Novel methods of volcanic gas measurement using drones and tree ring geochemistry at Turrialba volcano, Costa Rica

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Abstract

Turrialba is an historically explosive stratovolcano located at the southern end of Costa Rica's central volcanic range. Turrialba had been quiescent for nearly 150 years when the first signs of unrest, including degassing, began in 1996. Since 2010, Turrialba has emitted a near constant plume of gas, and there have been increasingly frequent explosions and ash emissions as activity continues to accelerate. In this work, I focus on two separate method development studies of measuring volcanic gases at Turrialba volcano. The first method is to indirectly measure fluctuations of gas output in the volcanic plume using an original method in dendrochemistry. A robust montane species, *Alnus Acuminata*, is found in abundance around the volcano, and a campaign of non-destructive sampling in 2016 produced a suite of cores showing traits suitable for dendrochronological analysis. We propose here that given their exposure to the volcanic gas plume, these trees contain a geochemical fingerprint of local atmosphere as recorded in seasonal tree rings, since exposure to high levels of SO_2 can affect the carbon and sulfur isotopic signatures in trees. Tree rings were analysed to provide a biannual record of fluctuating SO_2 output at Turrialba. In this way, $\delta^{34}S$ and $\delta^{13}C$ were measured both before and throughout the degassing episode, revealing a $\delta^{34}S$ shift of -5.2 ‰ and a similarly sharp $\delta^{13}C$ shift of +1.3 ‰ coinciding with the strongest degassing. Comparison between our results and the corresponding fluctuation of SO_2 from the plume during this time allows for calibration of this new proxy. The second method is direct measurement of real-time CO_2, SO_2, H_2S, and H_2O concentrations in the volcanic plume using a series of sensors mounted onto unmanned aerial vehicles (UAVs). This work may provide a revolutionary method for scientists looking to obtain a temporal record of degassing in order to better understand the state of an active magma body, helping to forecast the

type of eruptions likely to occur in the near future. This study aims to develop new and lasting methods such that plume studies can be used globally for studying the evolution of volcanic eruptions through discharged gases, both past and present.

Résumé

Turrialba est un stratovolcan historiquement explosif, situé au sud de la chaine volcanique centrale du Costa Rica. Turrialba était en repos pendant 150 années quand les premières indications de réveil, incluant le dégazage, ont commencé en 1996. Depuis 2010, Turrialba a émis un panache de gaz presque constant, et il y avait de fréquentes explosions et émissions de cendres alors que l'activité continue d'augmenter. Dans ce travail, je fais deux études de développement de la méthode en mesurant le gaz volcanique à Turrialba. Premièrement, les fluctuations des gaz dans le panache étaient évaluées en utilisant une nouvelle méthode en dendrochimie. Une espèce robuste, *Alnus Acuminata*, est trouvée en abondance autour du volcan Turrialba, et une campagne d'échantillonnage non-destructrice en 2016 a permis l'éxtraction d'une sélection de carottes ayant un potentiel pour la dendrochronologie. Nous proposons ici que ces arbres contiennent une trace géochimique de l'atmosphère local, entre autres parce que les arbres exposés à de fortes concentrations en SO_2 peuvent présenter une altération de leur composition isotopique ($\delta^{34}S$ et $\delta^{13}C$). Les cernes d'arbres étaient analysés pour qu'ils constituent une archive biannuelle des fluctuations de soufre à Turrialba. De cette façon, le $\delta^{34}S$ et le $\delta^{13}C$ étaient mesurés avant et pendant la période de dégazage, et nos résultats indiquent qu'il y a un déplacement de -5.2 ‰ en $\delta^{34}S$ et de +1.3 ‰ en $\delta^{13}C$ comme indices du dégazage fort à Turrialba. La comparaison entre nos résultats et les fluctuations correspondants de SO_2 du panache volcanique peuvent quantifier le réalisme de ce proxy. Deuxièmement, la mesure directe de CO_2, SO_2, H_2S, and H_2O dans la panache est possible en utilisant des sensors monté sur un UAV (véhicle aérien sans pilote). Ce travail peut révéler une méthode révolutionnaire pour les scientifiques qui recherchent une archive temporelle du dégazage afin de mieux comprendre un corps magmatique et prévoir les éruptions. Cette étude vise le développement des méthodes

nouvelles et durables pour mesurer les fluctuations des gaz dans un panache volcanique, même au présent et au passé, qui peuvent s’appliquer mondialement afin d’étudier l’évolution des éruptions volcaniques.

Preface

This thesis is composed of original research conducted by the author at the Department of Earth and Planetary Sciences, McGill University, under the supervision of Dr. John Stix. Fieldwork, sample preparation, laboratory analysis, and data interpretation were conducted by the author between 2015 and 2017. This thesis is based on two manuscripts, one long and one short, intended for publication in peer-reviewed journals. The author is the main contributor and first author of both articles. The first manuscript is entitled *Carbon and sulfur stable isotopes in tree rings as a proxy of volcanic degassing at Turrialba volcano, Costa Rica* and is co-authored by Étienne Boucher, J. Maarten De Moor, Jean-Francois Helie, Robert Piggott and John Stix. The second manuscript, entitled *Drones measure gases at volcanoes during international field campaign,* is a short science communication manuscript submitted for an online science magazine and is co-authored by Alfred Alan, Ernesto Corrales, Julian Rüdiger, J. Maarten de Moor, Jorge Andres Diaz, and John Stix. All co-authors have contributed intellectually and provided guidance in the collection, analysis, and/or interpretation of data.

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Table of Contents

List of Figures

List of Tables

1 Introduction

Volcanic degassing provides a key insight into the internal plumbing system of a volcano. Therefore, by monitoring the changes and output of the gases at the surface, it is possible to gauge deeper activity and thus interpret the warning signs of an imminent eruption. The gases are predominantly composed of H_2O, CO_2, SO_2, H_2S and halogens such as HCl and HF (A. Aiuppa et al., 2012; Burton et al., 2000, 2007; Taran & Zelenski, 2015). This surface degassing occurs at active vents and fumaroles, which may contribute to the formation of a larger plume. Fumaroles can be sampled directly (e.g., Taran & Zelenski, 2015; Vaselli et al., 2010; Zimmer et al., 2004), but this requires close contact which can put the researcher in danger, not only from the heat of the fumarole itself but also from possible eruptions. At times when direct access to the crater is not safe, new techniques are being sought to measure the larger-scale plume. Hence there is a need to develop novel methods to analyse volcanic plumes, and this study intends to do so with the use of isotopic dendrochemistry and drone plume mapping.

Fluctuations of stable carbon and sulphur isotopes, $\delta^{34}S$ and $\delta^{13}C$, of the surface degassing over time are examined using an original method in dendrochemistry. Trees surrounding the active Turrialba volcano in Costa Rica, which possess a yearly record of local atmosphere in their tree rings and have been sampled and analysed ring by ring. In this way, $\delta^{34}S$ and $\delta^{13}C$ measured both before and throughout the degassing episode can thus be used as

indicators of the volcanic activity. Since degassing at Turrialba is well-documented, comparison between my results and the corresponding fluctuations of CO_2 and SO_2 from the plume during this time can allow the development of a new proxy which can be applied here and at other volcanoes to obtain temporal records.

Currently, methods of studying past eruptions are limited to stratigraphic evidence which generally cannot account for degassing during non-eruptive or pre-eruptive periods. As a result, historical observations, if they exist, are often the only way of estimating degassing activity that precedes modern day science. Turrialba is no exception, considering that degassing associated with the most recent eruption of 1864-1866 was recorded only by eye-witness accounts (Reagan et al., 2006). Applying dendrochronology is an ideal solution to this problem, as Turrialba is surrounded by dense tropical forests which are strongly responsive to the changing environment (Martini et al., 2010; Tortini et al., 2017). One abundant species of tree in this area, *Alnus Acuminata* (locally known as the Jaul), is a robust candidate for my study and has been used in dendrochronological studies elsewhere (Morales et al., 2004). This study measures $\delta^{13}C$ and $\delta^{34}S$ in the tree rings, with comparison between these results and the degassing trends throughout the recent phases of activity at Turrialba.

Dendrochronology is a well-established field of study that allows relative dating between tree rings which contain a yearly record of environmental stresses. This has been used in many disciplines in order to study the past, from archeology to climate science. Dendrochemistry is the specific use of dendrochronology wherein chemical variations among rings are the sought variable, and can be particularly useful when studying atmospheric interaction with trees. Previous attempts have been made to link dendrochemistry to volcanogenic pollution; these studies examined trace elements and cations for the purpose of absolute eruption dating (e.g.,

Padilla & Anderson, 2002; Pearson et al., 2005; Sheppard et al., 2008; Unlu et al., 2009; Watt et al., 2007). I believe that an isotopic approach holds much promise for understanding volcanic gas impacts on vegetation, and for understanding cyclic degassing at volcanoes.

Different sources of sulfur produce distinct values of $\delta^{34}S$; -5 ‰ for fossil fuels, +21 ‰ for seawater and +5 ‰ for Central American arc volcanoes (De Moor et al., 2013). In studies of pollution, stable sulfur isotopes have been used to track anthropogenic industrial sources of SO_2 using $\delta^{34}S$ (e.g., Ishida et al., 2015; Kawamura et al., 2006; Thomas et al., 2013; Wynn et al., 2014). These studies have found that $\delta^{34}S$ in tree rings decreased (from +8 ‰ or higher) towards -5 ‰ (reaching as low as -1‰) as a result of increased fossil fuel burning in the 20th century. In this study we expect a shift from background atmospheric $\delta^{34}S$ as measured in trees distal from the crater, towards the magmatic value of +5 ‰ in those trees proximal to the plume.

Stable carbon isotopes also have been used as a proxy for anthropogenic pollution, since photosynthetic uptake is modified by SO_2 emissions, therefore changing $\delta^{13}C$ (Savard et al., 2002). With increased atmospheric SO_2 from smelter emissions, Savard et al. found there to be a shift of +3.5 ‰ above background values in trees exposed to the emissions. They explained this phenomenon as the result of persistent SO_2 exposure causing injury to the leaves and closing their stomata. Since these stomata are the pores by which CO_2 is exchanged with the atmosphere, their closure subsequently limits CO_2 availability for photosynthesis. With this decreased photosynthesis, the $\delta^{13}C$ approaches that of atmospheric CO_2 (-8.0 ‰), thereby resulting in ^{13}C enrichment. This study draws upon these principles, using $\delta^{34}S$ and $\delta^{13}C$ to track atmospheric fluctuations of volcanic gas. For the first time, a mechanism to relate volcanic gases with the isotopic chemistry of trees could be used to extrapolate the degassing history of a volcano. By

identifying $\delta^{34}S$ and $\delta^{13}C$ anomalies in prehistoric tree rings, it may be possible to identify periods of degassing and unrest at a periodically active and quiescent volcano.

