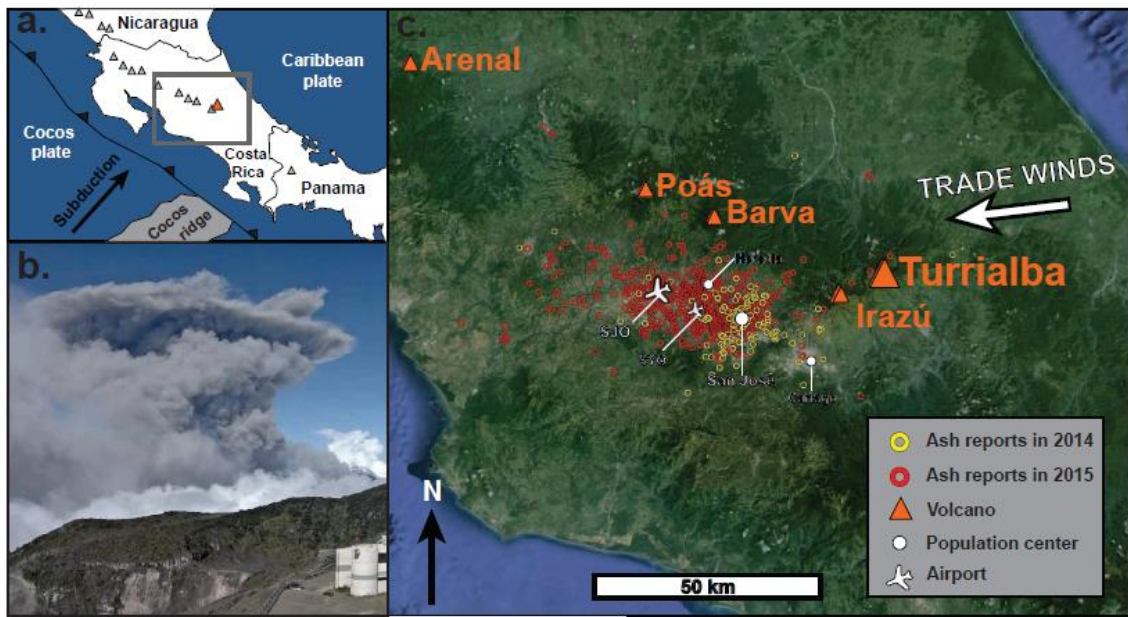


Figure 1. a. Tectonic setting of Turrialba volcano (orange triangle). Grey triangles indicate other volcanoes of the Central American Arc and the grey box indicates the area shown in panel c. b. Explosive eruption at Turrialba on 12 March 2015, as captured by an OVSICORI webcam located on the summit 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)

