Monitoring of volcanic gases in the field

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Volatiles in volcanic systems

Volatile elements are those that are stable in the gas phase at the pressure and temperature conditions of the Earth surface and are arguably the most important chemical components of volcanic and magmatic systems. The volatiles: mainly water, CO_2, sulfur, but also halogens and noble gases, control almost all aspects of volcanism. When dissolved in magma at high pressures, volatiles control the melting conditions that lead to magma generation, and play crucial roles in determining the physical properties of melt. As magma rises towards the surface, volatiles exsolve to form a gas phase that fuels volcanic eruptions. As exsolved volatiles escape the magmatic system, either during an eruption or passively during periods of quiescence, they are released to the atmosphere where they can drive climate response over short and long-time scales. This volatile release makes volcanoes a key interface between the Earth's interior and atmosphere, and important parts of the global geochemical cycle.

Subduction zones – volatile recycling

Different types of volcanoes communicate differently with Earth's interior depending on their tectonic setting. Continental arc volcanoes form at convergent tectonic plate boundaries, such as all around the Pacific Ring of Fire, where oceanic crust subducts below continental crust. At depth beneath the subduction zone, dehydration, metamorphic and melting reactions, in the down going slab, lead to enhanced generation of eruptible magma that can ascend through the overriding continental crust to build volcanoes and release some proportion of subducted and mantle volatiles. Petrologic and tectonic modelling can allow volatile inputs to such systems to be estimated but the outputs as volcanic degassing must be measured. This brings us to the key questions: How efficient is volatile recycling at subduction zones?

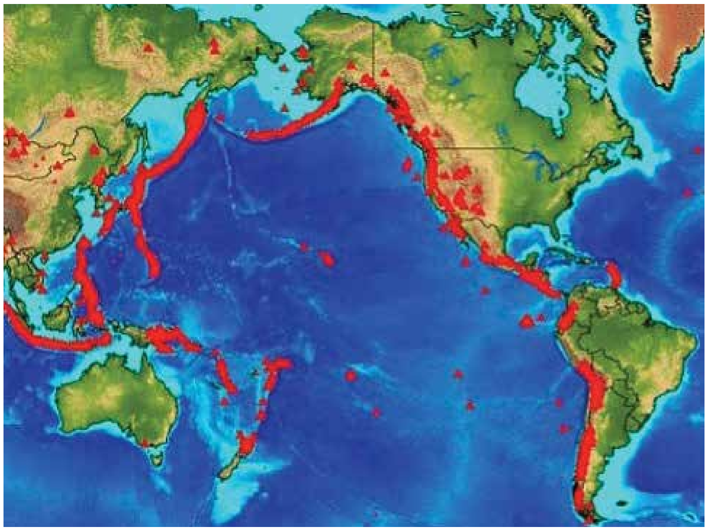

Figure 1. Pacific Ring of Fire.

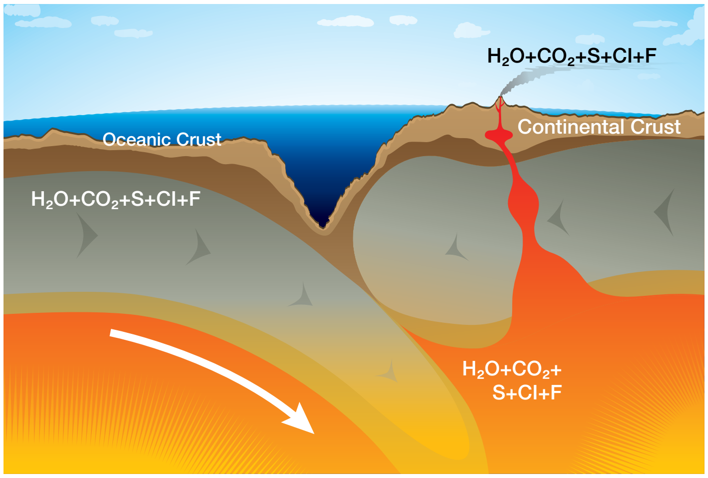

Figure 2. Volatiles are recycled at subduction zones.

$\delta^{13}C$ – key to identifying sources of CO_2

Even though all volatile elements are recycled to some degree at subduction zones, CO_2 is of particular interest, as it is part of the global carbon cycle. Components of the subducting slab, and the underlying mantle itself both contribute CO_2 to arc volcanoes. Conveniently the main sources of CO_2 have different isotopic signatures – or the ratio of C13, C12 in CO_2, expressed as $\delta^{13}C$.