Drones, also known as unmanned aerial vehicles (UAVs), have become increasingly accessible and affordable in recent years. These devices have been used to measure various environmental variables such as glacial ablation, temperature, soil erosion and greenhouse gases (e.g., Eltner et al., 2015; Immerzeel et al., 2014; Roldán et al., 2015) in areas which are too remote or too dangerous to be otherwise reached. Similarly, drones can be used in active volcanic areas to measure gases when eruptions prohibit safe access to the summit area (Muscato et al., 2012). CO_2 fluxes at Vulcano, Italy, have been monitored with the use of a UAV carrying infrared and UV spectrometers as well as electrochemical sensors (McGonigle et al., 2008). Similar studies have been performed at Kirishima volcano, Japan, in which a UAV with a Multi-GAS system was flown through the plume (Shinohara, 2013), and at Turrialba volcano, Costa Rica, where a mass spectrometer was added to a UAV along with other on-board sensors (Diaz et al., 2015). However, CO_2 remains one of the most difficult volcanic gases to measure due to its high concentration in the atmosphere which acts as background interference (Aiuppa et al., 2007). In this research, we use a compact UAV, the Turbo Ace Matrix I, with onboard instrumentation which measures CO_2 and SO_2 concentrations during the flight path. Using these measured concentrations, the CO_2/SO_2 ratio can then be determined. The CO_2/SO_2 ratio does not depend on windspeed and therefore provides a robust means of calculating the CO_2 emission rate if the SO_2 flus is known (Harris & Rose, 1996).

In conclusion, this research aims to apply novel methods which utilize dendrochemistry and drone plume mapping at Turrialba volcano, Costa Rica. By interpreting the geochemical signatures contained within these tree proxies as well as the direct gas measurements themselves,

a better understanding of the magmatic processes occurring beneath the volcano can be achieved. This work may have a profound impact on methods of studying historic volcanic eruptions as well as methods of forecasting future events. By extracting the stable carbon and sulfur isotopic variations from tree rings, I hope to pioneer a new technique which would enable chronologies of past eruptions to be deciphered without the need to rely on stratigraphic evidence or eye-witness accounts. This could open up a new field of study within the geosciences, and could be applied at other volcanoes to provide an unprecedented record of the past global flux of sulfur and carbon. This work is complemented by modern UAV technology applied for constraining the gas fluxes emanating from the crater. Overall, these methods have the potential to expand our ability to use gas geochemistry in studying the temporal evolution of volcanic degassing.

Preface to Chapter 2

Trees are excellent indicators of changes in the environment and are especially sensitive to atmospheric variations, which are recorded in annual tree rings as they grow. Volcanoes are capable of emitting thousands of tonnes of SO_2 to the atmosphere, although any emissions which pre-date the implementation of modern gas instrumentation are undocumented. In this chapter, we investigate the possibility of using trees to unravel past degassing histories at volcanoes by examining stable carbon and sulfur isotopes in tree rings. Core samples were collected from trees surrounding Turrialba volcano, Costa Rica, where a degassing crisis is ongoing. Samples were also collected from background sites to compare the dendrogeochemical variations with trees which are unaffected. The stable isotopic ratios of carbon, $\delta^{13}C$, and sulfur, $\delta^{34}S$, were analysed both before and throughout the degassing episode by manual dissection of tree rings and analysis by isotope ratio mass spectrometry. This new method could be used to reconstruct past volcanic activity and unrest, making this a useful proxy.

2 Carbon and sulfur stable isotopes in tree rings as a proxy of volcanic degassing at Turrialba volcano, Costa Rica

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Key words: Tree rings, Volcanic degassing, Sulfur isotopes, Carbon isotopes, Turrialba volcano

2.1 Abstract

Trees are useful archives of past atmospheric conditions. They have most commonly been used to infer large-scale changes in climate, industrial pollution, and the magnitude and frequency of geological hazards. While geochemical changes in tree rings have been linked to localized anthropogenic smelter pollution, their potential to track geochemical changes in volcanic plumes has not yet been fully realized. Here we apply a new proxy using sulfur and carbon isotopes in tree rings to examine fluctuations of gas output in the volcanic plume of Turrialba volcano, Costa Rica. Turrialba is an historically explosive stratovolcano located at the southern end of Costa Rica's central volcanic range; it is currently in a phase of heightened activity since 1996 which has developed into a severe degassing crisis over the past eight years. Since 2010, Turrialba has emitted a near constant plume of gas, and there have been increasingly

frequent explosions and ash emissions as activity continues to accelerate. Previous studies have shown that exposure to high levels of SO_2 can affect stable carbon and stable sulphur isotopes, $\delta^{34}S$ and $\delta^{13}C$, in trees. Cores from a species of alder tree, *Alnus Acuminata*, have been collected at several key locations surrounding the volcano and at two background sites, and have undergone biannual isotopic analysis both before and during the degassing episode. After onset of the strong degassing in 2010, a strong $\delta^{34}S$ shift of -5.2 ‰ and a similarly sharp $\delta^{13}C$ shift of +1.3 ‰ is observed in trees downwind of the plume. We propose that these shifts correspond to the isotopic values of the tree approaching those of the volcanic SO_2 and CO_2, and in the case of the $\delta^{13}C$, an additional fractionation caused by leaf damage from exposure to volcanic SO_2. This new proxy can be applied to other volcanoes as a novel method of obtaining a temporal record of degassing, a crucial tool for volcano monitoring.

2.2 Introduction

Dendrochronology has long been used to identify volcanic eruptions indirectly through the impact of climate on tree ring growth, but never has an eruption sequence been reconstructed using trees directly affected by volcanic emissions. Major eruptions during which stratospheric sulfur injection was sufficient to cause a global cooling signal can be dated by examining ring width index (RWI), often coupled with latewood density and frost ring morphology (e.g., Briffa et al., 1998; D'Arrigo et al., 2013; LaMarche & Hirschboeck, 1984; Gennaretti et al., 2014). More recently, these techniques have been combined with the Normalized Difference in Vegetation Index (NDVI) from satellite imaging to correlate ring damage with past lahars as a dating technique (Salaorni et al., 2017) or to correlate tree growth with opening of fractures in the ground prior to lava flows (Houlié et al., 2006; Seiler et al., 2017). However, lava flows and eruptions are discrete events which emit a finite amount of volatiles on a short timescale, while

steady degassing is known to account for a significant proportion of global volatile transfer over time, especially in arc settings (e.g., Aiuppa et al., 2012; Allard et al., 2016).

Dendrochemistry is a rapidly evolving field which examines variations in elemental abundance within tree rings which, when combined with dendrochronology, can provide a temporal record of chemical variations as a response to environmental pollution. Like other methods, it can be applied to discrete events, although it should be most effective in cases of long-term exposure such that the tree can absorb the elements of interest during the growing season. Similarly to dendrochronology, dendrochemistry has been applied to date large-scale historic eruptions (Hall et al., 1990; Pearson et al., 2005; Unlu et al., 2009) using trace metals. At Etna, volcanogenic cations in proximal trees were found to be generally inconsistent proxies for volcanic activity (Watt et al., 2007), although some qualitative comparisons could be drawn between long-lasting periods of elevated metal concentration and flank eruptions (Sergio et al., 2008). Studies elsewhere have reported a similar overall lack of correlation between metal concentrations in tree rings and local events, whether environmental (Padilla & Anderson, 2002) or volcanic (Sheppard et al., 2008; 2010). Metal behaviour in wood structure is not well understood (Watmough, 1997), and discrepancies are likely caused by translocation of the foreign elements within the tree, while organic elements such as sulfur and carbon are incorporated into the structure of the wood systematically as cellulose and cysteine (Kawamura et al. 2006) as the active ring is grown.

In this study, we examine sulfur and carbon isotopes within tree rings at Turrialba volcano, Costa Rica, as a proxy of volcanic degassing. Stable isotopes have proven to be successful archives of paleoclimate and drought in tree rings (e.g., McCarroll & Loader, 2004; Treydte et al., 2009), and dendrogeochemical studies have successfully tracked anthropogenic

pollution using stable carbon isotopes (Savard et al., 2002) and stable sulfur isotopes (Kawamura et al., 2006; Thomas et al., 2013; Wynn et al., 2014). Carbon from atmospheric CO_2 enters the tree through diffusion in leaf stomata, resulting in a fractionation of -4.4 ‰, and is then fractionated an additional -27 ‰ when the carbon is photosynthesized into leaf sugars (McCarroll & Loader, 2004). In addition to uptake of sulfurous gases through leaf diffusion, sulfur is also acquired by sulfate absorption in the roots of trees (Krouse, 1977). Diffusion of SO_2 through leaf stomata causes little fractionation, and it will dissolve and metabolize thereafter to organic compounds, while root assimilation produces a 1-2 ‰ fractionation (Wynn et al., 2014 and references therein). Speleothem studies show that unlike stalactites, tree rings show no lag in uptake of environmental sulfur so long as root systems are shallow (Wynn et al., 2010).

In this paper, we examine whether volcanogenic pollution may be recorded in a similar fashion by studying the tree rings from a volcano before and during a degassing crisis. We measure both stable carbon and sulfur isotopes in the tree rings in order to identify correlated changes to better understand the impact of volcanic gas on vegetation growth.

2.2.1 Turrialba degassing crisis

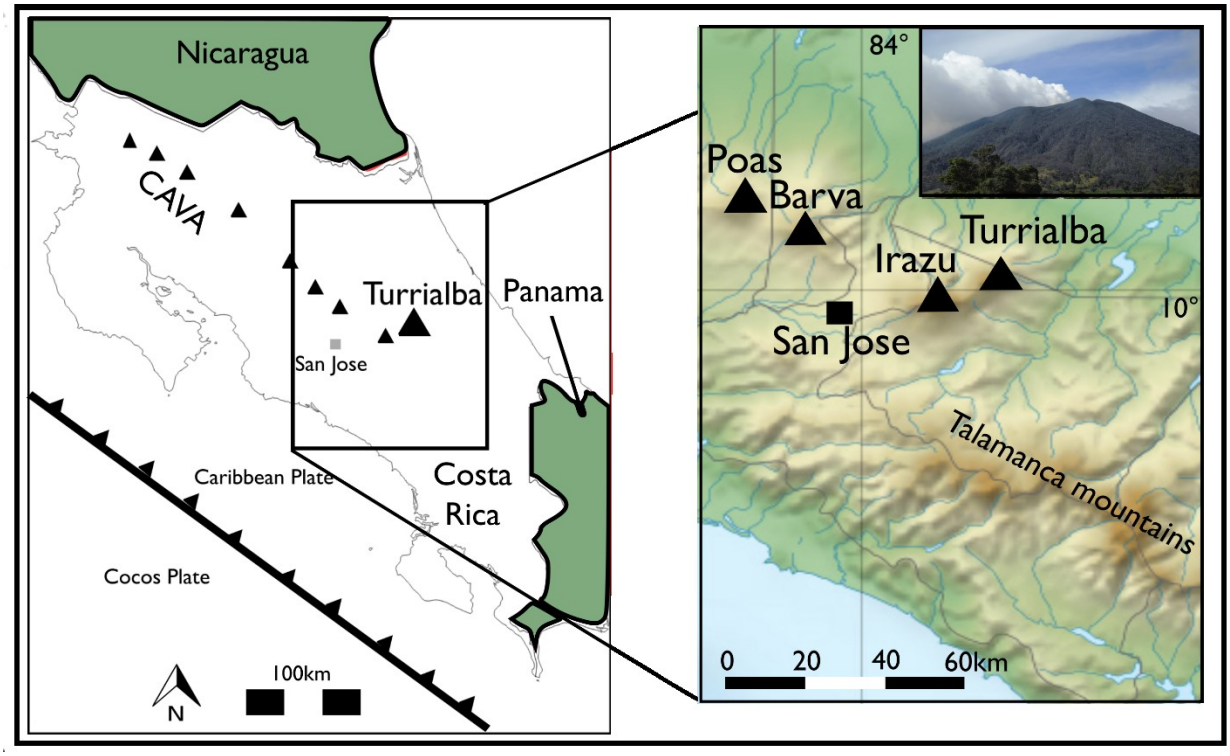
At 3340 m above sea level, Turrialba is Costa Rica's second tallest volcano and historically one of its most active. The stratovolcano is located above the populous Central Valley and 30 km from the capital city of San José and the main international airport. It is part of the Central American Volcanic Segment (CAVS), a chain of arc volcanoes formed as the result of the subduction of the Cocos plate beneath the Caribbean plate (Figure 1) (Zimmer et al., 2004). At least 20 past eruptions of Turrialba are documented in the stratigraphic record, ranging from short-lived phreatic episodes to larger plinian events (Reagan et al., 2006). Ejecta

from Turrialba spanning the last 10 ka of its eruptive history range from basaltic andesite through andesite to dacite, most likely having evolved by fractional crystallization (Di Piazza et al., 2015). Following a period of violent eruptions throughout the Holocene and the most recent activity in 1864-1866, there was a hiatus of activity at Turrialba for over a century which ended in 1996 when changes in seismic and fumarolic activity were noted (Conde et al., 2014). The summit area consists of three craters, two of which (the Central and West craters) have hosted increasingly active fumarolic activity along with seismic swarms and inflation since re-awakening more than 20 years ago (Martini et al., 2010). Consequently, gas emissions from Turrialba have been well-studied during this time.

