Chapter 57

Hazards of Volcanic Gases

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GLOSSARY

aerosol A colloidal dispersion of liquid particles in a gas, e.g., SO2, which will react with the OH radical in the atmosphere to form tiny droplets of sulfuric acid (H2SO4).

hazard In a volcanic context, hazard refers to the phenomena produced by a volcanic event and is directly related to Risk, where Risk = Hazard × Vulnerability, with vulnerability referring to the consequences for population and infrastructure.

PEL The recommended permissible exposure limit to a given chemical compound above which health risks may occur. The exposure limit is generally averaged over an 8-h day, 40-h week. It is measured in parts of compound (e.g., CO2) per million parts of air (ppm).

Gas solubility The maximum amount of a gas that can be dissolved in a given amount of water at 20 °C; measured in g/L.

δgas The vapor density of a gas relative to air (density = 1); measured in g/L.

1. INTRODUCTION

Gases are the invisible yet often continuous products of volcanic activity. Even volcanoes in a state of quiescence, not actually erupting or showing signs of unrest through seismic activity, are able to degas continuously. Eruptions can produce lethal quantities of toxic gases, but long-term exposure to a lower dose also can pose a significant hazard. Although volcanic gases are only directly responsible for 1–4% of volcano-related deaths, they are nevertheless hazardous and responsible for deaths every year. They have an important effect on the regional and global environment and may contribute greenhouse gases to the atmosphere. Indirectly, through the destruction of crops, volcanic gas emissions have resulted in starvation and disease (40% of volcano-related deaths between 1600 and 1982).

The composition of volcanic gases depends on the type of volcano and its eruptive state. However, the most common volcanic gases in order of abundance are water (H2O, 30–90 mol%), carbon dioxide (CO2, 5–40 mol%), sulfur dioxide (SO2, 5–50 mol%), hydrogen (H2, <2 mol%), hydrogen sulfide (H2S, <2 mol%), and carbon monoxide (CO, <0.5 mol%). Some of these, when emitted from active vents (Figure 57.1), react in the atmosphere or volcanic plume to form aerosols, the most important being hydrochloric acid (HCl), hydrofluoric acid (HF), and sulfuric acid (H2SO4).

2. TOXICITY OF VOLCANIC GAS SPECIES

It is difficult to determine accurately the contribution of gases to volcano-related deaths, since much of the data reflect deaths during eruptive periods, whereas the majority of gas-related deaths occurred during noneruptive periods. The long-term health effects of volcanic gases are poorly understood; they may be responsible for or accelerate epidemic diseases because of their irritant and depressing effects.
effects, which reduce the resistance of ocular, respiratory, and digestive systems to microbial attack. From a health perspective, the most important volcanic gases and aerosols are CO₂, SO₂, Rn, H₂S, HCl, HF, and H₂SO₄ (Table 57.1). Exposure to these has been the cause of the majority of volcanic gas-related fatalities.

### TABLE 57.1 Toxicology of Volcanic Gases and Aerosols—cont’d

<table>
<thead>
<tr>
<th>Sulfur dioxide (SO₂)</th>
<th>Characteristics</th>
<th>Effects of overexposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics</td>
<td>Colorless gas or liquid (&lt;−10°C) with characteristic pungent odor. Perceptible odor at 0.3−1.0 ppm and easily noticeable at 3 ppm. δgas = 2.26 g/L. Gas solubility = 10 g/L. PEL = 5 ppm in air; 13 mg/m³ of air.</td>
<td></td>
</tr>
<tr>
<td>Effects of overexposure</td>
<td>Inflammation and irritation of the eyes and respiratory tract resulting in burning of the eyes, coughing, and difficulty in breathing. Approximately 90% of inhaled SO₂ is absorbed in the upper respiratory tract, where it forms sulfurous acid which then oxidizes to form sulfuric acid. Concentrations of 6−12 ppm cause immediate irritation of nose and throat. Exposure to &gt;20 ppm causes irritation of the eyes, while concentrations of 10,000 ppm irritate moist skin within minutes.</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydrogen sulfide (H₂S)</th>
<th>Characteristics</th>
<th>Effects of overexposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics</td>
<td>Colorless, flammable gas with offensive odor (rotten eggs). Characteristic odor perceptible at 0.77 ppm and easily noticeable at 4.6 ppm. δgas = 1.19 g/L. Gas solubility = 2.9 g/L. PEL (averaged over 10 min) = 20 ppm in air; 28 mg/m³ of air.</td>
<td></td>
</tr>
<tr>
<td>Effects of overexposure</td>
<td>Inhalation of 20−150 ppm may cause eye irritation, while slightly higher concentrations cause irritation of upper respiratory tract. In low concentrations, exposure may result in headache, fatigue, dizziness, excitement, staggering gait, diarrhea, followed sometimes by bronchitis and bronchopneumonia. In small amounts the gas acts as depressant and as stimulant in larger amounts. Very large amounts result in paralysis of the respiratory center and death; exposure to 1000−2000 ppm may cause coma after a single breath.</td>
<td></td>
</tr>
<tr>
<td>Long-term</td>
<td>Prolonged exposure to concentrations as low as 50 ppm may cause pharyngitis and bronchitis, while concentrations &gt;250 ppm may result in pulmonary edema.</td>
<td></td>
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</tbody>
</table>
### TABLE 57.1 Toxicology of Volcanic Gases and Aerosols—cont’d

