

Neutron Activation Analysis and Volcanoes

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Abstract

To gain a better understanding of what mankind has done to the world, we must know the natural system very well. One important aspect of the natural atmospheric system is the source of aerosols or particles in the air that are involved with cloud formation and visibility (light scattering). Volcanoes are natural phenomena that have affected local and regional systems. Volcanoes produce aerosols and sulfur species that eventually form aerosols in vast quantities. Nuclear techniques (neutron activation analysis) have been used to study volcanoes for years, and these analyses tell us much about volcanic emissions and potential impacts upon the earth. The problems of how to sample and analyze volcanic emissions will be the focus of this presentation as well as the results of such studies at different volcanoes around the world.

Volcanoes have held mankind's attention since the very earliest days. In ancient times, people were mystified by volcanoes. Eventually we learned more about them and now have a much better understanding of how they work and their impact upon the world. Chemically, very little was known about volcanoes other than the fact that they release sulfur and lava or ash and are dangerous. Over the last few decades, samples have been carefully collected at erupting volcanoes that, upon chemical analysis, have shown that volcanoes are very active sources of volatile compounds and are definitely having an impact upon the world and, in particular, the atmosphere.

The two best-known effects are from ash and/or aerosols produced in volcanic eruptions. Some of the earliest writings of volcanic phenomena deal with their impact upon daylight by clouds of ash blocking the sunlight and darkening the sky. The second large effect of volcanoes upon the atmosphere is that of the sulfur gases forming sulfate aerosol and either blocking incoming sunlight or forming cloud-condensation nuclei (CCN) and affecting the clouds by causing more nuclei to be present. This latter effect would obviously be much more pronounced for local effects upon weather, cloud cover, and/or precipitation. Recently Charlson et al. (1987) showed that this latter impact of volcanoes was rather small because most of the

sulfur of natural origin in the atmosphere is produced by phytoplankton in the oceans, and volcanoes would have only a local impact for a short period of time. Therefore, volcanic impacts due to normal eruptions and the sulfur gases are probably not involved with climatic control, but only short-term and localized effects due to sulfur are likely to occur. Very large, cataclysmic eruptions are still believed to be important in the forcing of climatic changes, but these are due to aerosols and, again, may only be temporary and localized unless the eruption is truly massive.

In this talk, we will look at how samples are collected from volcanoes and how they can be analyzed for their trace element composition by neutron activation analysis. The releases of volatile species by volcanoes yields patterns that can be used to identify various types of volcanoes and their products in the environment. These "chemical fingerprints" have been used in the past to measure the impacts of volcanoes upon the atmospheric aerosol in remote areas of the world. In addition to these points, studies of volcanoes are interesting to many people due to the place volcanoes have in our imaginations with respect to their explosive and destructive histories. They are, therefore, a good place to train new students in the environmental sciences (atmospheric) and hold their attention during the work because of the high interest level in volcanoes. Therefore, let us look at the things that one can learn in these studies and what one learns about how to and how not to do the sampling safely. In addition, we will see how we can use radioactivity as a very powerful analytical technique in studying volcanic phenomena. In general today, radioactivity has very bad connotations for many people and in most cases is poorly understood except by a few people who work with it on a routine basis.

How do you sample a volcano? We will consider two ways, both of which we have used at numerous volcanoes with very favorable results. The first is by aircraft and the second is on the ground in or very near the volcano. To discuss these two methods, let us use a few examples of volcanoes that should be familiar to most people. Let us look at Mount St. Helens in Washington State, which erupted violently in 1980, and El Chichon in Mexico, which had it's cataclysmic

eruption in 1982. Because of the interesting chemistry associated with "hot spot volcanism," we will also look at the chemistry of the Hawaiian volcanoes, Mauna Loa and Kilauea, both of which have been sampled numerous times in the last seven years. At these volcanoes we used both sampling techniques with very favorable results.