The presence of SO_2 was first detected in November 2001 at the Central crater and in September 2002 at the West crater, followed by the opening of fissures in the summit area (Vaselli et al., 2010). Fumarolic activity increased, reaching magmatic-dominated geochemical signatures between 2005 and 2008, and establishing a baseline of ~360 metric tons SO_2 per day before emissions peaked at 3500 metric tons SO_2 per day in the months preceding a vent-opening phreatic eruption in the West crater in January 2010 (Campion et al., 2012; Conde et al., 2014; Martini et al., 2010). Another vent was opened in the West crater in January 2012, and an SO_2 flux of ~450 metric tons per day was recorded two months prior to a phreatic eruption from both vents on 21 May 2013 (Moussallam et al., 2014). Further eruptions in October to November 2014 led to the collapse of the West crater, and escalating eruptive activity throughout 2015, 2016, and 2017 have been accompanied by a persistent gas plume, with an estimated total output of over 2 Mt of SO_2 since 2008 (de Moor et al., 2016). In addition to ground-based measurements, SO_2 emissions also have been monitored by satellite since 2005 and yield a similar estimate of > 3 Mt of SO_2 emitted to date (Fioletov et al., 2016). Satellite imagery also

has been used to evaluate the effects of activity upon the surrounding vegetation (Tortini et al., 2017), making Turrialba an ideal site at which to test our new tree ring proxy.

Figure 1: General location of Turrialba volcano



2.3 Materials and Methods

2.3.1 Tree species

The species selected for this study was *Alnus Acuminata*, a tall tree of the Alder genus which is locally known as the jaul. This species is native to the area and found in abundance surrounding Turrialba volcano, growing both wild in the national park and as a silviculture crop planted by dairy farmers to maintain the soil and grass quality of their pastures (Russo, 1990). Growing between 1300 to 2500 metres above sea level, this species is found as far south as Argentina, where it has been used successfully in subtropical dendrochronology due to its

reliable and clearly visible annual rings (e.g., Grau et al., 2003; Morales et al., 2004). These rings are formed as a result of water availability during the growing season (wet season) at high elevation (Morales et al., 2004) in addition to temperature variations, while growth shuts down during the dry season of montane Argentina (Grau et al., 2003). Precipitation is similarly a limiting factor in the dry season of the Costa Rican highlands, which experience a dry season from January to April and a wet season from May to December. Therefore, the same concept should apply to this species in the tropics. Dendrochronological studies have proven successful in tropical environments at high elevation (e.g., Ballantyne et al., 2011; Cook et al., 2010; Stahle, 1999; Worbes, 1995), hence this species is a suitable candidate for this study.

2.3.2 Tree sampling

Over eighty cores were collected in April and May 2016 from thirty *A. Acuminata* trees on the flanks of Turrialba and a background site 50 km distant. One to two 5 mm cores and one 10 mm core were sampled at chest height from each tree using increment borers. To avoid contamination, no lubricant was used, and bark was carefully scraped away with a steel knife to avoid contamination from ash or moss. Cores were handled with nitrile gloves and stored in parafilm in aluminum tubes for transport; the cores were opened in order to dry them and avoid growth of mold before they arrived at the lab.

Seventeen trees were located 1.5-10 km from the crater at varying upwind and downwind locations surrounding the volcano, at elevations between 2200-2800 m above sea level. No dead trees were sampled from within the dead zone produced by acid rain (Tortini et al., 2017), as our 2014 sampling campaign revealed these trees to be bleached internally and therefore not viable for this type of study.

Sampled trees ranged from 25-45 years in age and were located predominantly on slopes where the surrounding vegetation consisted of other *A. Acuminata* trees, ferns and grass. In addition, an entire tree slab (sample LP01) was collected from a line of trees planted in the 1950's by the owners of a dairy farm, who felled the tree to aid in this study. Thirteen trees were also sampled in a distal background site located 50 km south of Turrialba, perpendicular from the plume direction and upwind of the populous Central Valley, so that no volcanic influence would be expected and anthropogenic influence would be similar to that experienced at Turrialba (Figure 2d). This background site, San Gerardo de Dota, is a valley in the Talamanca Mountains which hosts *A. Acuminata* at a similar elevation and microclimate. Hence, trees at this background site were also sampled from grassy slopes and forest between 2200-2500 m above sea level, and also ranged from 25-40 years in age.

2.3.3 Sample selection and preparation

All cores were dried in an oven at 60°C for 24 to 48 hours, then sanded, polished, and scanned on one side. The 5 mm core samples were first mounted onto grooved slats with glue to hold them in place. Ring widths were identified and measured for all samples electronically and verified visually for any discrepancies. Viable samples were cross-dated, and a master chronology was created using Past5 software. In addition to creating a master chronology for annual dating of tree rings, we compared ring width with our isotopic data to assess the effect of environmental factors on physical tree growth (Appendix I).

Of the trees sampled and dated, four trees were selected for dendrogeochemical isotopic analysis (Appendix II). These were chosen based on location, age, and sample quality. Sample TJ05 was chosen as the exposed tree, and is located 1.5 km southwest of the volcano's summit

crater (Figure 2d), just at the edge of the kill zone area most affected by degassing. Sample LP01 is located 2.5 km south of the summit in an area which is sometimes affected by the plume. This sample was donated from a felled tree on a dairy pasture, and was selected based on its age and sizeable volume of material available, even though it could not be ascertained beforehand whether it would be expected to behave as an affected tree or as a control. Sample TJ13 is located 3.5 km southeast of the summit and is considered a background control sample for the volcano. Sample SG08 is from San Gerardo de Dota and is a distal background sample. From these four samples, rings were sanded and manually dissected with a steel scalpel. To avoid contamination, nitrile gloves were worn when handling the samples, and steel blades and tweezers were wiped with methanol between samples. The wood was ground using a steel ball mill, using the same procedures to avoid contamination as above. Tree rings were pooled into two-year sample increments to yield biannual resolution when processing trees for dendrogeochemical analysis, in order to compensate for any one-year errors from a missing or extra ring.

2.3.4 Mass spectrometry

Geochemical analysis of wood powders was performed by isotope ratio mass spectrometry in continuous flow mode with an elemental analyser (EA-CF-IRMS) at the Geotop light stable isotope lab of the Université du Québec à Montréal. Carbon and sulfur isotopes were analysed separately in order to accommodate the large carbon to sulfur ratio in wood.

For carbon, 1.1-1.5 mg of wood powder were combusted in tin capsules with an Elementar Vario Microcube and the $\delta^{13}C$ in the resulting CO_2 gas measured by an Isoprime 100

mass spectrometer. Two internal standards were used for calibration (-42.16 ‰ and -17.14 ‰) and cross-checked with a third internal standard (-28.75 ‰). Per mil values were calculated as

$$\delta^{13}C\ (‰) = \{(\ ^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1\} \times 1000$$

and normalized on the VPDB scale (NBS19-LSVEC).

For sulfur, 25-40 mg of wood powder were weighed into tin boats and combusted in the Elementar Pyrocube, releasing N_2, CO_2 and SO_2. Due to the large sample mass, a carbo-sorb trap was added to immobilize excess CO_2 not trapped by the Pyrocube's own purge and trap system, so that $\delta^{34}S$ in the SO_2 could be analysed by the Isoprime 100. Peak heights varied between 0.2-1.2 nA, so an amplitude correction was calculated to detrend the raw $\delta^{34}S$ signal in relation to peak size. The instrument was calibrated with three international standards: IAEA S1 (-0.3 ‰), IAEA S2 (22.63 ‰), and IAEA S3 (-32.49 ‰). Standards and blanks were included throughout the run to account for any drift and baseline changes, although sulfur contents of blanks were negligible. Final $\delta^{34}S$ values, defined as

$$\delta^{34}S\ (‰) = \{(\ ^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard} - 1\} \times 1000$$

were normalized on the V-CDT scale. Sulfur concentrations were measured concurrently from the Elementar pyrocube using a Thermal Conductivity Detector (TCD).

2.3.5 Errors and reproducibility

A test for $\delta^{13}C$ analytical error was performed on eight whole wood powders. Each was analysed twice, and yielded a pooled standard deviation of 0.06 ‰ between duplicates. The analytical error for carbon was rounded to 0.1 % for error bars. A separate test was performed to assess $\delta^{34}S$ analytical error, in which one whole wood powder was split into four capsules which were each analyzed. The standard deviation for the quadruplicate $\delta^{34}S$ run was 0.93 ‰, which

was rounded to 1 ‰ for error bars. Full results of the eight duplicate wood powders for $\delta^{13}C$ and one quadruplicate powder for $\delta^{34}S$ can be found in Appendix III. In addition to errors from the mass spectrometry and processing, a fundamental step in any dendrogeochemical study requires an assessment of error between trees and within trees. To address these concerns, a series of duplication tests were performed on homogenized wood from two trees located 5 km apart. Results are presented in Appendix III and discussed below.