<table>
<thead>
<tr>
<th>Compound</th>
<th>Characteristics</th>
<th>Effects of overexposure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radon (Rn)</strong></td>
<td>Colorless, odorless, tasteless, radioactive gas, formed from the radioactive decay</td>
<td>Short-term: Extreme irritation and corrosion of the skin and mucous membranes. Contact</td>
</tr>
<tr>
<td></td>
<td>of uranium. $\delta_{\text{gas}} = 9.73 \text{ g/L}$. Gas solubility $= 51 \text{ g/L}$. PEL = 200 Bq/m³.</td>
<td>with the eyes will cause deep-seated burns, and if the chemical is not removed immediately, permanent visual impairment or blindness may result. Skin exposure produces severe burns, which are slow to heal. Subcutaneous tissues may be affected becoming blanched and bloodless, which may result in gangrene. A severe irritant to the nose, throat, and lungs, inhalation of the vapor may cause ulcers of the upper respiratory tract; concentrations at 50–250 ppm are dangerous even for brief exposures.</td>
</tr>
<tr>
<td><strong>Hydrochloric acid (HCl)</strong></td>
<td>Colorless gas or colorless fuming liquid with an irritating pungent odor. Detectable odor by most people between 1 and 5 ppm. $\delta_{\text{gas}} = 1.27 \text{ g/L}$. Gas solubility $= 62 \text{ g/L}$. PEL $= 5 \text{ ppm in air}; 7 \text{ mg/m}^3 \text{ of air.}$</td>
<td>Long-term: Repeated or prolonged exposure may cause changes in the bones as well as chronic irritation of the nose, throat, and lungs.</td>
</tr>
<tr>
<td><strong>Hydrofluoric acid (HF)</strong></td>
<td>Clear, colorless, fuming corrosive liquid or gas with strong irritating odor. Irritation of nose and eyes at low concentrations. $\delta_{\text{gas}} = 0.7 \text{ g/L}$. Gas solubility $= \text{miscible in all proportions. PEL} = 3 \text{ ppm in air, 2 mg/m}^3 \text{ of air.}$</td>
<td>Short-term: Irritation of eyes, nose, and throat. Severe burns with rapid destruction of tissue and erosion of teeth may occur. Inhalation may also lead to difficulty in breathing and inflammation of upper respiratory tract.</td>
</tr>
<tr>
<td><strong>Sulfuric acid (H₂SO₄)</strong></td>
<td>Clear, colorless, fuming liquid or gas with strong irritating odor. Irritation of nose and eyes at low concentrations. $\delta_{\text{gas}} = 3.4 \text{ g/L}$. Gas solubility $= \text{miscible in all proportions. PEL} = 20 \text{ ppm in air, 1 mg/m}^3 \text{ of air.}$</td>
<td>Long-term: Repeated or prolonged exposure to the vapor may cause erosion of the teeth, chronic irritation of the eyes, nose, throat, and lungs.</td>
</tr>
</tbody>
</table>

3. **HAZARDS TO POPULATION AND THE ENVIRONMENT: CASE STUDIES**

The relative degree of hazard from volcanic gases is dependent upon the type of gas emitted. Some gases are poisonous, while others are dangerous only if present in such high concentrations that they block oxygen respiration. The dispersion of a given gas species is also directly related to the hazard. Emission of gases at high elevations (e.g., Mt Etna, Italy) will have less direct impact on population than low-level gas plumes (e.g., Masaya, Nicaragua; Kilauea, USA). Relatively short-lived eruptions may eject significant amounts of gases into the stratosphere.
with short-term global consequences (e.g., Mt Pinatubo, Philippines). Persistently active volcanoes, however, degas continuously and may present a long-term hazard (e.g., Ambrym, Vanuatu). In some instances, even dormant volcanoes can pose a threat to human health and the local environment (e.g., Long Valley, USA).

