SOURCES OF VOLCANIC GASES FROM DOMINICA, LESSER ANTILLES

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INTRODUCTION

Dominica boasts nine young volcanic complexes, five of which have associated geothermal fields. Volcano hydrothermal monitoring provides information on temperature, origin, and secular changes in chemical composition of volcanic fluids and informs on potential volcanic hazards to which the public may be exposed. We sampled low temperature fumaroles and measured bulk gas composition and isotope ratios of N, He, S, and C for hydrothermal areas across the island. Isotope ratios enable us to track the gas sources for each hydrothermal system. Gas source components of a subduction zone volcano include the subducting slab with subducted sediment, the earth's mantle, crustal rocks just below the volcano, and the ubiquitous ambient air contamination.

SOURCE COMPONENTS FROM STABLE ISOTOPE SYSTEMATICS

The general isotopic compositions of volcanic gases from different tectonic settings is well established and can help define their source components (Poorter et al., 1991; Giggenbach 1991, 1992). The $\delta^{15}\text{N}$ of mid-ocean ridge basalts (MORB) is approximately -5‰, whereas atmospheric N_2 is 0‰, and terrigenous sediments typically have values of +6 to +7‰ (Fischer et al., 2002). The contrasts in $\delta^{15}\text{N}$ values of the gases allow this isotope system to be used as a potential tracer of volatile recycling from subducted sediments along the Lesser Antilles arc.

The $^3\text{He}/^4\text{He}$ ratios can be used to discriminate between mantle and crustal gases. An air-normalized $(^3\text{He}/^4\text{He})_{\text{R}}$ of mantle gases ~ 30 has been used as evidence for the existence of a 'primordial' undegassed deep mantle reservoir, whereas MORB has $(^3\text{He}/^4\text{He})_{\text{R}} = \sim +8 \pm 1$ (Class and Goldstein, 2005). Terrigenous sediment rich in U and Th results in high ^4He concentrations and low $(^3\text{He}/^4\text{He})_{\text{R}}$. Thus, $(^3\text{He}/^4\text{He})_{\text{R}}$ can aid in identifying different mantle volatiles from recycled subducted sediment sources: Low $(^3\text{He}/^4\text{He})_{\text{R}}$ reflects recycled terrigenous material enriched in radiogenic ^4He , whereas high $(^3\text{He}/^4\text{He})_{\text{R}}$ values indicate a magmatic mantle component.

Cosmochemical constraints suggest that sulfur may make up ~ 9 -12% of the Earth's core whereas the remaining S cycles through the rest of the solid Earth (Dreibus and Palme, 1996). Mantle $\delta^{34}\text{S}$ values are close to 0‰, with a value of -1.28 ± 0.33 ‰ proposed by Labidi and Moreira (2013). Subducted marine sediment may carry sulfate (gypsum, anhydrite) with near seawater $\delta^{34}\text{S}$ values (+18 to +25 ‰), whereas altered sea floor and organic rich shales may be rich in sulfides with $\delta^{34}\text{S}$ values down to -15‰ or lower. Thus, either very high or very low $\delta^{34}\text{S}$ values may point to recycled sedimentary sulfur, whereas values close to 0‰ represent mantle sulfur contributions. High temperature, volcanic sulfur-bearing gases consist mainly of SO_2 with minor amounts of H_2S , whereas low temperature fumaroles and geothermal gases are rich in H_2S and carry little to no SO_2 . The $\delta^{34}\text{S}$ of H_2S in fumaroles at arc volcanoes ranges from +1.6 to -5.2‰ in the eastern Indonesian arc (Poorter et al., 1991) and was found to be relatively uniform

($2.5 \pm 0.28\%$) at Milos in Greece (Gillhooly et al., 2014). Many low temperature fumaroles precipitated native S as a result of the oxidation of H_2S , which may range in $\delta^{34}\text{S}$ from -4.7 to +3.2‰ in Eastern Indonesia (Poorter et al., 1991).

Carbon occurs in the upper mantle as CO_2 , CO, CH_4 and COS (Deines, 1992). The $\delta^{13}\text{C}$ of mantle carbon is $-5 \pm 2\%$ (Schidlowski, 1995). Subducted sedimentary carbon may consist of carbonates ($\delta^{13}\text{C} = \sim 0\%$) or shales rich in organic matter ($\delta^{13}\text{C} = -20$ to -30%), whereas the altered ocean slab may carry substantial carbonate of marine derivation ($\delta^{13}\text{C} = 0\%$). Most arc volcanoes carry up to 75% of their CO_2 from recycled sedimentary carbon (Varekamp et al., 1992). Ambient atmospheric CO_2 , currently at ~ 411 ppmv has $\delta^{13}\text{C} = -8.5\%$.