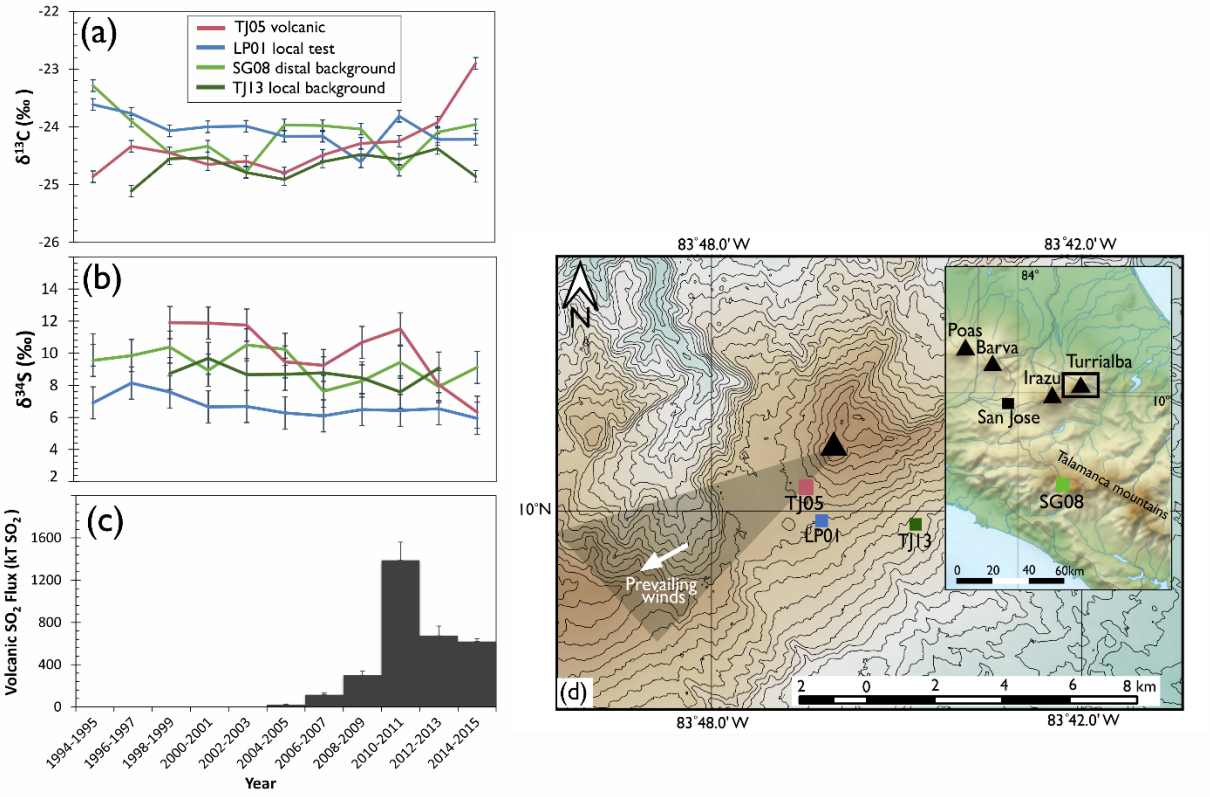
2.4 Results

Stable carbon and sulfur isotope values of the pooled biannual tree rings are plotted in Figure 2 with associated volcanic SO_2 output. The $\delta^{13}C$ values have been adjusted to correct for the atmospheric depletion as increased fossil fuel emissions lower the amount of ^{13}C over time (McCarroll & Loader, 2004). The $\delta^{13}C$ values range from -22.9 ‰ to -25.1 ‰, which fall within the expected range of -20 ‰ to -30 ‰ for wood and leaves of trees (McCarroll & Loader, 2004). Sample LP01 generally mimics the behaviour of sample SG08, with the largest difference occurring in 2010/2011 when they differed by 0.9 ‰. In general, all four samples follow a trend towards more depleted values from 1994/1995 until 2004/2005, and samples TJ13 and TJ05 closely parallel one another during this time, with the exception of 1996/1997. After 2004/2005, samples SG08, LP01, and TJ13 generally remain stable for another 10 years, while sample TJ05 becomes more enriched in $\delta^{13}C$. This enrichment trend in TJ05 is especially pronounced from 2010/2011 to 2014/2015, when it reaches a peak value of -22.9 ‰, a shift of +1.3 ‰. The full shift for this sample from 2004/2005 to 2014/2015 is +1.9 ‰.

The $\delta^{34}S$ values range from 5.9 ‰ to 11.9 ‰. Although very little literature is available for sulfur isotopes in wood, our results are comparable to values obtained by two previous

studies (Kawamura et al., 2006; Yang et al., 1996), and somewhat enriched compared to three other studies which range from 0 ‰ to 6 ‰ (Giesemann et al., 2005; Thomas et al., 2013; Wynn et al., 2014). Sample LP01 is the most depleted sample, remaining very stable throughout the entire series and never exceeding +8 ‰. Sample TJ05 is generally the most enriched sample until 2010/2011. Samples TJ13 and SG08 change little and occupy a mid range spanning from +7.5 to +10.5 ‰. In general, all values appear to be decreasing slightly with time; in 2010/2011, however, a marked change occurs in sample TJ05. The $\delta^{34}S$ peaks at +11.5 ± 1 ‰ in 2010/2011, after which time a sharp decrease occurs. By 2014/2015, sample TJ05 reaches +6.3 ± 1 ‰, nearly the lowest value observed for any sample. Furthermore, this shift of -5.2 ‰ coincides with the similarly sharp +1.3 ‰ shift in $\delta^{13}C$ in the same time frame.

Figure 2: (a) Biannual $\delta^{13}C$ values relative to VPDB with analytical error of ± 0.1 ‰. These values have been corrected for the Suess effect of global atmospheric ^{13}C due to fossil fuel consumption. (b) Biannual $\delta^{34}S$ values relative to VCDT with analytical error of ± 1 ‰. (c) Total estimated biannual SO_2 output from OMI satellite data (Fioletov et al., 2016). (d) Sampling locations of trees used for dendrochemical analysis. DEM contours derived from ASTER GDEM data, a product of METI and NASA. Trade winds are northeasterlies, and the mean plume direction heading is 247° ± 19° as estimated by Conde et al., (2014).



2.5 Discussion

At Turrialba, carbon and sulfur isotopic ratios in tree rings affected by volcanic degassing have shown a remarkable shift soon after the onset of degassing, which contrasts with trends seen in background samples. These findings support the potential use of tree rings as archives of volcanic activity. We now examine volcanic and background trends in $\delta^{13}C$ and $\delta^{34}S$, as well as compare affected and control trees and discuss uncertainty.

2.5.1 Carbon isotopes in tree rings as a proxy of strong volcanic degassing

While there are minor fluctuations in $\delta^{13}C$ on the order of ±0.5 ‰ in all samples, and a generally flat overall trend in SG08, LP01, and TJ13, there is a striking +1.3 ‰ increase after 2010 observed for our proximal downwind volcanic sample, TJ05. This sample first starts to diverge to more enriched values than that of the local background sample, TJ13, after 2004/2005. This divergence is concurrent with the first significant SO_2 emissions and notable sulfate content in rainwaters from Turrialba, marking a change from hydrothermal to magmatic discharge at the volcano (Martini et al., 2010). Therefore, the $\delta^{13}C$ may be sensitive to relatively subtle changes occurring at the volcano during the early stages of the degassing crisis, before the main eruptive and degassing phase began in 2010. We note that this early enrichment in TJ05 from 2004/2005 (a) is of the same order of magnitude as background fluctuations, and (b) is paralleled by a similar, though notably weaker, enrichment of TJ13 from 2004/2005 to 2008/2009. Therefore, the early enrichment of TJ05 may or may not be significant. The strongest $\delta^{13}C$ enrichment began in 2010/2011, which corresponds with the peak in volcanic SO_2 output, resulting in a shift of +1.3 ‰ between 2010 and 2015. This is about a third as much as the shift of +3.5 ‰ reported by Savard et al. (2002) in a study of tree rings downwind from a strong source of SO_2 from the Horne smelter in northern Quebec. However, despite a sharp onset of pollution at the smelter, the observed shift occurred over a period of 15 years, while in our study the +1.3 ‰ shift occurs over ~5 years. Therefore, both studies have a near identical rate of change in $\delta^{13}C$ when considering the generally similar emission rates of the two SO_2 point sources for the time periods studied (average of 1000 Kt SO_2 per year for the Horne smelter and an average of 600 Kt SO_2 per year for Turrialba).

Various sources of CO_2 each contribute a unique carbon isotopic signature to the atmosphere. Any local atmospheric variations will be reflected in the isotopic ratios of vegetation

which photosynthesize the carbon. At the same time, strong fumigation of trees by SO_2 will have a direct impact on the health of a tree by damaging the leaves (Martin et al. 1988), and it is therefore expected that carbon isotopic fractionation will be altered by the resulting physiological changes. This is the mechanism for the abrupt ^{13}C enrichment caused by onset of local SO_2 pollution as described by Savard et al. (2002), since the damage to the leaves causes closure of stomata (the pores through which trees exchange gases with the atmosphere) which in turn causes $\delta^{13}C$ to approach that of the atmosphere (-8.0 ‰). While the background atmospheric CO_2 at Turrialba has an average $\delta^{13}C$ of -9.2 ± 0.1 ‰, the carbon isotopic signature of the magmatic plume of Turrialba is -2.6 ± 1.4 ‰ (Malowany et al., 2017). This more enriched source may explain why the rate of tree ring ^{13}C enrichment observed at Turrialba is similar to that of trees downwind of the Horne smelter, despite the smelter's emitting 400 Kt more SO_2 on average annually than Turrialba.

Just as $\delta^{13}C$ values can be corrected to a pre-industrial standard to account for the increase in global atmospheric ^{13}C due to burning of fossil fuels (McCarroll & Loader, 2004), the same empirical formula can be applied to account for volcanically enriched ^{13}C atmospheric values from local volcanic degassing:

$$\delta^{13}C_{corrected} = \delta^{13}C_{plant} - (\delta^{13}C_{atm} + 9.2)$$

where $\delta^{13}C_{corrected}$ is the theoretical value without the influence of the volcanic CO_2 source and we assume a pre-degassing value of -9.2 ‰. Assuming a moderately dense plume value for $\delta^{13}C_{atm}$ of -8.5 ‰ (Malowany et al., 2017), we calculate the theoretical $\delta^{13}C_{corrected}$ value should leaf damage be the only mechanism at work. The difference between this value and the TJ05 value for 2010/2011 is the shift in per mil caused by leaf damage. If we then subtract the background noise (the shift of -0.4 ‰ that TJ13 undergoes from 2010 to 2015), we can estimate

that ~1.0 ‰ of the enrichment in TJ05 was caused by leaf damage, while ~0.3 ‰ was caused by the volcanic CO_2.

2.5.2 Sulfur isotopes in tree rings

Sources of sulfur isotopes will influence the isotopic ratios of vegetation in a similar way to carbon, depending on the relative proportion of direct atmospheric uptake through the leaves to sulfur uptake in the root system. As volcanic SO_2 flux peaked in 2010/2011 and remained relatively high through 2014/2015, the $\delta^{34}S$ underwent a very large shift of -5.2 ‰ in TJ05 during this time. This shift is in good agreement with the observed shifts of -4 ‰ (Thomas et al., 2013), -5 ‰ (Kawamura et al., 2006; Wynn et al., 2014), and -1.9 % (Ishida et al., 2015) reported in tree rings after the onset of high anthropogenic SO_2 emissions from industrial sources. These studies tracked anthropogenic pollution from the early to mid 20th century, demonstrating that this depletion trend persisted until the late 1970's and early 1980's when emissions were regulated and then declined. These shifts are much more gradual than seen in our study, occurring over several decades, while the shift we observe takes place over the course of 5 years. However, the trees in those studies were not located close to point source SO_2 emissions but rather tracked the general pollution in urban areas from increased fossil fuel consumption. Therefore, we can reasonably assume that the local and persistent volcanic pollution may explain the more sudden onset of ^{34}S depletion observed. While fossil fuels possess a $\delta^{34}S$ isotopic signature of -8.2 to +7.2 ‰ (Ishida et al., 2015), the shift at Turrialba approaches the average $\delta^{34}S$ signature of the gas plume at Turrialba of +3.4 ± 0.5 ‰ (de Moor et al., 2016). In contrast to the gradual $\delta^{13}C$ response seen in TJ05 starting in 2004/2005 prior to the heaviest degassing phase of the volcano, there does not appear to be a similarly early response in $\delta^{34}S$. In fact, $\delta^{34}S$

in TJ05 actually increases by 2.3 ‰ during this time, similarly to SG08 but inversely to TJ13. Therefore, $\delta^{34}S$ may only record the strongest degassing at Turrialba. Spruce trees subject to high concentrations of SO_2 or stress have been shown to respond by emitting H_2S, which would cause an enrichment of ^{34}S as compared to input values (Jędrysek et al., 2002). However, this is apparently not a mechanism in our study since $\delta^{34}S$ in TJ05 decreases sharply from 2010/2011 to 2014/2015, perhaps because of the different species and climate.

