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CASE STUDY Thermo Scientific Delta Ray IRIS

The Trail by Fire expedition A continent-scale transect of volcanic degassing

#AboveAndBeyond

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20 Volcanoes. 6 Scientists. 1 Mission. This is the Trail by Fire.

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The atmosphere that allowed our planet to spark and sustain life formed as a result of gases emitted by volcances early in the Earth's history. These volatile elements, mainly water and carbon dioxide, are constantly recycled back into the deep earth at subduction zones – points where tectonic plates sink into the mantle. During this process, the sinking plate is subjected to increasing heat and pressure, releasing volatiles. When added to the mantle, volatiles induce melting and fuel volcanic explosions, completing the cycle. We've had this picture of the earth's system for quite a while, yet the actual flux of volatiles in and out of the deep earth still remains poorly quantified. One of the outstanding questions with profound implications for the Earth system regards how much of the subducted volatile budget is released back to the atmosphere, and how much remains trapped at depth.





Objective

Objective was to provide the first accurate estimate of the flux of volatile species (H_2O , CO_2 , SO_2 , H_2 , CO, HCI, HF, H_2S and OCS) emitted by volcanoes along the entire length of the Nazca plate subduction zone (~6000 km), from the southern tip of Chile all the way to the equator. With nearly 200 active volcanoes (20 in a state of unrest), the South American Andes is one of the world's most tectonically and volcanically active regions. The remote locations, high elevations (up to 6.893 m) and lack of established trails to the summit of most of these volcanoes means that few scientific studies have been done. There's been very little data on this region in the global database of volcanic gas emissions, and we wanted to correct that.



Figure 1. Location map of active volcanoes in South America. The nearly-continuous line results from the subduction of the Nazca Oceanic plate.

Instrumentation

To measure volcanic flux, we used ultraviolet cameras and ultraviolet scanning differential optical absorption spectroscopy (DOAS). These uses scattered UV light from the sun, comparing the absorbance of a band specific to SO_2 in the ultraviolet for light transmitted through the plume of gases emitted from the volcano to light that is not. This gives us the concentration of SO_2 . Then we factor in the speed of the plume movement to get the SO_2 flux in kg/s or tons per day. SO, is the only species we can do this with, as it's the only one that absorbs strongly in the ultraviolet. To complement the SO₂ flux measurements, we then make direct measurements of the complete chemistry of the volcanic emissions (H₂O, CO₂, SO₂, H₂, CO, HCI, HF, H₂S and OCS) using either open-path FTIR, electrochemical and non-dispersive infrared (NDIR) "multi-gas" sensors, filter-packs or direct sampling. From these direct measurements, we get a ratio of each species to SO₂, then use those ratios in combination with the SO₂ flux to determine the flux of the other gases. Many of these techniques can be either operated manually or placed on drones to be transported in places inaccessible to humans. Finally, we used an infrared isotope ratio spectrometer to measure the isotopic composition of the volcanic CO₂.



Figure 2: A. Example of processed UV camera image showing the SO₂ concentration in a volcanic plume. B. Direct sensing measurements by Multi-Gas and bag sampling for IRIS analysis. C. Matrix quadcopter equipped with an UV-spectrometer and Multi-GAS.

Isotope Ratio Infrared Spectrometry

The traditional method for measuring isotopes in volcanic gases is to take a sample of the gas free of any air contamination and bring it back to the laboratory for analysis. This method is time-consuming but mainly, it is unpractical for most volcanoes were the vent is inaccessible and the gas plume cannot be sampled free of air contamination. The advantage of the Thermo Scientific[™] Delta Ray[™] Isotope Ratio Infrared Spectrometer is that analyses can be done in the field and therefore the number of samples is not restricted. Our approach was therefore to take series of samples from the air-diluted volcanic plumes and analyse them back at our camp site (a cosy Land Rover Defender) at the flank of each volcano. By analyzing samples with various concentrations of atmospheric versus volcanic CO, we could then determine the isotopic composition of the pure volcanic CO_2 end member (Fig. 3).



Figure 3a: Photograph of the Delta Ray IRIS installed at the back of our field vehicle.

Results

The expedition provided the first gas measurements at many Andean volcanoes and yielded a series of valuable results (Moussallam et al., 2018, 2017a, 2017b, 2016; Schipper et al., 2017). On the isotope front, our main finding was to show that the δ^{13} C signature of volcanic CO₂ in northern Chile is heavy (isotopic composition close to carbonate), suggesting that most the CO₂ coming out of these volcanoes is indeed derived from the recycling of subducted sediments.



Figure 3b: Delta Ray IRIS data as δ^{13} C in CO₂ (VPDB) versus 1/CO₂ for samples collected with variable mixing ratios of volcanic to atmospheric CO₂. The regression line (dotted) intercept to the y-axis gives the δ^{13} C value of the pure volcanic CO₂.

Conclusion

Results from our expedition have helped further constrain the flux, composition and isotopic signature of volcanic degassing along the Nazca plate subduction zone but these results are punctual and cannot easily be extrapolated over time. To do this we've been working with colleagues at NASA during the entire expedition, scheduling satellite acquisition concurrently with our ground-based measurements. We are now working on using our ground measurements to better calibrate measurements made by satellite and extend our observations in space and time.

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