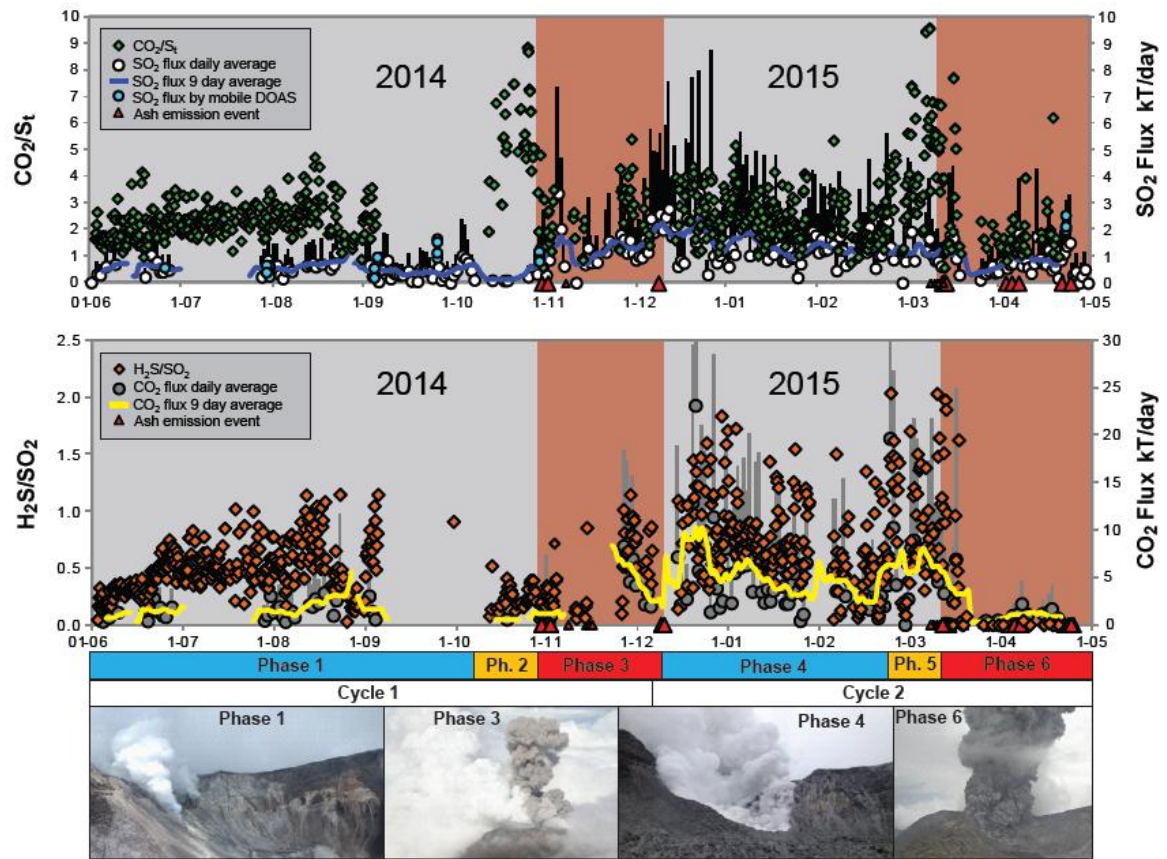


Figure 2. Time series of gas fluxes and gas compositions at Turrialba volcano from June 2014 until May 2015. Daily mean flux values are indicated by circles and associated bars indicate the 75th percentile of individual days. Blue and yellow lines indicate 9 day moving average of the gas flux. Diamonds 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 SO₂ flux measured by scanning DOAS and CO₂/S_{total} where S_{total} represents SO₂+H₂S. Importantly, clear peaks occur in CO₂/S_{total} weeks prior to both eruptive periods. The highest SO₂ fluxes occurred after the vent-opening eruptions in 2014 followed by a relatively steady decrease. Lower time series plot shows CO₂ flux (calculated based on SO₂ flux and CO₂/SO₂) and H₂S/SO₂ as measured by Multi-GAS. Importantly, H₂S/SO₂ drops to purely magmatic values after the first series of eruption in 2015. H₂S tracks the influence of hydrothermal fluids at Turrialba, and the time series shows that the peak in CO₂/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 H₂S/SO₂. Phases 2 and 5 precede the eruptive phases and display high CO₂/S_t with variable hydrothermal influence. Phases 3 and 6 are defined by eruptive activity and

show low CO_2/S and low $\text{H}_2\text{S}/\text{SO}_2$ 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

