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Carbon and sulfur isotopes in tree rings as a proxy for volcanic degassing

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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 degassing has not yet been fully realized. Here, we applied a new proxy using sulfur and carbon isotopes in tree rings to examine fluctuations in gas emission at Turrialba volcano, Costa Rica. Since 2009, Turrialba has emitted a persistent gas plume and increasingly frequent explosions and ash eruptions as activity has accelerated. We collected cores from a species of alder tree, *Alnus acuminata*, at several locations surrounding the volcano. Biannual isotopic analysis of rings demonstrated a notable $\delta^{34}S$ shift of –5.2‰ and a similarly sharp $\delta^{13}C$ shift of +1.3‰ in trees downwind of the plume following the onset of strong degassing in 2009. We propose that these shifts in the isotopic values of the tree correspond to those of the volcanic SO_2 and CO_2, and in the case of the $\delta^{13}C$, an additional fractionation caused by leaf impairment 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.

INTRODUCTION

Dendrochemistry is a rapidly evolving field examining variations in elemental abundance within tree rings, which can provide a temporal record of external pollution. It has been applied to date volcanic eruptions using trace elements absorbed from soil, both from distal trees (e.g., Hall et al., 1990; Pearson et al., 2005) and local trees (Sheppard et al., 2008; Watt et al., 2007). While trace elements such as metals may be used to date single events, their mobility both in soils and within trees limits their functionality for reconstructing eruption sequences at highly active volcanoes. Volcanic plumes carrying CO_2 and SO_2 supply a source of sulfur and carbon that can rapidly enter trees. Carbon enters solely through the pores, called stomata, in the leaves, and is systematically incorporated into the structure of the wood as cellulose (McCarroll and Loader, 2004). Sulfur enters both as SO_2 through the stomata and as SO_4 through the root system (Wynn et al., 2014) and is predominantly structurally fixed within the cell wall (Fairchild et al., 2009).

In this study, we examined sulfur and carbon isotopes in 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 and Loader, 2004; Treydte et al., 2009), and dendrochemical studies have successfully tracked anthropogenic pollution using stable isotopes of carbon (Savard et al., 2002) and sulfur (Wynn et al., 2014; Thomas et al., 2013; Kawamura et al., 2006; Ishida et al., 2015).We examined whether volcanogenic emissions may be recorded in a similar fashion by studying the tree rings from a volcano before and during a degassing crisis. We measured both carbon and sulfur isotopes in tree rings to correlate changes with nearby volcanic gas output.

Turrialba Degassing Crisis

At 3340 m above sea level, Turrialba is Costa Rica's second tallest volcano, which reawakened in A.D. 1996 following an ~150 yr hiatus. The presence of SO_2 was first detected in fumaroles in 2001–2002 (Vaselli et al., 2010), with gas emissions reaching a baseline of ~360 metric tons (Mt) SO_2 per day by 2008 (Conde et al., 2014). Emissions peaked at 3500 Mt SO_2 day^{-1} in the months preceding a vent-opening phreatic eruption in January 2010, with an average of 1000 Mt SO_2 day^{-1} through 2012 (Conde et al., 2014). Another vent opened in January 2012, and further eruptions in 2014 led to the collapse of the West crater. Escalating eruptive activity during 2015–2019 has been accompanied by a persistent gas plume. An estimated output of 2 Mt of SO_2 was emitted from 2008 to 2015 ($\delta^{34}S$ = +3.4‰ ± 0.5‰), and 0.86 Mt of CO_2 was emitted from 2014 to 2015 as higher CO_2/S ratios dominated (de Moor et al., 2016), with a volcanic plume source $\delta^{13}C$ of –3.9‰ ± 0.4‰ (Malowany et al., 2017).

MATERIALS AND METHODS

We collected more than 80 cores in April and May 2016 from 30 *Alnus acuminata* (alder) trees on the flanks of Turrialba and from a background site 50 km away. In subtropical regions and at high elevation, rings in this species are formed as a result of water limitation in the dry season (Grau et al., 2003; Morales et al., 2004), which occurs in the Costa Rican highlands from January to April. We constructed the first dendrochronological record for the region and compared this record with environmental data (see Appendix DRI in the GSA Data Repository[1]).