2.5.3 LP01: control or affected tree?

Although samples TJ05 and LP01 both come from trees growing in soils of pH 5 to 6, the principal uptake path of sulfur in sample TJ05 is through atmospheric exchange as demonstrated by the rapid response to the volcanic degassing, while the consistently low $\delta^{34}S$ signature and elevated sulfur concentration of sample LP01 (Figure 3d, in Appendix I) suggest that it may be receiving sulfur primarily through root uptake. If so, it may be heavily affected by variations in the soil caused by one of three factors: an effect of low pH due to heavy use of fertilizer, the tree's location in a valley increasing volcanic runoff at this site, or the age and soil depth of the tree. Soil acidification caused by anthropogenic SO_2 pollution has been shown to increase sulfur concentration in tree rings (Tendel & Wolf, 1988), and soil acidification also occurs at nitrogen-fertilized pastures (Noble et al., 1998). Sample LP01 was located on a well-established dairy pasture in a fertile valley directly on the southern flank of the volcano. This acidity may explain the elevated sulfur concentration in the rings of LP01, but reducing conditions are expected to cause an enrichment in residual sulfate (Chambers & Trudinger, 1979). Since LP01 was located in a relatively flat area where soil depth is greater and the tree was relatively old (59 years, as compared to ~30 year age of the other trees), the uptake and mobility of sulfur may be affected

by these conditions (Pearson et al., 2005). If the roots have grown sufficiently, they may reach the saturated zone in deeper soils, tapping a source of sulfate dissolved in deeper groundwater (Yang et al., 1996). Nonetheless, LP01 may simply not be an ideal candidate for dendrogeochemistry, as it appears to be less sensitive to environmental fluctuations. In this study, therefore, it is not necessarily considered a volcanically influenced tree nor a control sample.

2.5.4 Sources of uncertainty

Although some studies suggest that sulphur will be concentrated in the outermost rings (Fairchild et al., 2009), this may not be the case for *A. Acuminata*. Our background samples, as well as TJ05, show relatively similar sulfur concentrations (Figure 3d, in Appendix I), increasing confidence that the trend we see for TJ05 is a result of volcanic emissions affecting the tree environment. Other than the volcanic pollution-induced shift seen for TJ05, year-to-year $\delta^{13}C$ shifts of +0.5 ‰ to +0.8 ‰ are observed in each sample at varying times (1994/1995 to 1996/1997 for TJ05, 2002/2003 to 2004/2005 for SG08, and 2008/2009 to 2010/2011 for LP01). These shifts are not persistent, however, and may be attributed either to analytical uncertainty or to short-term variability caused by natural fluctuations as seen in other studies (e.g., Savard et al., 2002). These minor enrichments may be caused by precipitation or temperature fluctuations, as they appear to correspond to years of unusually high rainfall (Fig. 3f, in Appendix I). In 2004/2005, SG08 produced narrow rings, which correspond with a plateau in $\delta^{13}C$ and may support the hypothesis that these minor effects are rainfall induced.

In preliminary tests (Figure 4, in Appendix III), an offset in carbon isotope values between cellulose and whole wood of +0.1 to +0.3 ‰ was noted in two test trees. This would

imply that cellulose is more enriched in ^{13}C than whole wood for this species and climate, likely due to a systematic fractionation of carbon between cellulose and other compounds in the tree. No corrections to our data set have been made to correct for this offset. In the same test trees, a $\delta^{34}S$ shift of +1.5 to -2.5 ‰ between whole wood and cellulose is observed, which reflects a proportion of water soluble sulfur in the tree resin. In both cases, these variabilities are less than the isotopic shifts induced by volcanic degassing but should be addressed in future studies.

2.6 Concluding remarks

This is the first study linking sulfur and carbon isotopes to proximal volcanic activity, as well as one of the first to combine carbon and sulfur stable isotopes in understanding the effects of SO_2 emissions on the environment. We have found that tree rings have high potential to be used as a proxy for past degassing. Coinciding with the onset of strong volcanic degassing between 2010 to 2015, a rapid and large $\delta^{34}S$ shift of -5.2 ‰ and a similarly sharp $\delta^{13}C$ shift of +1.3 ‰ are observed in tree rings downwind of the emissions, while no such trends occur in background samples. These substantial shifts far exceed the analytical uncertainty of our isotopic measurements. Additionally, a subtle $\delta^{13}C$ enrichment begins earlier at the onset of low-level volcanic emissions in 2004/2005. These results indicate that both sulfur and carbon isotopes may be useful archives of volcanic degassing. Carbon isotopes may be more sensitive to early changes, and also require less sample mass (~1 mg whole wood for carbon vs. ~40 mg whole wood for sulfur) for analysis by EA-CF-IRMS. Variations between trees and within trees should be assessed in future studies in order to understand the details and limitations of this technique.

Sulfur concentrations did not vary significantly with $\delta^{34}S$, although we recommend evaluating sulfur concentration, rainfall, and ring width to better understand background trends.

This new proxy has the potential to overcome the limitations of understanding historical eruptions beyond the rock record. Degassing is a key precursory signal at many arc volcanoes, and there is currently no way of retroactively extrapolating a degassing history other than relying on circumstantial historical accounts, if they exist. It is important to understand the evolution of past eruptions and unrest at volcanoes to better forecast the type of eruption sequence which is likely to occur in the future. Therefore, a means of examining degassing during non-eruptive or pre-eruptive periods is crucial, and our results provide a way forward. Both carbon and sulfur isotopes in tree rings of trees proximal to degassing respond rapidly to high levels of degassing. Therefore, detailed degassing chronologies can be constructed from the tree rings. This work also extends the application of carbon and sulfur isotopes in dendrochronology, demonstrating their versatility as tracers of paleo-atmospheric fluctuations in tropical trees. The viability of *A. Acuminata* for dendrochronological studies in the tropics is a valuable discovery in the field of tree ring science.

We recommend further application of this technique at other volcanoes in different climates to validate and extend the method. Alder trees (*Alnus Incana*) have been collected by the first author in Kamchatka, Russia, downwind from Mutnovsky volcano, which hosts a continuously degassing active funnel vent (Zelenski & Taran, 2011). These samples are currently undergoing analysis. Recent advances in MC-ICP-MS and LA-ICP-MS allow for lower detection limits, such that heavy stable isotopes including Pb and Hg could also be used to fingerprint atmospheric sources.

2.7 Appendix I: Dendrochronological dating and environmental conditions

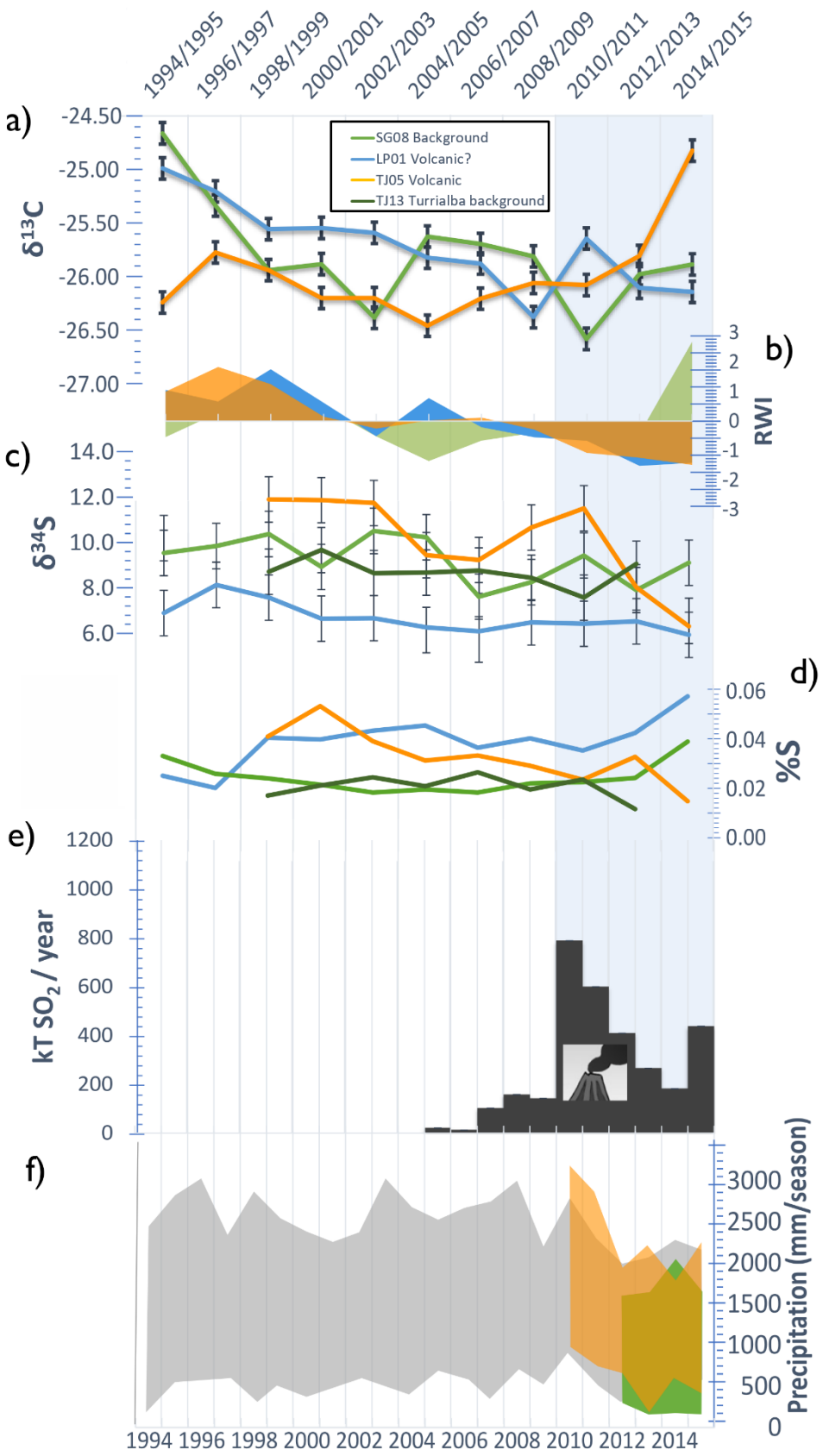
Since no tree ring data exist for this region, the master chronology we created was limited to trees collected during this study. Occasionally, faint and narrow rings were observed which could not be placed with statistical confidence as annual in nature. In general, however, rings were well-developed. The annual nature of the tree rings is supported by the age of LP01. The owner of the tree provided the exact year (1959) when it was planted on their farm, and this date was verified upon cutting the tree and counting the rings.

Each tree which underwent isotopic analysis was grouped with trees from the same site, where applicable, and chronologies from each site were averaged and normalized to yield ring width indices (Fig. 3b). Ring widths are expected to become smaller towards the outer edges of the tree as the circumference increases, which is normally accounted for by detrending functions which remove this long-term decrease on chronologies including trees of various ages (Briffa et al., 1998). In our study, rings were not detrended due to the large size (0.2 to 2 cm) of the rings and also because these chronologies span less than a century. From 2010/2011 onwards, rings are narrow in LP01 and TJ05, while in SG08 they are larger. Ring width is highly variable both within single trees or sites and between them. Ring widths of samples TJ05 and LP01 generally are antipathetic to ring widths of SG08 throughout the chronology.