Mount St. Helens erupted violently on May 18, 1980, in an eruption not soon to be forgotten by most people in this country and, in particular, the residents of Washington and Oregon. Following the eruption, we asked NASA to fly a U2 stratospheric sampling aircraft to collect samples of the plume that had been injected into the stratosphere. This was not tremendously interesting to us, as we did not get to fly on the aircraft, but only received the samples in the mail. These were collected on cellulose filters and analyzed in our laboratory at the University of Maryland (where I taught in 1980) by neutron activation analysis. The results of these chemical analyses showed the presence of ash, sulfur and numerous chemicals. But in general, the results were very boring when one is looking for interesting chemistry. Table 1 gives the concentrations of the elements determined along with their chemical enrichment factors. The enrichment factor is defined as the ratio of the element of interest to a marker element that is not expected to undergo chemical fractionation. We have used aluminum (or occasionally scandium) as the marker element since it is very easy to measure using neutron activation analysis and is normally not enriched by natural processes occurring in nature. This ratio is normalized to the same ratio for either crustal rock or magma, or the rock type characteristic of the volcano. The enrichment factor is given by the following equation:

$$EF_{(crust)} = \frac{(X/AI)_{sample}}{(X/AI)_{standard}}$$

In this equation X refers to the concentration of the element of interest, and the standard can be an average crustal abundance or the lava from the volcano. If the enrichment factor (EF) is unity, this would indicate that no significant chemical fractionation has occurred. If the EF is greater than unity, then some chemical fractionation has occurred for the element of interest. The results from the stratospheric U2 samples were not

extremely interesting as the EF values were all near unity (Vossler et al., 1981).

Since everyone wanted to see the remains of the volcano and get out there to see the destruction, we arranged (a few weeks later) to fly out in a NASA Lockheed Electra to sample the plume. This was a very interesting mission, as we were able to see the crater and much of the destroyed region around the mountain. These samples showed impressive enrichments as compared with the first U2 samples. The results (Phelan et al., 1982) are also given in Table 1 along with those of the U2 flight.

Table 1. St. Helens Air Samples

Element	Stratospheric Samples May 19, 1980 ^a		Quiescent Plume September 1980 ^b	
	Conc (µg/m ³)	EF _{ash}	Conc (µg/m ³)	EF _{ash}
Na	79	0.93	270	1.20
Al	220	—	660	—
S	5.6	2.70	3100	740
Cl	3.5	1.37	370	50
Ca	56.00	0.76	170	0.56
Sc	0.019	0.97	0.023	0.35
V	0.082	0.72	1.6	3.7
Mn	0.90	0.74	6.00	1.0
Fe	72.00	0.96	410	1.6
Zn	0.22	1.82	260	600
As	0.026	5.6	65	8,000
Se	0.00072	1.08	1.1	2,400
Cd	0.00015	6.4	1.2	1,700
Sb	0.00105	3.5	2.4	4,600
Ba	1.10	1.18	30	15
Th	0.0039	0.75	0.06	2.8

^a T. Vossler, D. L. Anderson, N. K. Aras, J. M. Phelan, and W. H. Zoller, Trace Element Composition of the Mount St. Helens Plume: Stratospheric Samples from the 18 May Eruption, *Science*, 211, 827 (1981).

^b J. M. Phelan, D. L. Anderson, D. S. Ballantine, and W. H. Zoller, Airborne Aerosol Measurements in the Quiescent Plume of Mount St. Helens: September 1980, *Geophysical Res. Lett.*, 9, 1093 (1982).

Now that we had seen the crater, the next step was to fly out and obtain a permit to land in the crater and sample the gases and particles being emitted. This was done a month later, and we were able to sample some of the gases being emitted from the hot fumeroles near the throat of the volcano (now a lava dome!). Measurements over the next two years showed similar results, and we were able now to watch the crater change as a large lava dome grew over the active throat of the volcano. In all samples, we were able to

observe higher enrichments for many elements than seen previously as the volcano was definitely releasing volatile elements from the cooling magma in the dome and system below ground. What we have observed is that the volcano enriches or releases the volatile elements (or their compounds, which are volatile) in quantities higher than would be expected based upon the abundance of the elements in the rocks themselves. This enrichment process depends upon the temperatures involved, the halogen content, and the volatility of metal halide compounds.

The same was true for the volcano El Chichon in Mexico. We sampled it first with a manned research aircraft (Lockheed Electra, operated by NASA) and then went down to Mexico and landed in the crater to sample the current emissions from the volcano. The main difference with this volcano was its emissions of H₂S, a toxic gas that was released from the acid lake that occupied about half of the crater floor. The pH of the lake was 0.5, which meant that it had a sulfuric acid content equal to a solution about 0.01 M acid! Under these conditions, the H₂S will not ionize, but instead will be emitted from the lake as a gas. So much was released from the lake within the crater that birds flying overhead were killed and fell into the crater. The floor of the crater contained many rotten or decaying birds that had been killed by the H₂S gas!