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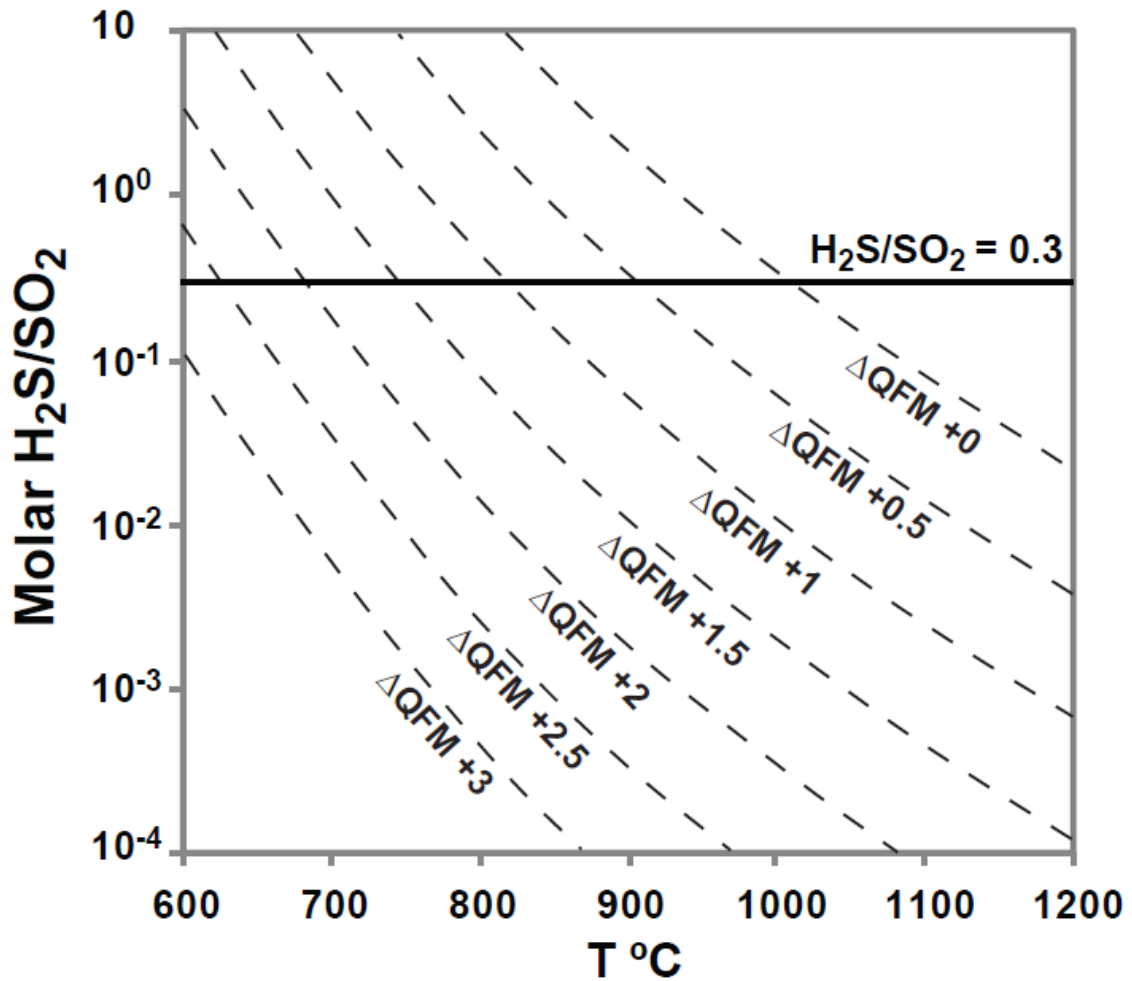


Figure 3. Plot of modeled $\text{H}_2\text{S}/\text{SO}_2$ as a function of temperature and oxygen fugacity ($f\text{O}_2$), at 1 bar pressure for a volcanic gas composition containing 95% H_2O . The equilibration $f\text{O}_2$ of the Turrialba gas emissions was estimated by Mousallam et al. (2014) to be between $\Delta\text{QFM} +1.5$ and $+3$, and the temperature of Turrialba gas vents has been between 600°C and 800°C prior to the October 2014 eruption (robust T measurements have not been possible thereafter). Thus, at reasonable $f\text{O}_2$ and temperature conditions for the period of MultiGAS measurements ($\Delta\text{QFM} > +1.5$ and $T > 600^\circ\text{C}$) magmatic gas emissions are strongly dominated by SO_2 . For the purposes of discussion, we assume that $\text{H}_2\text{S}/\text{SO}_2 > 0,3$ reflects relatively unambiguous contribution of hydrothermal H_2S to gas emissions, acknowledging that this value is rather arbitrary. See de Moor et al., (2013) for full modeling methods and relevant references.