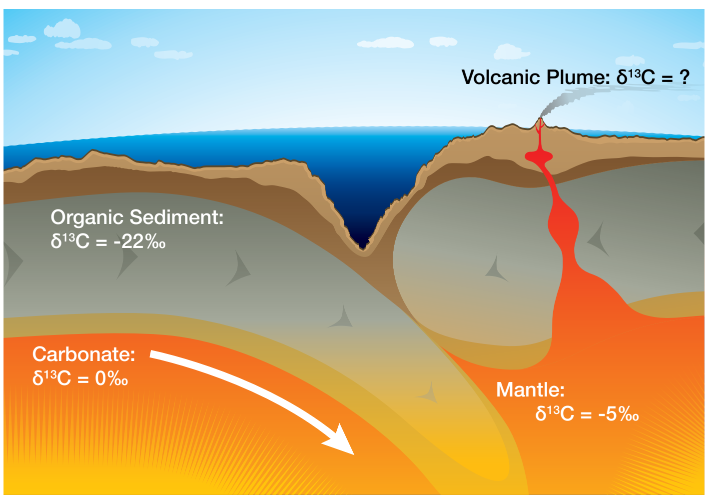

Figure 3. $\delta^{13}C$ is the key to identifying sources of CO_2.

Subducting slabs carry mainly marine carbonate with $\delta^{13}C$ of 0‰ and organic sediments with $\delta^{13}C$ of -22‰. The mantle on the other hand has a $\delta^{13}C$ of -5‰. Therefore, if we are able to get accurate and precise $\delta^{13}C$ from the volcanic plumes, we can look at mixing proportions of recycled (slab) versus primordial (mantle) contributions to the total CO_2 flux. And this can help us determine the efficiency of CO_2 recycling.

Field measurement of volcanic gas flux

For general field measurements of volcanic gas flux there are established tools. Because SO_2 has convenient strong absorptions in the ultraviolet, we use ground or satellite based spectroscopic techniques to measure SO_2 flux. The direct measurement of flux of other volatiles is not as straightforward. Usually we use geochemical sensors such as in a MultiGAS instrument, which is a pump driven instrument containing a host of IR and electrochemical sensors to determine total plume concentrations and the relative concentrations of different volatile compounds. By combining SO_2 flux and the ratios of other gases to SO_2, we can estimate the flux for all the different plume components.

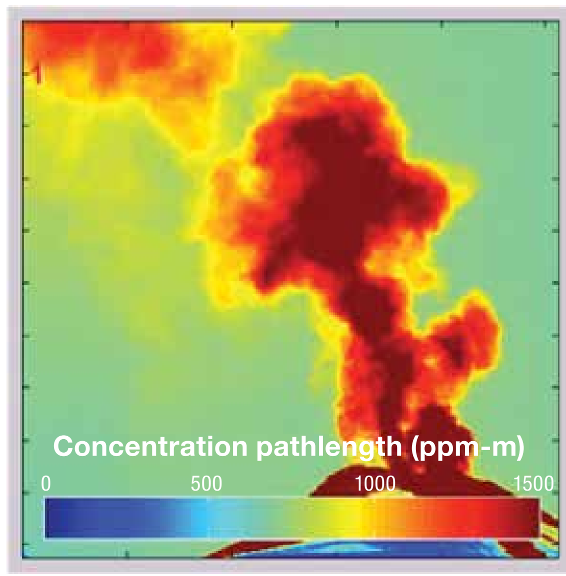

Figure 4. SO_2 flux can be measured by ground or satellite based spectroscopic techniques.

Measurement of volcanic $\delta^{13}C$-CO_2

The measurement of carbon isotopes of CO_2 at volcanoes traditionally required that samples were collected in glass flasks and returned to the laboratory for analysis by isotope ratio mass spectrometry (IRMS). This can become complicated, especially when working on remote volcanoes. It significantly limits the number of samples that can be collected, and the results of that sampling cannot be assessed in the field. Furthermore, sampling in flasks is usually limited to fumaroles that can be accessed on foot. These are often high in CO_2 but are also affected by local hydrothermal processes that can mask true volcanic signals. Despite of decades of work on volcanic carbon, the first plume measurements by IRMS were only achieved in 2011 (Chiodini et al. 2011 Bull Volc 73:531-542).

Figure 5. Measurement of volcanic δ^{13}C-CO_2.

Figure 6. Mount Etna. A vehicle mounted IRIS was driven into the volcanic plume at Mount Etna, Sicily.