[1]GSA Data Repository item 2019295, Appendix DR1 (dendrochronological, analytical, and statistical methods used in this paper, as well as sample locations and isotopic data tables) and Appendix DR2 (all raw and processed data), is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

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Of the trees sampled and dated, four trees were selected for dendrochemical analysis (Appendix DRII). Sample TJ05 was chosen as the exposed tree that was most affected by degassing, located 1.5 km southwest of the volcano's summit crater (Fig. 1) at the edge of the kill zone area (where nearly all vegetation has been killed by the intense volcanic activity). Wind direction is consistent at Turrialba, averaging 247° ± 19° NE (Conde et al., 2014). Sample LP01 came from a tree located 2.5 km south of the summit in an area that is sometimes affected by the volcanic plume. Sample TJ13 was taken 3.5 km southeast of the summit and is a background control sample for the volcano. Sample SG08 is a distal background sample from San Gerardo de Dota (50 km from Turrialba), a valley in the Talamanca Mountains that hosts *A. acuminata* at similar elevations. It was collected perpendicular from the plume direction and upwind of the populous Central Valley, so that no volcanic or anthropogenic influence would be expected (Fig. 1).

From these four samples, rings were dissected with a steel scalpel and ground into powders using a steel-ball mill. We chose to use whole wood, as is commonly used in dendrochemical studies (McCarroll and Loader, 2004). Tree rings were pooled into 2 yr sample increments to yield biannual resolution, in order to compensate for any 1 yr errors from a missing or extra ring, and to provide sufficient material for sulfur isotope analysis. Geochemical analysis of wood powders was performed by isotope ratio mass spectrometry in continuous-flow mode with an elemental analyzer (EA-CF-IRMS) at the Geotop Light Stable Isotope Laboratory of the Université du Québec à Montréal. Details and an error analysis can be found in Appendix DRIII.

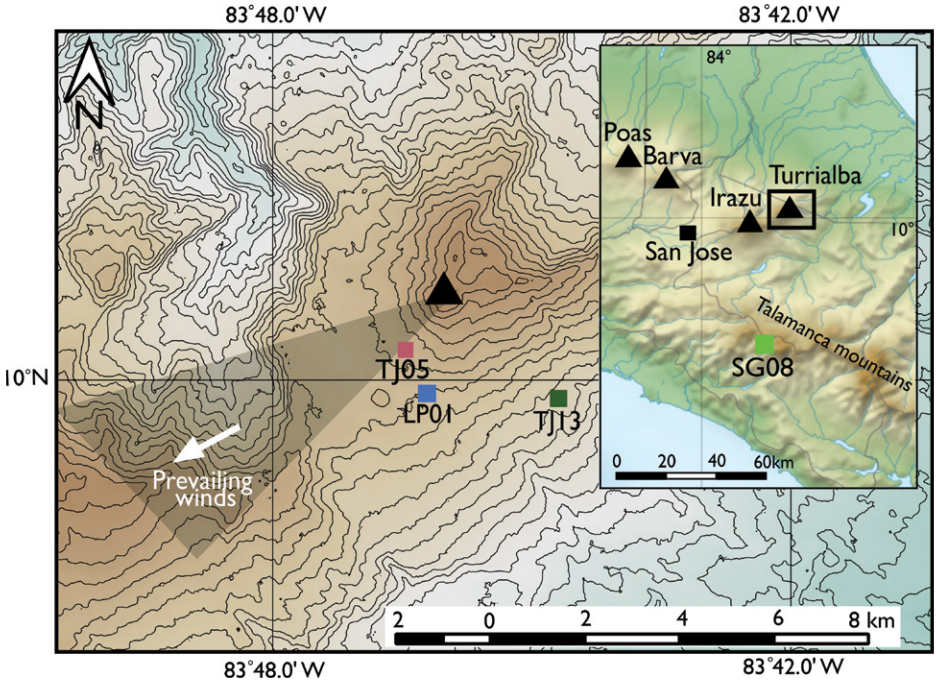

Figure 1. Sampling locations at Turrialba volcano, Costa Rica, of trees used for dendrochemical analysis. Digital elevation model (DEM) contours were derived from Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) Global Digital Elevation Model (GDEM) data, a product of the Ministry of Economy, Trade, and Industry of Japan (METI) and NASA. Trade winds are northeasterlies, and mean plume direction heading is 247° ± 19°, as estimated by Conde et al. (2014).

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 decrease in $\delta^{13}C$ due to fossil fuel emissions (McCarroll and 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 and Loader, 2004). In general, all four samples follow a trend toward lower 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 remained stable for another 10 yr, while sample TJ05 became more enriched in ^{13}C. This positive trend in TJ05 is especially pronounced from 2010/2011 to 2014/2015, when it noticeably diverged from the local background sample, reaching 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 data display significant correlation ($r = 0.80$, $p < 0.05$, $N = 9$) between the cumulative SO_2 emissions and $\delta^{13}C$ of TJ05 for 1998–2015, unlike the data from the other trees.