The combination of S and C isotope systematics of volcanic gases enables us to distinguish between volatile recycling of subducted black shales (low $\delta^{13}\text{C}$ and low $\delta^{34}\text{S}$) versus carbonates – terrigenous sediment with high $\delta^{34}\text{S}$ and close to 0‰ for $\delta^{13}\text{C}$.

STUDY AREA

Gas samples were taken from five geothermal sites on Dominica. Four of the five sites are located in the southern portion of the island and the Cold Soufriere is located on the northern tip of the island. The best-known site, the Valley of Desolation (VoD), has numerous fumaroles and bubbling pools over an area of $\sim 0.5\text{km}^2$ (Joseph et al., 2011). Reported fumarole temperatures from the VoD over the last century have been between 91°C and 99°C while bubbling water pools have temperatures in the range 40°C - 96°C (Joseph et al., 2011). The 2017 temperature observations are consistent with these historical records, with the VoD having some of the hottest features with temperatures of 99°C for both the Bubbling Pool South and the Black Bubbler.

Sulfur Springs is the second hottest site at 91°C , characterized by sulfurous fumaroles and hot pools with a plethora of bright yellow sulfur deposits surrounding gaseous vents. Galion is the third hottest fumarolic site at 87.5°C . Many bright yellow sulfur deposits were present around gaseous vents. Sulfur Springs and Galion activity is part of the Plat Pays

volcanic complex (Joseph et al., 2011). Watten Waven is characterized by numerous bubbling pools and fumaroles with a temperature of 59°C , and its activity is part of the Watten Waven/Micotrin volcanic complex. The coldest hydrothermal site, at 24°C , is aptly named Cold Soufriere. It lacks fumaroles, H_2S odors, and kaipohan geothermal features (Joseph et al., 2011).

METHODOLOGY

Cleaned, empty Giggenbach flasks were weighed before being prepared for sampling. Approximately 50ml of a 5M NaOH solution was then funneled into each Giggenbach flask. The Giggenbach flasks next were evacuated with a hand pump, and then re-weighed. A separate set of Giggenbach flasks were prepared as well and bulk gas composition was analyzed at the INVG laboratory in Palermo, Sicily.

Gas from bubbling pools were sampled at the VoD, Cold Soufriere and Watten Waven sites. Dry fumarolic vents were sampled at Sulfur Springs and Galion. Thus, the standard methods described by Giggenbach and Goguel (1989) had to be adapted for the variation in the type of geothermal feature sampled. For bubbling pool sites, a funnel was attached to the end of a tube covering the most vigorously bubbling spots in the pool which was connected to the inlet of the Giggenbach flask. The Giggenbach flask was opened and gases seeped up the tube and into the flask. The flask was held open as long as gases bubbled through the NaOH solution. Once bubbling in the flask slowed down, the flask was closed to allow absorption of soluble gases, and after a few seconds, the flask was opened again to allow more gas to bubble through the flask. This process is repeated four to five times to ensure that as much gas was collected as the flask could hold. Careful attention was paid that no liquid from the pool entered the flasks.

For the fumarolic vents at Galion and Sulfur Springs, a $\sim 1\text{m}$ titanium tube was gently hammered into the surface layer as close as possible to the hottest portion of the fumarole. A glass connector was fitted to the top of the Ti-tube, and the Giggenbach flask fitted with a ground glass joint onto the connector. The same protocol of opening and closing the flask when bubbling intensity decreased was followed. We paid

Figure 1: Manifold that was used to draw headspace gases from the Giggenbach flasks. The glass manifold was first evacuated, then the headspace gas in the Giggenbach flask was allowed to expand into the glass syringe before isolating the volume above the upper green valve. The gas was then injected into the Exetainer. This process was repeated as many times as possible for each sample.

attention to the high temperatures of the fumaroles as well as avoided H_2S inhalation during sampling.

Ambient air samples were collected with a 100ml syringe at varying distances from the vents and then injected in pre-evacuated ‘Exetainers’ for $\delta^{13}\text{C}(\text{CO}_2)$ analysis. The syringe was pumped full and emptied several times to avoid sample carry-over and contamination. At bubbling pool sites, the syringe was filled as close to the most vigorously bubbling portion of the pool; at fumarolic vents, filled as close to the opening as possible. For atmospheric samples, the syringe was pumped at least 0.5km away from any fumarole or bubbling pool site. Analyses for $\delta^{13}\text{C}(\text{CO}_2)$ and CO_2 concentrations were done at the UC Davis Stable Isotope Lab.