Sulfur concentrations range from 0.015 % to 0.06 % sulfur (Figure 3d). These are typical values for wood, which is around 50 % carbon. Sulfur concentrations do not show clear correlations with $\delta^{34}S$ (correlation coefficient of 0.12). LP01 and TJ05 have the highest sulfur concentrations after 1999, and while LP01 has the lowest $\delta^{34}S$ overall, TJ05 has the highest $\delta^{34}S$ overall. In 2014/2015, $\delta^{34}S$ decreases for both of these samples, while sulfur concentration

increases sharply in LP01 but decreases sharply in TJ05. Some studies have reported an inverse trend between $\delta^{34}S$ and concentration (Wynn et al., 2014), while others have reported no significant change in sulfur concentration despite large variations in $\delta^{34}S$ (Thomas et al., 2013).

Figure 3: (a) Biannual $\delta^{13}C$ values relative to VPDB with analytical error of ± 0.1 ‰. These values are not corrected for the Suess effect of global atmospheric ^{13}C depletion due to fossil fuel consumption. (b) Ring width index normalized for comparison between different tree sites. (c) Biannual $\delta^{34}S$ values relative to VCDT with analytical error of ± 1 ‰. (d) Percent sulfur as calculated from Elemental Analyser results for wood powder analysis. (e) Total estimated annual SO_2 output from OMI satellite data (Fioletov et al., 2016). (f) Total precipitation for Costa Rica (gray), Turrialba volcano weather station (orange) and Talamanca Mountains Cerro Buenavista weather station (green), where the upper limit represents rainy season precipitation (May to December) and the lower limit represents dry season precipitation (January to April) (data provided by the Institutuo Meteorológico Nacional).



2.8 Appendix II: Tree sample locations

Table 1: List of tree samples chosen for dendrochemical analysis. Soil ph was determined using litmus paper in the field when soil humidity was sufficient. Trade winds are northeasterlies, and the mean plume direction heading is 247° ± 19° (Conde et al., 2014). Locations are in decimal degrees using the WGS84 datum.

Tree name	Latitude (decimal degrees relative to WGS84)	Longitude	Elevation (m)	Distance to crater (km)	Heading from crater	Type	Soil pH
TJ05	10.00610°	-83.77373°	2772	1.5	215°	Forested slope	4-5
LP01	09.99791°	-83.77053°	2598	2.5	192°	Dairy pasture	4-5
TJ13	09.99697°	-83.74500°	2251	3.5	153°	Grassy slope	7
SG08	09.57669°	-83.80103°	2442	50	184°	Rocky slope	Too dry to measure

2.9 Appendix III: Error analysis

Table 2: Error assessment of replications, intra-tree, inter-tree, and cellulose samples

Sample	δ34S	Mean	Deviation from mean	Sample	δ13C	Mean	Deviation from mean
Whole wood analytical error			**(Sulfur quadruplicate, carbon duplicates)**				
LP01-96-97	6.1	7.14	1.03	TJ 6a93x	-27.28	-27.25	0.04
LP01-96-97_1	8.0		0.85	TJ 6a93y	-27.22		
LP01-96-97_2	6.3		0.81	TJ 6b93x	-27.32	-27.34	0.03
LP01-96-97_3	8.1		1.00	TJ 6b93y	-27.36		
Std. Dev.			1.07	TJ 5c93x	-25.82	-25.95	0.19
				TJ 5c93y	-26.08		
				TJ 5d93x	-25.75	-25.84	0.13
				TJ 5d93y	-25.93		
				TJ 6a01x	-26.87	-26.90	0.04
				TJ 6a01y	-26.92		
				TJ 6b01x	-26.63	-26.66	0.03
				TJ 6b01y	-26.68		
				TJ 5c01x	-26.38	-26.34	0.05
				TJ 5c01y	-26.30		
				TJ 5d01x	-26.21	-26.25	0.06
				TJ 5d01y	-26.29		
				Pooled Std. Dev.			0.06
Whole wood intra-tree variation between cores							
TJ5d 01x	6.47	6.55	0.08	TJ5d 01x	-26.21	-26.29	0.08
TJ5c 01x	6.63			TJ5c 01x	-26.38		
TJ5c 93x	6.23	6.10	0.13	TJ5c 93x	-25.82	-25.79	0.03
TJ5d 93x	5.97			TJ5d 93x	-25.75		
TJ6b 01x	9.16	8.05	1.11	TJ6b 01x	-26.63	-26.75	0.12
TJ6a 01x	6.93			TJ6a 01x	-26.87		
TJ6a 93x	4.87			TJ6a 93x	-27.28		
TJ6b 93x	nd			TJ6b 93x	nd		
Pooled Std. Dev.			0.65	Pooled Std. Dev.			0.08
Whole wood inter-tree variation							
TJ5 2001-2013 average		6.55	0.75	TJ5 2001-2013 average		-26.29	0.23
TJ6 2001-2013 average		8.05		TJ6 2001-2013 average		-26.75	
Std. Dev.			1.06	Std. Dev.			0.32
TJ5 1993-2000 average		6.10	0.61	TJ5 1993-2000 average		-25.79	0.75

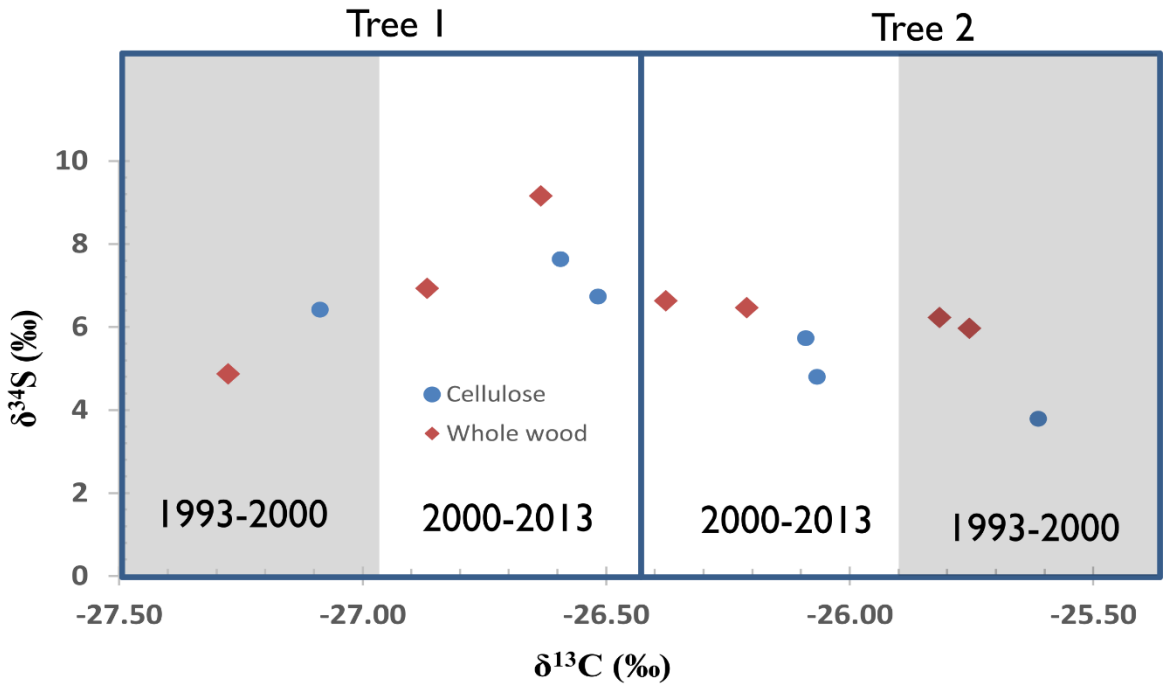
TJ6a 93x		4.87		TJ6a 93x		-27.28	
Std. Dev.			0.87	Std. Dev.			1.05
Whole wood (x) and holocellulose (s)							
TJ6a 93x	4.9	5.65	0.78	TJ6a 93x	-27.28	-27.18	0.09
TJ6a 93s	6.4			TJ6a 93s	27.09		
TJ5c 93x	6.2	5.01	1.22	TJ5c 93x	-25.82	-25.71	0.10
TJ5c 93s	3.8			TJ5c 93s	-25.61		
TJ5c 01x	6.6	5.72	0.91	TJ5c 01x	-26.38	-26.22	0.16
TJ5c 01s	4.8			TJ5c 01s	-26.07		
TJ6a 01x	6.9	7.29	0.35	TJ6a 01x	-26.87	-26.73	0.14
TJ6a 01s	7.6			TJ6a 01s	-26.59		
TJ5d 01x	6.5	6.10	0.37	TJ5d 01x	-26.21	-26.15	0.06
TJ5d 01s	5.7			TJ5d 01s	-26.09		
TJ6b 01x	9.2	7.95	1.21	TJ6b 01x	-26.63	-26.58	0.06
TJ6b 01s	6.7			TJ6b 01s	-26.52		
Pooled Std. Dev.			0.88	Pooled Std. Dev.			0.11

Two trees were selected for error analysis, and two cores from each tree were cut and ground into pre-2000 and post-2000 bulk wood. By comparing the results of the same sets of years from each tree, a temporal comparison can be made between trees. Then, by comparing the results from two cores taken from different sides of the same tree, we can assess the variations in the dendrogeochemistry within the tree. The pooled standard deviation between duplicate cores for $\delta^{34}S$ whole wood was 0.65 ‰, with only the duplicate analysis from tree 1 (TJ6) possessing a deviation from the mean exceeding 0.2 ‰. The pooled standard deviation between cores for $\delta^{13}C$ was 0.08 ‰. The largest variability is observed between trees, with a standard deviation of 1.1 ‰ for carbon and 0.87 ‰ for sulfur from the 1993-2000 bulk wood. The standard deviation of the 2000-2013 bulk wood is 0.3 ‰ for carbon, and 1.06 ‰ for sulfur.

Although either whole wood, lignin, or cellulose may be used in carbon isotopic analysis, softwoods are sometimes processed through a cellulose extraction step in order to remove any resins (McCarroll & Loader, 2004). In cedar trees, it was also shown that water soluble sulfur, presumably in resins, is much less abundant than organically bound sulfur, but the two components differ in $\delta^{34}S$ caused due to either fractionation or translocation effects (Kawamura

et al., 2006). Even though alder trees are not softwoods, in order to assess the effect of resin extraction on isotopic results for *A. Acuminata* in this environment, a subset of the bulk wood powders underwent a Soxhlet chemical extraction to isolate holocellulose. The samples which underwent a Soxhlet extraction experienced a systematic $\delta^{13}C$ shift of +0.1 to +0.3 ‰, but a random $\delta^{34}S$ shift of +1.5 to -2.5 ‰. Results of the intra-tree, inter-tree, and cellulose tests are presented in Table 2, and plotted in Figure 4.

Figure 4: Stable isotopic ratios of bulk wood samples. $\delta^{13}C$ values are calculated relative to VPDB with analytical error of ± 0.1 ‰. $\delta^{34}S$ values are calculated relative to VCDT with analytical error of ± 1 ‰.