3.1. CO₂ Hazards

The most lethal CO₂-related events have been those in which CO₂, which is colorless, odorless, and denser than air, flowed downhill as a density current, collecting in low-lying areas and asphyxiating all lives in its path. The first recorded incident of this occurred in the Dieng Volcanic Complex (or Dieng Plateau), Indonesia: a complex of volcanic centers forming a large depression, approximately 14-km long and 6-km wide. On the morning of February 20, 1979, the inhabitants of the village of Batur felt three seismic shocks at 2:00 AM, 3:30 AM, and 4:00 AM and then observed a phreatic eruption at 5:15 AM, which ejected a dark gray cloud from the Sinila crater (a small water-filled vent, 3 km northeast of the village). This eruption, which formed a 90-m wide and 100-m deep crater, was accompanied by the ejection of blocks and mud, steam and gas, and a hot lahar (or mudflow) that flowed 3.5 km downslope. At 6:45 AM, a second minor eruption occurred 300 m west of Sinila and resulted in the formation of a new crater, Sigludung. Many of the villagers from Koputjukan fled west toward Batur and were killed by a gravity current of gas (probably CO₂ and H₂S), which was emitted from multiple small vents and fissures to the south and west of the two craters. Others, having witnessed the deaths along the Koputjukan—Batur road, retreated to a nearby elementary school, where they were also killed. In total, the gas killed at least 149 people and injured over 1000 people.

Some volcanic lakes can also pose significant risk due to the accumulation of CO₂ and CH₄ in thermally stratified waters, which when perturbed can lead to limnic eruptions or catastrophic gas discharge from the lakes. Lake Kivu (on the border between Rwanda and the Democratic Republic of Congo), Lake Monoun, and Lake Nyos (Cameroon) are the best examples, with Monoun and Nyos being the only two with recorded events. The CO₂ is believed to have originated from cold springs degassing below the lakes, which being thermally stratified, allowed for the gas accumulation. Although still somewhat controversial, it is generally believed that these two events may have been triggered by landslides, which caused the deep gas-rich layer to rise to a point in the lakes where the hydrostatic pressure was insufficient to keep the CO₂ in solution. Being denser than air, the CO₂ gas that was released formed a large density current, which flowed over the crater rim and downslope.

On August 15, 1984, at approximately 11:30 PM local time, a cloud of concentrated CO₂ burst from the crater in Lake Monoun and flowed down valley several hundred meters, where it settled along the Panke River depression. The emission was heralded by an explosion heard by the people in Njindoun village (1 km north of the lake) and by seismic shocks felt 6-km north in the village of Mbankouop. At approximately 3 AM, the majority of the victims (39 in total) had left the village of Njindoun and were heading south toward the Foumbot market. The location of the bodies indicated that the victims encountered and succumbed to the dense gas cloud near the bridges over the Panke River. When police arrived at the scene (~6:30 AM), a whitish smoky cloud still covered the area, drifting with the wind off Lake Monoun. They were only able to enter the area when the cloud had finally dissipated at approximately 10:30 AM. It was then that they noted that the bodies of the victims were covered with reddish first-degree burns and blisters and that mucous and blood had frothed from their noses and mouths. The surrounding vegetation was bleached yellowish and withered, yet the victims’ clothes were unaffected. The carcasses of domestic and wild animals were also found nearby.

Between 9:00 PM and 10:00 PM (local time) on August 21, 1986, just 2 years after the Lake Monoun event, a cloud of concentrated CO₂ was emitted from the lowest point of the Nyos Crater Lake and spread into the surrounding valleys, affecting an area approximately 20-km long and 15-km wide. The gas emission appears to have been preceded by the rise of a gas column at 4:00 PM and a weak explosion at 8:00 PM and then by two or three violent explosions between 9:00 and 10:00 PM. No seismic events were recorded. There was little or no damage to vegetation or housing, although taller vegetation was flattened in some areas between the lake and Lower Nyos. As with the Lake Monoun event, the carcasses of many domestic and wild animals were found in the affected area (Figure 57.2). The exact number of casualties is unknown, but according to government sources, at least 1700 people died, while...
approximately 5000 people in the affected area escaped exposure or survived its effects.