A third example of a volcano with interesting chemistry is in Hawaii, a pleasant place to visit and an interesting place to study volcanic chemistry. We discovered Kilauea's chemistry by accident in 1983 when it began a long series of eruptions at the Pu'u O'o Vent (still ongoing today), and some of the aerosols and gases released reached our "clean background sampling station" at NOAA's Mauna Loa Observatory. We saw an element we have never seen before on our air filters from any source, natural or man-made (Zoller et al., 1983). Since we have never seen the element iridium in samples collected anywhere in the atmosphere, we were intrigued as to what was occurring at this volcano. Obviously this curiosity would require a trip to study the volcano in person.

We then went out to Hawaii and—with the help of the USGS—sampled the fume and gases from the new vent (Pu'u O'o). The results of this initial volcanic study not only confirmed the finding of iridium, but we also saw rhenium, another element that we had never observed at volcanoes previously (Olmez et al., 1986). The element iridium is normally very rare on earth

and difficult to measure analytically, so we again needed neutron activation analysis to do the job.

Following this work, we decided it was such a rare thing that we had observed, that we would sample Kilauea several more times in the intervening years. Some of the data from Kilauea volcano are given in Table 2. The data from this table gives examples of the elemental concentrations and very large enrichment factors observed regularly at Kilauea (Olmez et al., 1986, and Crowe et al., 1987).

Table 2. Trace Elements from Kilauea Volcano

Elem.	Aircraft Samples			
	May 1983 ^a		March 1984 ^b	
	Conc (µg/m ³)	EF _{BHVO-1}	Conc (µg/m ³)	EF _{BHVO-1}
Sc	0.0082	1.0	0.0083	1.0
Al	20.7	1.0	5.5	0.26
Mn	0.96	2.7	0.35	0.98
Fe	65.6	2.8	43	1.8
Th	0.0021	6.9	—	—
V	1.4	16	0.47	5.3
Na	148	33	110	24.0
K	61	48	48	38
Zn	4.51	160	9.3	330
Ag	0.0036	230	0.30	19,200
Sb	0.0254	540	0.37	7,870
In	0.404	15,000	0.33	12,000
As	7.97	19,000	14	33,000
Au	0.0654	40,000	0.042	25,000
Cd	3.63	110,000	8.1	245,000
Sn	76.2	130,000	81	138,000
F	19,600	190,000	0.0036	41,700
Ir	0.0064	420,000	0.0036	240,000
Cl	30,700	1,200,000	12,000	470,000
S	93,600	3,400,000	490,000	17,800,000
Hg	19	17,000,000	—	—
Se	165	60,000,000	32	11,600,000

^a I. Olmez, D. L. Finnegan and W. H. Zoller, Iridium Emissions from Kilauea Volcano, *J. Geophys. Resch.*, 91, 653 (1986).

^b B. M. Crowe, D. L. Finnegan, W. H. Zoller, and W. V. Boynton, *J. Geophys. Resch.*, 92,13, 708, (1987).

In 1984 the main Hawaiian volcano, Mauna Loa, erupted, and again we were fortunate enough to get over to sample it by aircraft and on the ground. In this work we had added an additional sampling tool to those we had available. This was a treated filter pack using ⁷LiOH to trap acidic gases such as SO₂, HCl, HF, etc. The system was much more useful than we had anticipated as on the sampler we also were able to measure (by neutron activation analysis) the element osmium and, additionally, obtained data on gaseous

iridium, which has been helpful information to determine the volcanic chemistry of the platinum group elements.

We were able to measure the element osmium by neutron activation and analysis since we collected the "acidic gases" on $^7\text{LiOH}$, and the lithium-7 isotope has a very low cross section for neutrons, so we could use these samples for analysis by the technique. Like iridium, osmium is very sensitive to measurement by the nuclear techniques and could be done entirely by instrumental methods without prior or post-chemical separations. This gave us a very good chemical fingerprint of the phenomenon of "hot spot vulcanism" that has led to many very interesting implications in the chemical and environmental sciences.

There are obvious connections between these platinum group elements and large scale geological occurrences such as the dinosaur disappearance that occurred 65 M years ago. These points have led numerous investigators into theories of mass extinctions related to volcanic systems.

Out of this work that we will be discussing, the following points should be remembered. First, not all occurrences in science are planned by scientists. Secondly, that nuclear techniques offer remarkably sensitive analytical methods for some elements, allowing one to measure levels as low as femtogram quantities of the more sensitive elements routinely. Thirdly, that science, chemistry, and studies of the environment can be fun, exciting, and can lead one to learn things that can be applied to other things that are going on around us. They help us obtain a better understanding of the world around us and how we can work with it, learn from it, and move on to help others do the same.

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