2.10 Appendix IV: Isotopic data

Table 3: Biannual $\delta^{13}C$ values in per mil are relative to VPDB with analytical error of ± 0.1 ‰, and values are also shown with correction for the Suess effect of global atmospheric ^{13}C depletion due to fossil fuel consumption. Percent sulfur as calculated from Elemental Analyser results and accompanying biannual $\delta^{34}S$ values in per mil relative to VCDT, with analytical error of ± 1 ‰.

Sample	Year	Measured $\delta^{13}C$ (‰)	$\delta^{13}C$ Suess corrected* (‰)	% Sulfur	Amplitude-corrected $\delta^{34}S$ (‰)
SG_08_94_5	1994/1995	-24.7	-23.3	0.036	9.6
SG_08_97_6	1996/1997	-25.4	-23.9	0.030	9.9
SG_08_98_99	1998/1999	-26.0	-24.5	0.028	10.4
SG_08_00_01	2000/2001	-25.9	-24.3	0.026	8.9
SG_08_02_3	2002/2003	-26.4	-24.8	0.023	10.5
SG_08_04_5	2004/2005	-25.7	-24.0	0.024	10.2
SG_08_06_7	2006/2007	-25.8	-24.0	0.025	7.6
SG_08_08_9	2008/2009	-25.9	-24.0	0.026	8.3
SG_08_10_11	2010/2011	-26.6	-24.8	0.027	9.4
SG_08_12_13	2012/2013	-26.0	-24.1	0.028	7.9
SG_08_14_15	2014/2015	-25.9	-24.0	0.041	9.1
LP_01_94_5	1994/1995	-25.0	-23.6	0.029	6.9
LP_01_96_7	1996/1997	-25.3	-23.8	0.025	8.1
LP_01_98_99	1998/1999	-25.6	-24.1	0.043	7.6
LP_01_00_01	2000/2001	-25.6	-24.0	0.042	6.7
LP_01_02_3	2002/2003	-25.6	-24.0	0.045	6.7
LP_01_04_5	2004/2005	-25.9	-24.2	0.047	6.3
LP_01_06_7	2006/2007	-25.9	-24.2	0.039	6.1
LP_01_08_9	2008/2009	-26.4	-24.6	0.043	6.5
LP_01_10_11	2010/2011	-25.7	-23.8	0.038	6.4
LP_01_12_13	2012/2013	-26.2	-24.2	0.045	6.5
LP_01_14_15	2014/2015	-26.2	-24.2	0.058	5.9
TJ_05_94_5	1994/1995	-26.3	-24.9	nd	nd
TJ_05_96_7	1996/1997	-25.8	-24.3	nd	nd
TJ_05_98_99	1998/1999	-26.0	-24.5	0.043	11.9
TJ_05_00_01	2000/2001	-26.3	-24.7	0.054	11.9

TJ_05_02_03	2002/2003	-26.3	-24.6	0.042	11.8
TJ_05_04_5	2004/2005	-26.5	-24.8	0.035	9.5
TJ_05_06_7	2006/2007	-26.3	-24.5	0.036	9.2
TJ_05_08_9	2008/2009	-26.1	-24.3	0.033	10.7
TJ_05_10_11	2010/2011	-26.1	-24.2	0.028	11.5
TJ_05_12_13	2012/2013	-25.9	-23.9	0.036	8.0
TJ_05_14_15	2014/2015	-24.9	-22.9	0.020	6.3
TJ13_94_95	1994/1995	nd	nd	0.030	10.2
TJ13_96 97	1996/1997	-26.6	-25.1	nd	nd
TJ13_98 99	1998/1999	-26.1	-24.6	0.022	8.7
TJ13_00 01	2000/2001	-26.1	-24.5	0.026	9.7
TJ13_02 03	2002/2003	-26.5	-24.8	0.029	8.7
TJ13_04 05	2004/2005	-26.6	-24.9	0.025	8.7
TJ13_06 07	2006/2007	-26.4	-24.6	0.030	8.8
TJ13_08 09	2008/2009	-26.3	-24.5	0.024	8.5
TJ13_10 11	2010/2011	-26.4	-24.6	0.028	7.6
TJ13_12 13	2012/2013	-26.3	-24.4	0.017	9.1
TJ13_14 15	2014/2015	-26.8	-24.9	nd	nd

*The Suess correction involves subtracting the difference between the pre-industrial and global atmospheric $\delta^{13}C$ for each set of years: $\delta^{13}C_{corrected} = \delta^{13}C_{plant} - (\delta^{13}C_{atm} + 6.4)$ (McCarroll & Loader, 2004). Average global atmospheric $\delta^{13}C$ for each set of years was obtained from the Mauna Loa observatory (http://cdiac.ess-dive.lbl.gov/d13_flask_mauna_loa.html).

Preface to Chapter 3

Drones are becoming increasingly popular tools used by scientists to access remote or dangerous areas. Volcanic craters are certainly unpredictable areas that can be hard to reach, but volcano monitoring requires regular access to craters to fix instrumentation or collect gases. In this chapter, preliminary findings of the feasibility of using drones to measure volcanic gas fluctuations are presented. It is important to monitor volcanic gases as they provide valuable information on the current state of a magma body, and changes in their chemistry can signal an imminent eruption. If drones can be applied in these situations, the potential for loss of life is drastically reduced.

This manuscript has been accepted for publication in an science news journal which is peer-reviewed by specialists in the field. Science communication is becoming an especially important part of any scientific study, as sharing results with the general public through media and video are becoming integral parts the dissemination of research.

3 Drones Measure Gases at Volcanoes During International Field Campaign

A team of volcanologists, chemists, physicists, and engineers from around the world test novel techniques at Central America's two largest degassing volcanoes

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3.1 Introduction

Volcanic gases are important eruption forecasting tools that are often used in volcano monitoring. However, collecting gas samples requires scientists to enter high risk volcanic areas.

Figure 5: A drone equipped with compact gas instrumentation is flown toward the volcanic gas plume at Turrialba volcano in Costa Rica. Researchers are able to fly the drone from a safe distance while it measures key gases.

That's where drones come in. Drones are the perfect tool for volcanologists to access these danger zones and are becoming increasingly popular among the scientific community for photography and aerial mapping. But few studies have attempted to quantitatively measure gas emissions by drone.

A drone, or Unmanned Aerial Vehicle (UAV), is a remote-controlled device

which allows the pilot to remain a safe distance from the active crater while the drone is maneuvered to the site of interest, either piloted manually or with an autonomous navigation system. Compact gas sensors can be mounted onto the drone which make measurements while it is in the air.

In late April 2017, a team of researchers gathered in Central America for a two-week excursion to test a variety of instrument and drone combinations. The team included gas geochemists, volcanologists, physicists, engineers, and chemists from four institutions across Canada, Germany, and Costa Rica. Most, of course, doubled as drone pilots.

3.2 Why measure these gases

Figure 6: An octocopter flies a transect under the gas plume at Masaya volcano, 5 May 2017

There are three main reasons to measure volcanic gases.

The first is to measure changes in the ratios of certain gases which can indicate an imminent eruption. The concentrations of carbon dioxide (CO_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) can be measured by flying the drone right into the plume of gas as it disperses from the volcano.

The second reason is to understand which reactive species are coming out of the volcano so that the interactions between volcanoes, climate, and ozone can be better understood. These various compounds contain halogens such as chlorine and bromine, and their changing speciation as the plume ages can also be determined by hovering the drone directly in the gas at varying distances from the source.

The third reason is to measure the total amount of gas being emitted in order to calculate the exchange of volatiles between the deep earth and the atmosphere, and also to monitor volcanic activity. This is done by flying transects under the entire width of the gas plume to measure the output, or flux, of SO_2. This is usually done by driving or walking under the width of the plume, but is limited by road access and obstructions at ground level. The drone bypasses these problems, is faster, and can even directly measure wind speed at plume height, a key variable for the flux calculation, by passively drifting with the plume.

By combining gas concentration ratios and SO_2 flux measurements, the CO_2 flux can also be calculated.

3.3 Gas Giants

Turrialba volcano and Masaya volcano are Central Americas largest degassing volcanoes, with each emitting upwards of two million tons of SO_2, among other gases, over the past decade alone (Calculations based on data from de Moor et al., 2016 and Martin et al., 2010). Both of these gas giants are dangerously close to major cities, so they are key locations to test new measurement techniques.

Figure 7: The location of Masaya volcano and Turrialba volcano.

Turrialba was sculpted out by a series of violent eruptions during the past 10, 000 years, before all activity came to a halt in the year 1866. Then, in 1996, the volcano sprang to life once

Figure 8: Team members assess the data just collected atop Turrialba volcano

again. Fast forward twenty years, and explosive bursts of ash frequently rise several hundred meters above the summit, causing havoc at the international airport in San Jose, the capital. The opening of new vents and the escape of magmatic gas from intruding magma is the main driver of the ongoing volcanic crisis, and a small lava lake has been spotted forming at the bottom of the crater.

Masaya is a different kind of volcano altogether. It is composed of a large caldera complex formed 2500 years ago, with volcanic cones rising from the floor of the caldera. One of the craters atop the largest cone hosts a vigorously bubbling and convecting lava lake which has attracted a multitude of tourists in recent years.

Unlike Turrialba, Masaya has been persistently active throughout the past several hundred years, with a longstanding history of degassing from the surface of the lava lakes that have come and gone for centuries.

The prodigious degassing at these two volcanoes makes them the ideal locations to test new drone-mounted instrumentation, thereby improving hazard assessments.

3.4 Building compact instrumentation

Figure 9: The MiniGAS and MicroGAS mounted onboard a modified DJI S1000 Octocopter frame with Pixhawk flight controller (payload 5.1 kg on the rim of Turrialba volcano, 26 April 2017

For measuring concentrations of CO_2, SO_2, and H_2S, two compact variations of multiple gas analyzers (Multi-GAS) were designed for drone flights. The MiniGAS and MicroGAS each consist of a pump, electrochemical sensors, and on-board data loggers to store or, in the case of the MiniGAS, transmit the data by telemetry. These instruments weigh in at less than 1 kg each.

A lightweight gas diffusion sampling device also was deployed to measure halogen species and their compositional variation. This device uses a pump and glass tubes with reactive coatings, called denuders, designed to collect the desired halogen compounds. An SO_2 sensor and additional wiring which connects to the drone telemetry system allows the pilot to remotely start the sampling once high SO_2 levels are reached, signaling the drone is in the plume.

A drone-mounted mini-DOAS (Differential Optical Absorption Spectrometer) or "DROAS" was built for SO_2 flux measurements by drone. In addition to the telescope and UV spectrometer, this instrument contains a micro-computer running the data collection program.

3.5 Choosing the right drone

Two octocopters and two quadcopters were used for this expedition, in combination with different types of compact sensors and spectrometers. Choosing the right drone to fly each mission was based on the goals which needed to be achieved.

Figure 10: Masaya volcano, 6 May 2017. Left: A custom-built RAVEN (payload 1.3 kg) quadcopter with the denuder sampling unit mounted on board. Right: A DJI S1000 octocopter (payload 5.1 kg) with the DROAS unit in grey, and the MiniGAS unit in red, placed in front.

For example, is the goal to perform a DROAS traverse, which requires covering a large distance (a kilometre or more) beyond the line of sight? Then a sturdy octocopter with autonomous flying capability is ideal.

Or, is the goal to fly straight up until the gas plume is reached, and hover there as long as the battery allows? A manual flight by a lightweight quadcopter is best suited to this mission.