Another type of CO₂-related hazard is that seen at Mammoth Mountain, California, a large dacitic volcano located on the southwestern rim of the 760,000-year-old Long Valley caldera. Beginning in 1990, extremely high levels of CO₂ soil degassing (20–90% CO₂) on the flanks of Mammoth Mountain have resulted in tree-kill areas, which cover >500,000 m². The CO₂, which kills the trees during the winter by inhibition of root function and oxygen deprivation, originates from the degassing of intruded magma and gas release from magmatically heated metasedimentary rocks beneath the caldera. The CO₂ flux from Mammoth Mountain was estimated at 1200 metric tons per day (t/d) in 1995 dropping down to ~10 t/d in 2010, occurring principally in the tree-kill areas. This diffuse degassing may also be producing catastrophic acidification of the soil and mobilization of toxic Al³⁺ into local aquatic ecosystems. Furthermore, although CO₂ generally dissipates when it leaves the ground, its relatively high density causes it to collect in hollows, wells, and confined places, where it creates a serious asphyxia hazard. During the winter months, the relatively impermeable snow around Mammoth Mountain prevents CO₂ from escaping, dramatically increasing the hazard; a number of cases of asphyxia or near-asphyxia have been reported after skiers fell into snow-covered fumaroles or took shelter in small snow caves or snow-covered cabins.

Global CO₂ emission from subaerial volcanoes has been calculated, using CO₂/SO₂ ratios and SO₂ flux estimates, to be approximately 0.15−0.26 billion metric tons (Gt) of CO₂ per year, with over half of that coming from passively degassing volcanoes. Although only a fraction of that of anthropogenic emissions (36 Gt of CO₂ in 2013), volcanoes nevertheless contribute large amounts of CO₂ to the atmosphere. In earlier geologic times, catastrophic volcanic event such as the eruption of the Deccan Traps (India) may have added significant amounts of CO₂ to the atmosphere and therefore may be partially responsible for increased global warming.

### 3.2. SO₂ Hazards

When sulfur dioxide is released to the atmosphere, it oxidizes with the OH radical in air to form sulfurous acid (SO₃), which then reacts with water to produce sulfuric acid particles. At Masaya volcano, a basaltic complex of nested calderas and craters located in northwestern Nicaragua, the long-term degassing activity from the currently active crater, Santiago (Figure 57.1), has had a significant impact on the surrounding vegetation: high concentrations of SO₂ disturb stomatal respiration and cause necrosis. Sulfur dioxide fluxes from the crater have been measured at as much as 2500 t/d. The presence of this gas, as well as HCl and HF, has led to extensive fumigation and contamination of >1200 km² downwind of the volcano. Concrete and metal fences, telephone wires, and other metal equipment are also severely damaged in the affected areas (Figure 57.3). Since the nineteenth century, the significant economic impact from the degassing has led local coffee farmers to even demand the capping or destruction (by aerial bombardment) of the degassing vent; none of these attempts proved successful. Mixing of rain from Hurricane Mitch (late 1998) with the volcanic gas plume produced concentrated acid rain, which local farmers blamed for the damage to young palm trees and even the complete destruction of a soya field during a single afternoon.

On June 6, 1912, Novarupta, a dacitic volcano located on the Alaska Peninsula, explosively erupted ~13 km³ of magma and triggered the collapse of Mt Katmai volcano. The Katmai–Novarupta eruption released substantial amounts of gas, which created acid rains that appear to have greatly impacted the local environment. As with Masaya, acid rain was reported to have dissolved the metal work of buildings 400-km northeast at Seaward, while polished brass was tarnished 1100 km away at Cape Spencer. A month after the eruption, housewives in Vancouver, Canada (2400 km south), reported that clothes left out to dry had “turned to shreds” upon being ironed.