Bright yellow sulfur precipitates close to the vents were taken from VoD, Sulfur Springs, Galion, and Cold Soufriere. Samples were homogenized and analyzed for mineralogy by XRD at Wesleyan University, and for $\delta^{34}\text{S}$ at the OASIC Lab at Louisiana State University. The sulfur was precipitated as BaSO_4 and gravimetric analysis of the Giggenbach flask solutions followed the method of Fahlquist and Janik (1992). The BaSO_4 precipitate was analyzed for $\delta^{34}\text{S}$ at the OASIC Lab at LSU. Headspace gases were transferred into pre-evacuated exetainers using an extraction line and a gas-tight syringe as a pump (Fig. 1). Samples were balanced to near atmospheric pressures

with UHP He prior to analyses. Aliquots of the Giggenbach flask headspace gases were sent to the UC Davis Stable Isotope Lab for $\delta^{15}\text{N}-\text{N}_2$ analyses.

RESULTS

Bulk gas composition

Volcanic, magmatic, and hydrothermal gases are dominant in H_2O and CO_2 . Volcanic and magmatic gases are characterized by high SO_2 , HCl , HF , and CO while hydrothermal gases lack these constituents due to mixing with aquifers (Fischer and Chiodini, 2015). Gas compositions analyzed at INVG indicate N_2/Ar ratios typical of arc-type gases (Figure 2), as defined by Giggenbach (1996), suggesting N_2 addition from subducted sediments (Joseph et al., 2011). However, some of the hydrothermal fluids contain deeper source components as indicated by a significant excess of N_2 possibly due to the addition of nitrogen from the subducting slab (Fischer and Chiodini, 2015). This is especially true for discharges from Galion, Sulfur Springs, and VoD.

Nitrogen isotope composition

The $\delta^{15}\text{N}$ results are used to trace the possible sources of the excess N_2 in these gases.

The measured $\delta^{15}\text{N}$ values (Fig. 3) range from -0.84‰ (Galion) to $+0.24\text{‰}$ (VoD Black Bubbler). Galion,

Figure 2: Bulk gas compositions in a He-Ar-N₂ ternary plot, indicating bulk gas compositions with some excess N₂ (arc type gases) and some with stronger air influences.

Sulfur Springs (-0.25‰), Cold Soufriere (-0.19‰), and VoD South (-0.23‰). All these $\delta^{15}\text{N}$ values are considerably lower than the 0‰ of air and the typical values for terrigenous sediment (+6 to +7‰). These negative $\delta^{15}\text{N}$ values may have been sourced from the mantle (-5‰). Galion, Sulfur Springs, Cold Soufriere, VoD South have intermediate $\delta^{15}\text{N}$ values possibly the result of mixing between mantle, subducted-sediment, and the common air end member.

Helium isotope composition

After correction for air contamination, He isotope data range from 6.65 to 8.39 R/Ra. These analyses are just below to close to MORB values ($R/R_A = \sim 8$), indicating a mantle origin for the He with small contributions of subducted sediment. Lower R/Ra values at Sulfur Springs (6.77) and Cold Soufriere (6.65) especially could indicate addition of subducted sediments. Nonetheless, the helium isotope signature indicates largely a mantle derived gas with a small

Figure 3: The $(^3\text{He}/^4\text{He})_R$ and $\delta^{15}\text{N}$ isotopic diagram shows potential mixtures between mantle, and subducted components and mixing with ambient air. One sample suite plots on a mixing curve of ambient air with a component that is strongly leaning to mantle compositions, whereas some of the other samples show a larger contribution from the subducted complex.

input from recycled sediment.

Sulfur isotope composition

Sulfur isotope data of all the analyzed gases range from +2‰ to +12‰ (Fig. 4). Sulfur isotope values of the five bubbling pools have a great range: Cold Soufriere (+4.6‰), VoD Black Bubbler (+1.5‰), VoD South (+2.3‰) and Watten Waven (+12.1‰). The two dry fumarolic sites are Galion (+2.6‰) and Sulfur Springs (+4.3‰). The highest temperature features at VoD (99°C) and Galion (87.5°C), have $\delta^{34}\text{S}$ values closest to mantle values, with some indication of the presence of subducted marine sulfates in the source region.