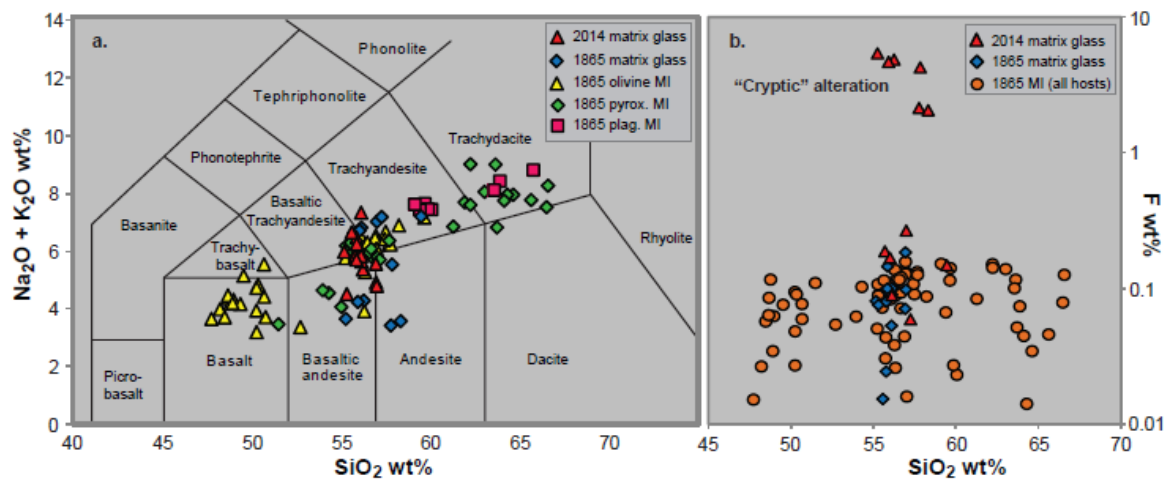


Figure 4. Plot a shows total alkalis vs silica classification diagram comparing the composition of fresh-looking clasts in the 29 October 2014 ash (2014 matrix glass) with 1864-1866 magma compositions (1865 matrix glass, olivine melt inclusions, pyroxene melt inclusions and plagioclase melt inclusions). Plot b shows fluorine concentration in wt% versus silica. Some of fresh-looking clasts in the 29 October 2014 ash show anomalously high F contents, interpreted to reflect “cryptic” alteration due to pre-eruptive (but post cooling below glass transition temperature) interaction with F-rich gas/liquid.