The $\delta^{34}S$ values range from +5.9‰ to +11.9‰. Our results are comparable to values obtained by two previous studies (Kawamura et al., 2006; Yang et al., 1996), and they are somewhat enriched in ^{34}S compared to three other studies, which ranged from 0‰ to 6‰ (Giesemann et al., 2005; Thomas et al., 2013; Wynn et al., 2014). Sample LP01 had the lowest range in $\delta^{34}S$, remaining very stable throughout the entire series and never exceeding +8‰. Samples TJ13 and SG08 changed little and occupy a midrange, spanning from +7.5‰ to +10.5‰. Sample TJ05 dropped by –2.3‰ in 2004/2005, and then increased by +2.3‰ from 2005–2007 until 2010–2011. After this peak at +11.5‰ ± 1‰ in 2010/2011, a sharp decrease occurred. By 2014/2015, sample TJ05 had dipped to +6.3‰ ± 1‰, falling under the 10th percentile of all measured values. Furthermore, this shift of –5.2‰ coincided with the similarly sharp +1.3‰ shift in $\delta^{13}C$ in the same time frame. There is significant correlation ($r = –0.72$, $p < 0.05$, $N = 9$) between the cumulative SO_2 emissions and $\delta^{34}S$ values of TJ05 for 1998–2015, while there is no significant correlation for the other tree series. The full data set is available in Appendix DRIV.

DISCUSSION

At Turrialba volcano, carbon and sulfur isotopic ratios in tree rings affected by volcanic degassing show 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.

Carbon Isotopes

While there are minor fluctuations in $\delta^{13}C$, on the order of ±0.5‰, in all samples, and a generally flat trend in samples SG08, LP01, and TJ13, there is a striking +1.3‰ increase after 2010 observed for our proximal downwind volcanic sample, TJ05. This sample first started to diverge to values higher than that of the local background sample, TJ13, after 2006/2007. This divergence immediately followed the first significant SO_2 emissions and notable sulfate content in rainwaters from Turrialba in 2005 (Martini et al., 2010). Therefore, the $\delta^{13}C$ values may be sensitive to relatively subtle changes occurring at the volcano during the early stages of the degassing crisis. The enrichment of sample TJ05 as compared to the background TJ13 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 one-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 (the

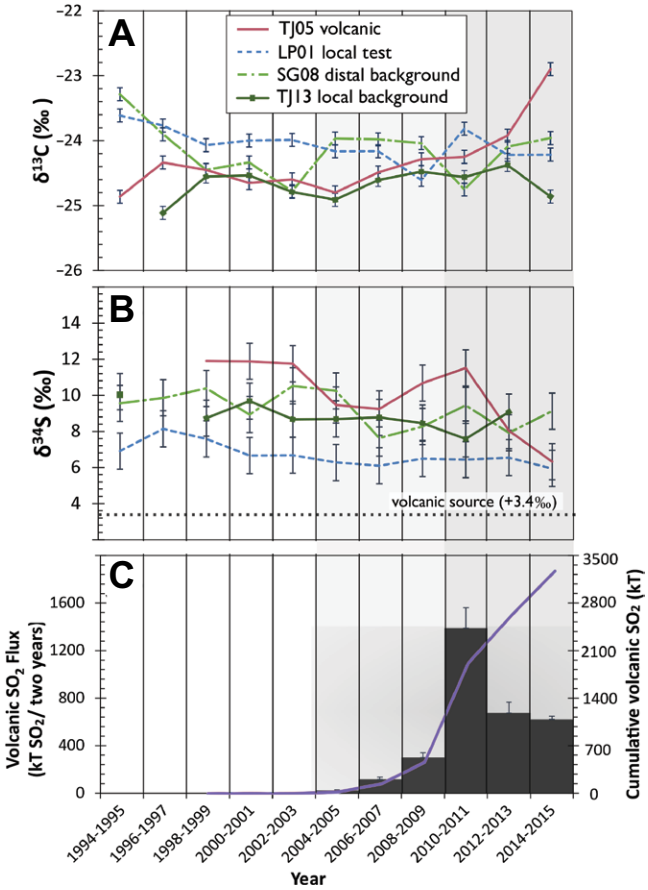

Figure 2. A: Biannual $\delta^{13}C$ values at Turrialba volcano, Costa Rica, relative to Vienna Peedee belemnite (VPDB), with analytical error of 0.1‰. TJ05, LP01, SG08, and TJ13 are tree sample numbers. B: Biannual $\delta^{34}S$ values relative to Vienna Canyon Diablo troilite (VCDT) with analytical error of ±1‰. C: Total estimated biannual SO_2 output (bar chart, left axis) and cumulative SO_2 of Turrialba volcano from NASA Ozone Monitoring Instrument (OMI) satellite data (purple line; Fioletov et al., 2016).