Field measurement of volcanic δ^{13}C-CO_2

Now the field measurement of carbon isotopes of CO_2 has become possible with the introduction of Isotope Ratio Infrared Spectroscopy (IRIS). Instruments, such as the Thermo Scientific™ Delta Ray™ IRIS are now field-deployable on active volcanoes. This has been done in several recent studies.

- A vehicle-mounted Delta Ray IRIS was driven into the volcanic plume at Mount Etna, Sicily (Rizzo et al. 2015 Chem Geol 411:182-191). Continuous, real-time, high frequency monitoring of δ^{13}C opened new fields of research in volcanology.
- Discrete samples were collected from a helicopter and returned to ground-based Delta Ray IRIS in the Western Aleutian Islands (Fischer & Lopez 2016 GRL 43:3272-3279). These scientists investigated Earth crust formation, conditions affecting volcanic activity, and volcanic carbon emitted to the atmosphere.
- The Trail by Fire expedition (http://www.trailbyfire.org) mounted a Delta Ray IRIS in a Land Rover 4x4, and used it during an expedition aiming to determine total volatile flux from the entire Nazca Subduction Zone – 15 volcanos in 5 months (Schipper et al. 2017 Bull Volc 79:65).

In all situations, the authors were able to achieve measurements of δ^{13}C-CO_2 of volcanic plumes in the field, which allowed results to be assessed in the field, and subsequent sampling protocols to be adjusted in response – a capability that was not possible before the availability of IRIS technology.

Figure 7. Western Aleutian Islands. Discrete samples were collected from a helicopter and returned to ground-based IRIS.

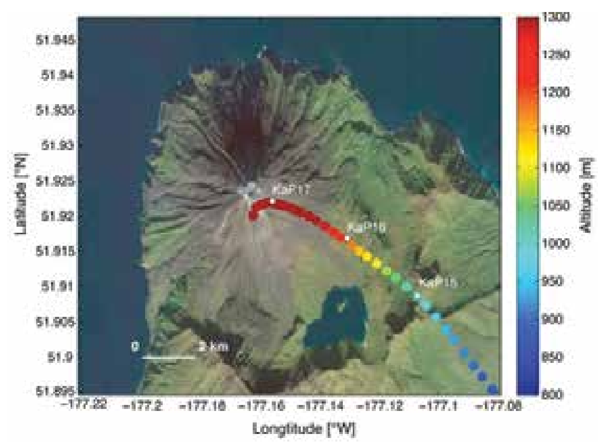

Figure 8. The Trail by Fire Expedition determined volatile flux from the entire Nazca Subduction Zone – 15 volcanos in 5 months.

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The future of IRIS on active volcanos

Researchers now have the ability to bring home data rather than samples from the field, which opens new avenues for research. It has been shown that the ratio of CO_2 and SO_2 in volcanic plume, can systematically rise in advance of explosive eruptions. Now that real-time IRIS implementation is possible in the field, researchers can investigate if there are also corresponding pre-eruptive changes in $\delta^{13}C$-CO_2. This holds potential to be a strong compliment to monitoring operations that wish to forecast volcanic eruptions.

Furthermore, current estimates of global volcanic carbon flux are rough. Rapid measurements from multiple volcanic systems will help refinement of this global geochemical cycle.

Correlation between measured plume $\delta^{13}C$-CO_2 and subduction parameters will allow ground-truthing of petrologic models, and forward modeling of volcano-specific contributions to the global carbon cycle. With enough data from different portions of a single subduction zone, or volcanic arc, researchers will be able to predict the outputs of completely inaccessible volcanoes, and estimate how they have contributed to the carbon cycle in the past, and how they will in the future.

Figure 9. Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer (IRIS).

Dr. C. Ian Schipper

Ian Schipper first became enamored with volcanoes when as an undergraduate engineering student at the University of British Columbia he gained a volunteer position at the Hawaiian Volcano Observatory. From this first introduction to volcanology, he has continued to chase the science and adventure of a volcanically inclined career. His PhD studies at University of Otago, New Zealand, took him to the bottom of the Pacific Ocean, to study submarine explosive volcanism at Loihi Seamount. Postdoctoral work at l'Université d'Orléans in France, and JAMSTEC in Japan gave him hands-on experience managing high-tech laboratories and using experimental techniques. Now, as a lecturer at Victoria University of Wellington, New Zealand, he is building a multidisciplinary research program that incorporates fieldwork and a wide variety of analytical techniques to address the physical and chemical signatures, nuances, and consequences of volcanic degassing.

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