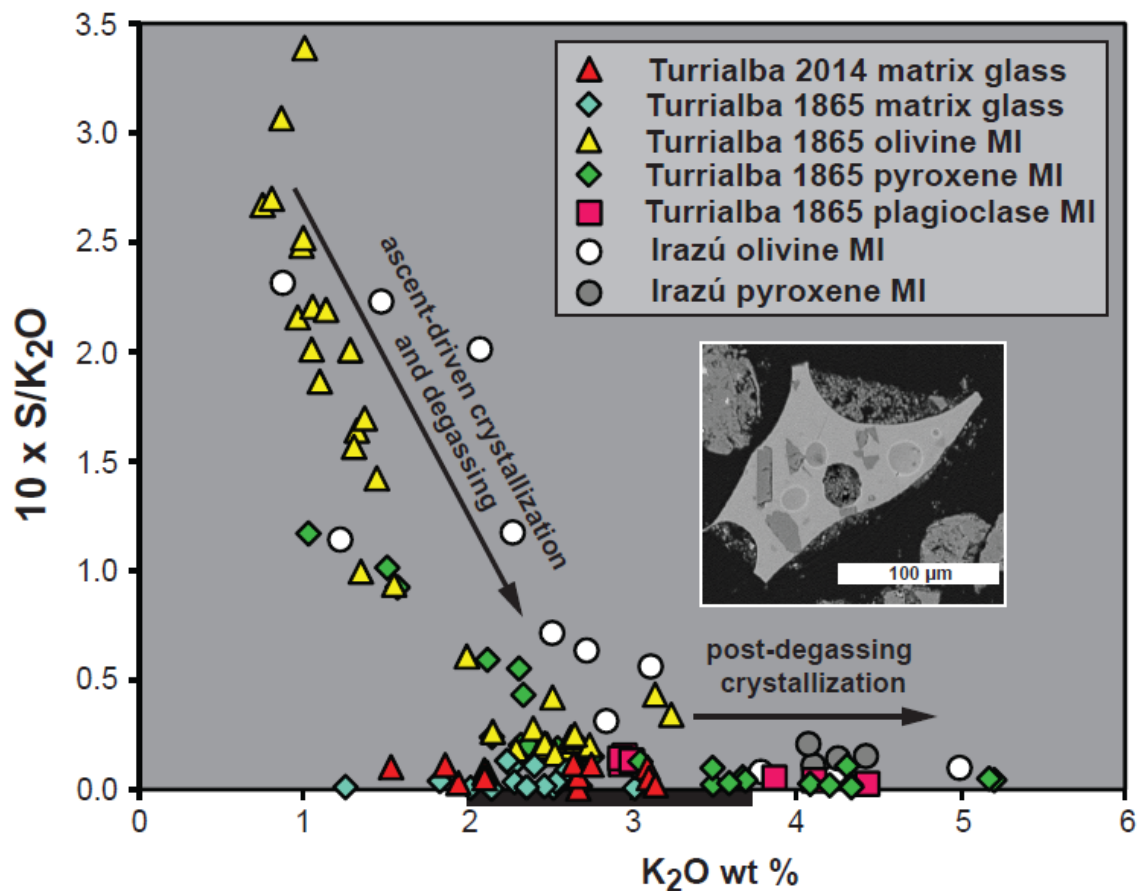


Figure 5. Plot of $10xS/K_2O$ versus K_2O with 2014 matrix glasses, 1865 melt inclusions and melt glasses, and melt inclusions from nearby Irazú volcano. Olivine-hosted melt inclusions (yellow triangles) from the 1865 eruption are sulfur-rich and K_2O -poor, representing primitive undegassed melt. Matrix 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_2O 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_2O content of Irazú matrix glasses [*Alvarado*, 1993], again overlapping with Turrialba compositions but extending to higher K.

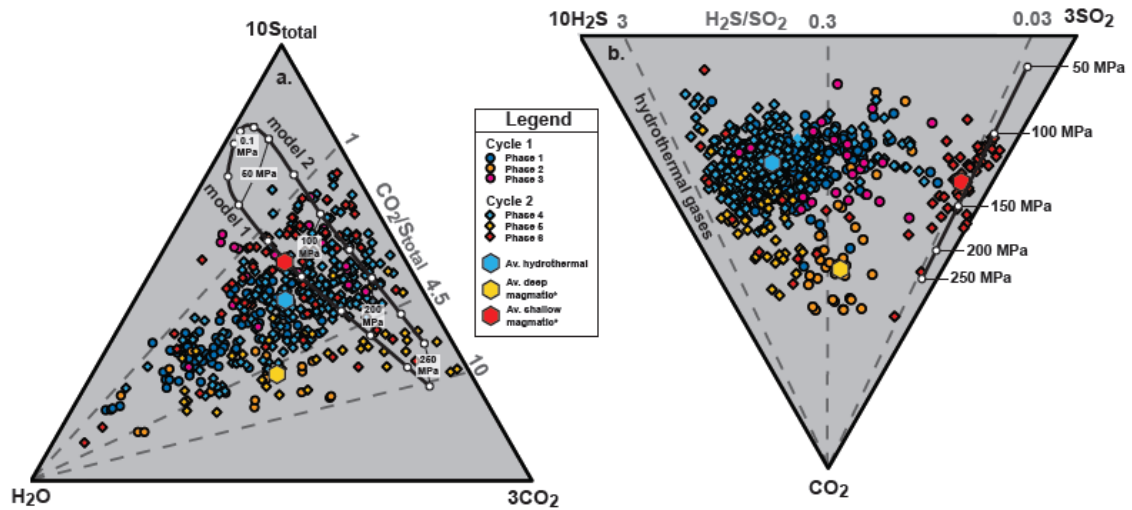


Figure 6. Triangular plots distinguishing gas sources and degassing trends. Plot a shows $S_{\text{total}} - \text{H}_2\text{O} - \text{CO}_2$ and plot b shows $\text{H}_2\text{S} - \text{SO}_2 - \text{CO}_2$. Panel c shows a conceptual model for the Turrialba plumbing system based on the gas compositions. In plot a, the only periods that show $\text{CO}_2/S_{\text{total}}$ compositions greater than 4.5 are the precursory periods (yellow-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. Initial undegassed melt composition are based on melt inclusion data (see supplementary material for details; Tables S2 and S3) from the 1864-1866 eruption at Turrialba (for major elements and S; supplemental materials; Table S2), as well as the available data for CO_2 and H_2O contents from nearby Irazú volcano (; Benjamin, et al., 2007; Wehrmann, et al., 2011]). The starting composition for Model 1 has 3 wt% H_2O , 200 ppm CO_2 , 2000 ppm S, whereas model 2 starting composition has 2.5 wt% H_2O , 200 ppm CO_2 , 2000 ppm S. In plot a, high H_2O compositions are mostly associated with gases from hydrothermal and precursory phases indicating meteoric (hydrothermal) 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; Moussallam et al., 2014). At these conditions the $\text{H}_2\text{S}/\text{SO}_2$ ratio is fixed at ~ 0.02 independent of original $\text{H}_2\text{S}/\text{SO}_2$ composition, which is a function of T, P, H_2O , and $f\text{O}_2$. High $\text{H}_2\text{S}/\text{SO}_2$ ratios are indicative of hydrothermal fluid input or reactions