The surficial native sulfur has more negative $\delta^{34}\text{S}$, while the gas phase sulfur has more positive $\delta^{34}\text{S}$. During equilibrium isotope partition, the higher oxidation state species will have the highest $\delta^{34}\text{S}$. An exception to this rule is the precipitation of native S through oxidation of H_2S : under equilibrium conditions at 200-400°C, where S_8 binds with itself and S_2^- oxidizes to S_0 and the precipitate on the ground is “isotopically lighter”. During this process, the remaining gas will become heavier (Rayleigh fractionation), which may

Figure 4: Temperatures of the various sampling locations with $\delta^{34}\text{S}$ values, both for gases and associated solid sulfur. The latter are always isotopically lighter than the gases. Also shown are two different temperature Rayleigh fractionation curves for the crystallization of solid sulfur from H_2S ; the temperature scale is then used as the % of remaining gas. These curves show the heavier $\delta^{34}\text{S}$ values in the remaining gas with progressive extraction of solid sulfur during precipitation in the air.

drive up gas sulfur values to high extremes with extensive sulfur fractionation. The $\delta^{34}\text{S}$ values for solid sulfur from Cold Soufriere (+2.6‰), Galion (-1.1‰), Sulfur Springs (-0.2‰), and the VoD Black Bubbler (-2.2‰) evidence this type of fractionation, as all of the solid sulfur values are more negative than their respective gas counterparts (Figure 4).

The $\delta^{34}\text{S}$ value of +12‰ of the Watten Waven sample is of interest due to its “isotopically very heavy” nature compared to all other samples that are $< +4.62\%$ in $\delta^{34}\text{S}$. This outlier data point may be the result of extreme sulfur extraction from its gas (unlikely) or the result of SO_2 disproportionation deep in the crust at high temperatures (200–400°C). The two samples with the highest $\delta^{34}\text{S}$ are from cool bubbling pools (Watten

Waven, +12.1‰) and Cold Soufriere, +4.62‰) and fractionation at modest temperature between aqueous and gas sulfur species may be another explanation. Watten Waven solid sulfur deposits were lacking in 2017 but should be looked for during the next field campaign.

Carbon isotope composition

The air samples have contributions from ambient CO_2 and from geothermal/volcanic CO_2 and a $1/\text{CO}_2$ versus $\delta^{13}\text{C}(\text{CO}_2)$ (Keeling plot) is a suitable tool to derive potential mixing endmembers (Figure 5). Plotting $\delta^{13}\text{C}(\text{CO}_2)$ vs $1000/\text{CO}_2$ (in ppmv) results in a more or less linear mixing array between the volcanic and ambient endmembers. The ambient pole plots at 400 ppm and -8.5‰ and the array of data intersects the y axis (‘100% CO_2 ’) near the -2.5‰ value, close to standard mantle $\delta^{13}\text{C}$ values of $-5 \pm 2\%$. Samples (Fig. 5) taken close to Nancy’s Pool at Cold Soufriere (-4.6‰) and the fumarole at Sulfur Springs (-1.7‰)

Figure 5: Keeling diagram with $\delta^{13}\text{C}(\text{CO}_2)$ vs $1000/\text{ppmv CO}_2$. A mixing line is drawn between ambient air and the samples, providing a best estimate for the volcanic component of $\delta^{13}\text{C}(\text{CO}_2) = -2.5\%$, well within the mantle range.

have CO₂ concentrations well above ambient and $\delta^{13}\text{C}(\text{CO}_2)$ closer to mantle values. Samples taken ~0.5km away from any geothermal site plot well within the ambient CO₂ endmember. All other points plot between the two endmembers, indicating mixing between ambient and volcanic CO₂.

CONCLUSIONS

The suite of gas and stable isotope analyses shows a variation between gases with strong mantle affinities, as indicated by high ($^3\text{He}/^4\text{He}$)_R, low $\delta^{13}\text{C}(\text{CO}_2)$ and $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$, and a suite of gases that point more towards small contributions derived from subducted sediment. These hydrothermal gases of Dominica are rich in N₂, H₂, H₂S, and CH₄, pointing more to a geothermal origin than pure volcanic gases directly derived from the underlying magma. It appears that these gases have partially equilibrated in an intermediate geothermal reservoir prior to their emission at the surface. Continued monitoring of these fumarolic sites will allow for greater insight into the geothermal processes in the subsoil of Dominica and possibly may aid in the monitoring of future volcanic activity.

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