Horne smelter in northeastern Canada). However, despite a sharp onset of pollution at that smelter, the increase of +3.5‰ occurred over a period of 15 yr; in our study, the increase of +1.3‰ occurred over a period of 5 yr. Another point to consider is that, while the smelter emits only SO_2, the volcano is also emitting CO_2 with a unique end-member value. 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 –3.9‰ ± 0.4‰ (Malowany et al., 2017). This relatively enriched source of ^{13}C likely contributed to the increase in tree ring $\delta^{13}C$ observed at Turrialba. This makes sense physiologically, since any local atmospheric variations will be reflected in the isotopic ratios of vegetation, which photosynthesizes the carbon. At the same time, strong fumigation of trees by SO_2 will have its own direct impact on the physiology of a tree. The exposure causes closure of stomata (the pores through which trees exchange gases with the atmosphere), which in turn causes preferential uptake of ^{13}C (Martin et al., 1988). This may also explain why the cumulative SO_2 output correlates with $\delta^{13}C$ in TJ05; as aerosols and ash accumulate on the foliage and in the surrounding environment, the stomatal pores may be increasingly obstructed and/or damaged. Stomata obstruction was also observed by Savard et al. (2002) for trees strongly affected by an SO_2-emiting smelter, and it is likely the other main driver of the increase in tree-ring $\delta^{13}C$ observed in our study. While volcanic hydrogen fluoride can cause fatal leaf injuries (Delmelle et al., 2002), we expect that because TJ05 is in the transition zone, rather than in the kill zone (Tortini et al., 2017), stomatal blockage during the study period is related to the strong SO_2 exposure.

Sulfur Isotopes

Sources of sulfur influence the isotopic ratios of vegetation in a similar way to carbon, depending on the proportion of direct atmospheric uptake through the leaves versus sulfur absorption through the roots. The $\delta^{34}S$ of TJ05 demonstrates a decrease in ^{34}S resulting in a shift of –5.2‰ following the peak in degassing in 2010/2011, while trends prior to this are on the order of background changes, as seen in SG08 and TJ13. This shift is in good agreement with the observed shifts of –4‰ (Thomas et al., 2013), –5‰ (Wynn et al., 2014; Kawamura et al., 2006), 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 middle 20th century, demonstrating that this depletion trend persisted until the late 1970s and early 1980s, when emissions were regulated and then declined. While SO_2 emitted from fossil fuels has $\delta^{34}S$ values ranging from –3‰ to +9‰ (Mayer, 1998), the depletion in ^{34}S at Turrialba approaches the average $\delta^{34}S$ of the gas plume at Turrialba of +3.4‰ ± 0.5‰ (de Moor et al., 2016). However, the tree-ring $\delta^{34}S$ values do not fully reach the SO_2 end-member value of the plume, and trees may require prolonged exposure in order to reach end-member values, which may explain why the $\delta^{34}S$ of TJ05 correlates with total SO_2 output. We cannot ascertain whether this gap in $\delta^{34}S$ between trees and the plume is caused by a lag in atmospheric forcing or sulfate accumulation, or whether there is dilution in the soil prior to root uptake. Alternatively, it has been shown that spruce trees subject to high concentrations of SO_2 respond by emitting H_2S, which causes a relative enrichment of ^{34}S in the wood as compared to input values (Jędrysek et al., 2002). This fractionation process would partially dampen the volcanically induced ^{34}S depletion of the tree rings, although this response has not been shown experimentally in *A. acuminata*.

CONCLUDING REMARKS

This is the first study linking sulfur and carbon isotopes to proximal volcanic activity. We have found that tree rings have a high potential to be used as a proxy for past degassing. A rapid and large $\delta^{34}S$ shift of –5.2‰ and a similarly sharp $\delta^{13}C$ shift of +1.3‰ were observed in tree rings downwind of emissions at Turrialba volcano, coinciding with the onset of strong volcanic degassing between 2010 and 2015, while no such trends occurred in background samples. These substantial shifts far exceed the analytical uncertainty of our isotopic measurements. Additionally, a subtle $\delta^{13}C$ increase began 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. Our work extends the application of carbon and sulfur isotopes in dendrochemistry, demonstrating their versatility as tracers of paleo-atmospheric fluctuations in tropical trees.

This new proxy has the potential to overcome limitations in 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 historical accounts, if they exist. It is important to document and understand the evolution of past eruptions and unrest at volcanoes to better forecast the type of eruption sequence that is likely to occur in the future. Therefore, a means of identifying and dating degassing episodes provides crucial insight into a volcano's activity over time scales of 100–1000 yr.

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