converting SO_2 to H_2S in the reducing hydrothermal environment. Thus, in both plots deviations from the modeled gas compositions can adequately be explained by hydrothermal input of H_2O and H_2S . Importantly, the $\text{H}_2\text{S}/\text{SO}_2$ clearly distinguishes hydrothermal phases 1 and 4 and magmatic degassing, which is characterized by $\text{H}_2\text{S}/\text{SO}_2 < 0.3$. Average hydrothermal, deep magmatic, and shallow gas compositions are shown as hexagons. The deep magmatic and shallow magmatic averages are calculated using phase 2 and phase 6 gas compositions only, because phases 3 and 5 show significant hydrothermal overprint.

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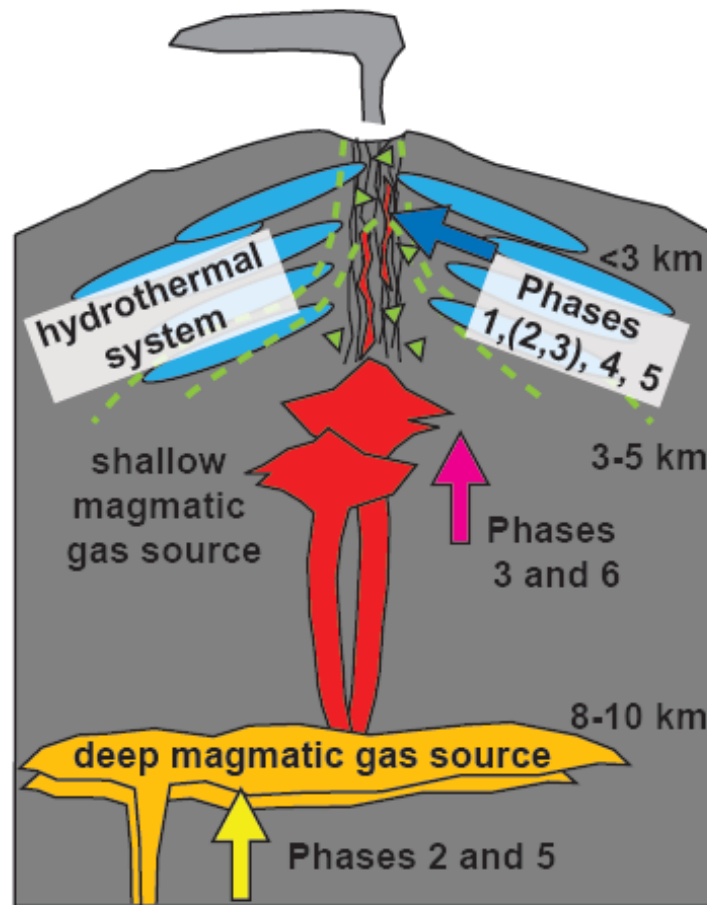


Figure 7 Conceptual model of Turrialba volcano showing the plumbing system as envisioned from gas compositions and modeling. Pulses of new magma arrive at mid-crustal depths (8-10 km) during phases 2 and 5, producing CO₂-rich gas pulses and destabilizing a lower magma reservoir. Shortly thereafter, magma, volatiles, and heat are injected to the shallow magmatic system, triggering phreatic and phreatomagmatic eruptions. An extensive hydrothermal system contributes volatiles and modifies magmatic gas compositions mostly during phases 1, 4, and 5, and to lesser extent during phases 2 and 3. Phase 3 eruptions (particularly the 29 October 2014 event) ruptured hydrothermally sealed breccia (green triangles) previously sealed at chemical and thermal interfaces between magmatic vapor and hydrothermal liquid zones, allowing massive degassing of hydrothermally-stored volatiles during stage 4.

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 ₂ O 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 ₂ O	3.52	0.65	3.12	1.16
K ₂ O	2.31	0.41	2.55	0.48
P ₂ O 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	

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

SO₂ emitted Tons	H₂S emitted* Tons	Total S emitted Tons	Melt S content wt%	Mass melt degassed kg	Magma vol km³
2.04 x 10 ⁶	6.12 x 10 ⁵	1.60 x 10 ⁶	0.2	7.99 x 10 ¹¹	0.296

* The average H₂S/SO₂ ratio of 0.6 from Multi-GAS data (Figure 2) is assumed in order to estimate total H₂S emissions

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