The team discovered the suitability and limitations of each drone, and created an effective protocol for assessing when and where it was suitable, or too dangerous, to fly each type. A pre-flight checklist was used to ensure that wind, fog, and other hazards are considered and that bystanders in the area are in a safe viewing location.

3.6 Flying High

We flew a dozen missions at Turrialba and Masaya from the crater rim, base, and downwind from the plume at each volcano. Each of the instruments was deployed, sometimes in tandem, on at least one drone.

During these flights, we were able to successfully enter the volcanic plume to measure SO_2 and CO_2 concentrations. We also conducted several flight transects to estimate SO_2 flux values. Examples of these missions can be seen in Figures 11, and 12.

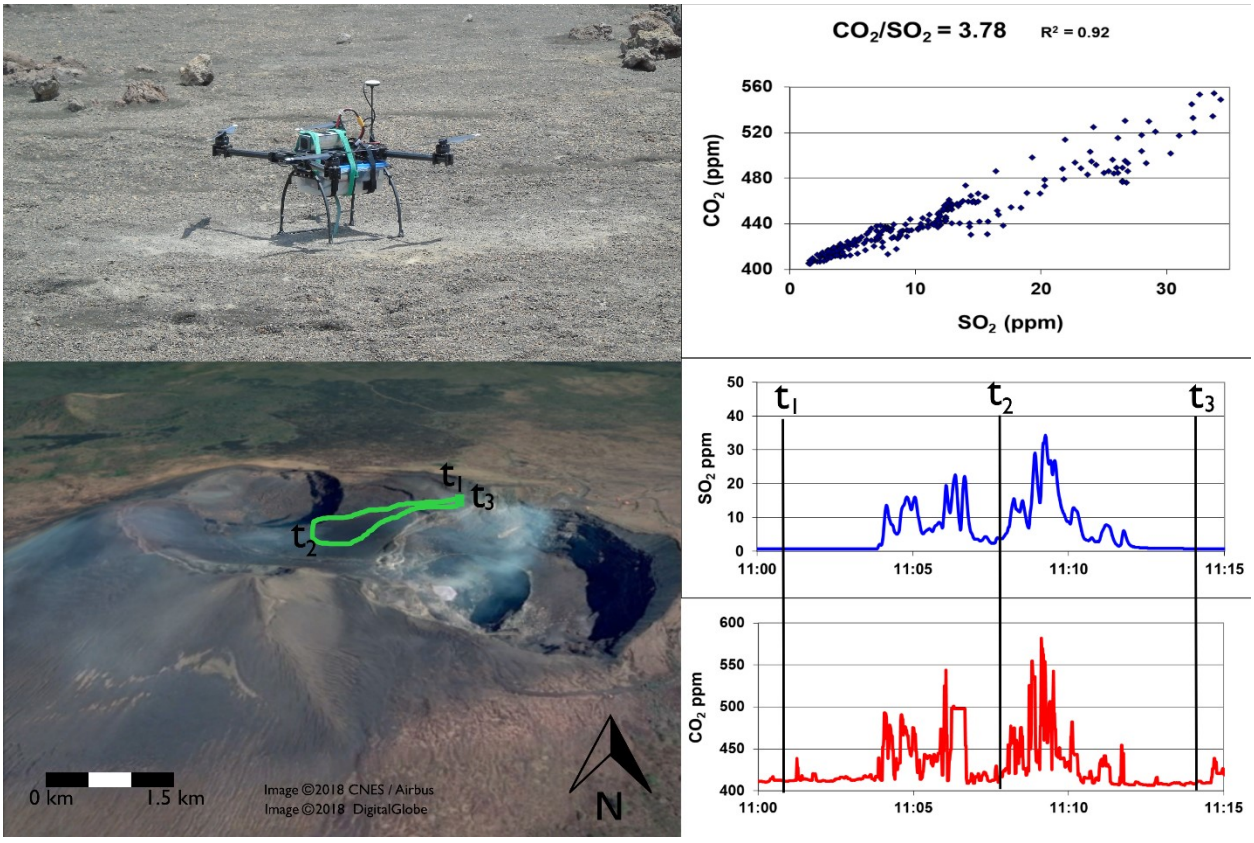

Figure 11: Sample flight mission showing the CO_2/SO_2 ratio measured in the plume of Masaya volcano. At t1, the drone takes off from the edge of the crater. At t2, the drone has passed through the plume and turns around for the return journey through the plume again. At t3, the drone lands back at the start location.

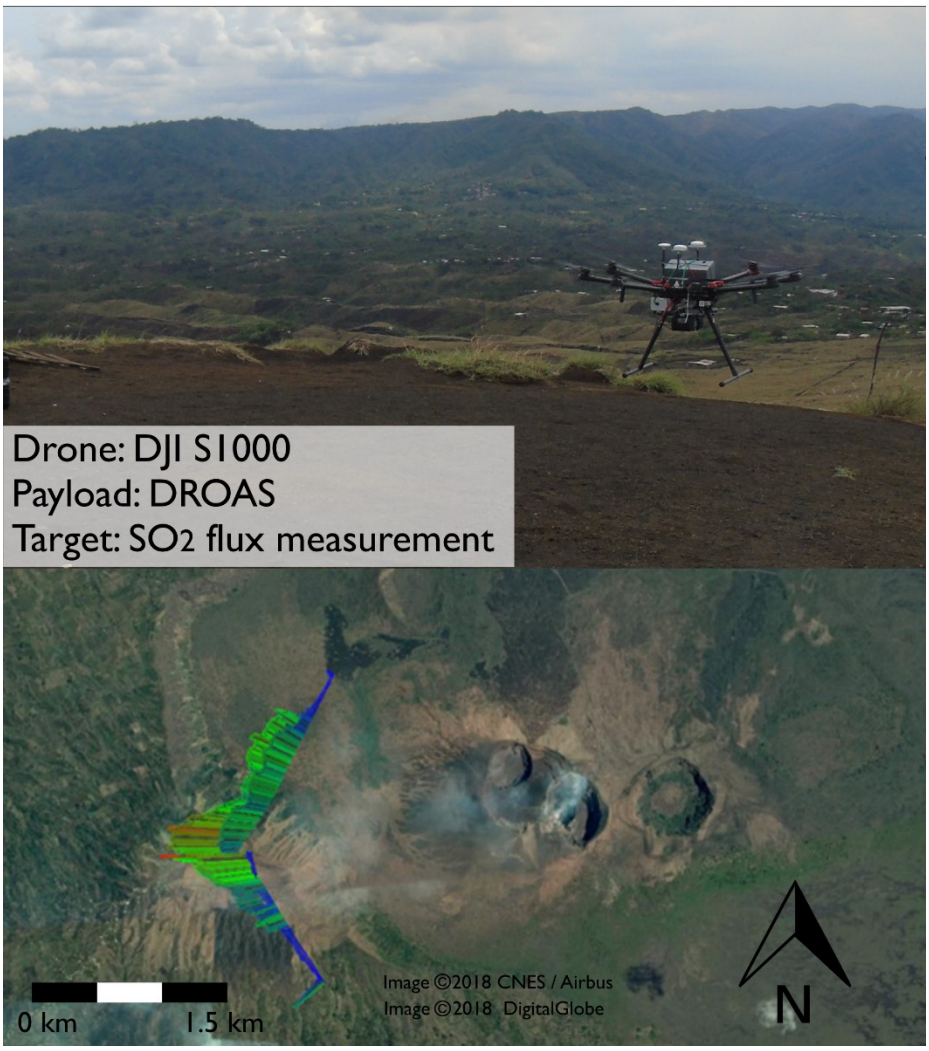

Figure 12: Sample flight mission showing the SO_2 flux measured in a downwind transect of the plume of Masaya volcano.

3.7 Soaring into the Future

Researchers were able to demonstrate an array of drone and sensor capabilities in volcanic gas plumes during two weeks of field testing in Costa Rica and Nicaragua. At the same time, countless lessons were learned as to the adaptability and preparedness needed to undertake such a task. In addition to acquiring permits, customs letters, plane-approved batteries, and spare parts prior to travel, coordinating with local authorities proved vital to dealing with the surprises which abounded at every stage of the fieldwork.

With proper safety measures and permissions in place, this kind of work could revolutionize volcanic gas measurements made at volcanoes without ever putting the researchers in danger. New ash deposits and crater lakes could be sampled during eruptive periods. Instrumentation could be deployed in craters by drone. The possibilities are endless.

Figure 13: A researcher pilots an octocopter toward the gas plume at Turrialba volcano.

4 Conclusion and Future work

This thesis has examined two unique methods of measuring volcanic gases: an indirect method using isotopes in tree rings as a proxy, as well as a direct method using UAVs and compact sensors. Both have proven to be promising new techniques when applied at Turrialba volcano, are ready to be tested at other volcanoes, and have potential for a wider application beyond volcanology.

In the first study (chapter 2), stable carbon and sulfur isotopes were successfully measured by EA-CF-IRMS and a biannual record of $\delta^{13}C$ and $\delta^{34}S$ was created for 1994/1995 to 2014/2015. The $\delta^{13}C$ values of the *A. Acuminata* trees range from -22.9 ‰ to -25.1 ‰, while the $\delta^{34}S$ values range from 5.9 ‰ to 11.9 ‰. Background samples show minor variations and an overall slightly decreasing trend in $\delta^{13}C$ and $\delta^{34}S$. Sample TJ05, the tree exposed to the volcanic plume, follows the same trends until 2004/2005. At this time, $\delta^{13}C$ begins to increase gradually. This coincides with the onset of significant SO_2 emissions from Turrialba. From 2010/2011 to 2014/2015, a remarkable shift is seen in $\delta^{13}C$ and $\delta^{34}S$ for sample TJ05. The $\delta^{13}C$ increases drastically, resulting in a shift of +1.3 ‰, while the $\delta^{34}S$ undergoes a sharp shift of –5.2 ‰. These shifts correspond with the strongest degassing. The mechanism proposed to explain this is a combination of the strong degassing closing the stomata of the leaves, thereby altering the carbon fractionation, and the additional volcanic source to the atmosphere providing a distinct sulfur signature which influences the composition of sulfur in the tree rings. Duplication produced an analytical standard deviation of 0.06 ‰ for $\delta^{13}C$ and a standard deviation between duplicate cores of 0.08 ‰. A quadruplicate analysis produced an analytical standard deviation of 0.923 ‰ for $\delta^{34}S$ and a standard deviation between duplicate cores of 0.65 ‰.

In the second study (chapter 3), a compact mini-GAS sensor was mounted onto multiple drones and deployed in the field. Automated flight of the drones was achieved and multiple transects were conducted through and under the volcanic plumes of Turrialba volcano, and Masaya volcano. During these test flights, SO_2 and CO_2 concentrations were successfully measured in the plume, demonstrating the potential of this new method for application at volcanoes around the world.

Both of these method development studies have shown preliminary results that recommend them for future application. In particular, the tree ring study should be applied to other volcanoes and on different species of tree to constrain the limitations of the proxy. Furthermore, future field campaigns are planned to measure volcanic gases by drone in order to quantify the variation within the plume. Both studies are inter-disciplinary and could be applied outside the realm of volcanic gas measurement. For example, stable sulfur and carbon isotopes in tree rings have been applied as archives of industrial pollution, therefore the use of drone-mounted gas sensors should be expanded to include testing at smelters and industrial sites to monitor pollution and greenhouse gas emissions. The tree ring proxy could be combined with other proxies such as ice cores or pollen if local lakes or glaciers exist, which would further strengthen this proxy.

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