The conversion of volcanic sulfur dioxide into aerosol particles is often responsible for formation of an acid smog or “vog” (e.g., Kilauea, Hawaii; Figure 57.4). This acid vog is slowly neutralized by ammonia in the atmosphere to form a haze that may block solar ultraviolet rays from reaching the lower atmosphere, which in turn may lead to a cooling effect (e.g., Mt Pinatubo, Philippines). The volcanic haze may also act as cloud condensation nuclei and perhaps even as sites for the catalytic destruction of ozone with obvious global implications.
3.3. H2S Hazards

Hydrogen sulfide is an extremely toxic gas, which has been responsible for at least 46 fatalities (since the early twentieth century) at Rotorua (New Zealand) and a number of volcanoes in Japan, where it is believed to be the most common cause of volcanic gas accidents. This has led many volcano observatories in Japan to install H2S detectors and automated warning systems in areas frequented by the public.

One such incident occurred in 1971 on the flanks of Kusatsu-Shirana volcano, Honshu, when six downhill skiers died almost instantly after passing through a depression filled with H2S. Being denser than air, the gas may accumulate in snow-covered depressions or caves which are breached from time to time, releasing lethal concentrations to the surface. Another more recent accident occurred on Adatara volcano, Honshu, a basaltic-to-andesitic volcano, which forms part of the volcanic front of northeastern Japan. On September 15, 1997, 4 hikers, from a party of 14, were killed after inhaling volcanic gases on the floor of the Numano-taira crater. The group had become disoriented because of fog and left the trail, which had signs warning of volcanic gas hazards in the area. Three of the hikers fell into the crater, where they succumbed to noxious gases that had accumulated on the crater floor due to calm wind conditions. The fourth hiker died, after succumbing to the gases while attempting a rescue. Scientists from the Kusatsu-Shirane Volcano Observatory reported that the fumarolic gas from the southwest rim of the crater was composed of 0.5% SO2, 33–37% CO2, and 60–65% H2S.

3.4. HCl Hazards

Although there are few cases of hydrochloric acid being solely and directly responsible for volcano-related fatalities, it is nevertheless an important component because of its effects on the environment. HCl is highly soluble in water and is therefore easily removed by rain from a volcanic plume, resulting in low-pH acid rains (e.g., Kilauea, USA; Masaya, Nicaragua). Significant amounts of HCl may also have been injected into the stratosphere during the cataclysmic eruption of El Chichon (Mexico) in 1982 with potentially serious environmental implications. In Hawaii, clouds of lava haze or “laze” are formed from the boiling and vaporization of seawater when lava flows enter the sea. These large white laze plumes contain a mixture of HCl (up to 10–15 ppm) and seawater and produce acid rains (pH 1.5–2), which pose a hazard to the local population.

3.5. HF Hazards

Hydrogen fluoride is highly soluble and with excessive intake leads to dental and skeletal degradation and is indirectly responsible for the most lethal gas-related volcanic event. The Laki fissure (Iceland), a NE-trending 27-km-long row of cones and craters, was the source of the Grimsvötn caldera eruption, which lasted from June 8, 1783 to May 26, 1785. The second largest historic basaltic fissure eruption since the ~AD 935 Eldgjá eruption, it was preceded by tremors and earthquakes starting on May 15. The eruption involved at least 19 km3 of basaltic magma of which 15 km3 was erupted as lava and tephra covering 565 km². Lava fountains are thought to have risen as high as 1400 m and were accompanied by convecting eruption columns, which rose to a maximum altitude of ~15 km, resulting in an atmospheric loading of 219 Mt of SO2, 7.0 Mt of HCl, and 15.0 Mt of HF over an 8-month period. A low-altitude gas haze caused grasses contaminated by fluorine to be stunted, leading to the loss of over 50% of Iceland’s grazing livestock. This consequently lead to the “Haze Famine,” which, in combination with various diseases and two severe winters, caused the death of 10,521 people, 22% of Iceland’s population. The injection of ash, gases, and aerosols into the lower stratosphere also affected parts of Western Europe, North Africa, and Western Asia and resulted in cooling of the Northern Hemisphere by 1–2 °C.

Ambrym is a persistently and vigorously degassing island volcano (>17,000 t/d SO2; ~950 t/d HCl; 3400 t/d HF) in Vanuatu, which is having a significant impact on the health of its 9000 residents. Since rainwater is used by the majority of residents for cooking and drinking, fluoride contamination is important with concentrations in rainwater tanks reaching 9.5 ppm F; the WHO-recommended F concentration in drinking water is 1 ppm. This has led up to 96% of the population suffering from moderate to extreme dental fluorosis, and it is known that prolonged exposure to F concentrations of 4–6 ppm can lead to skeletal fluorosis.
4. GAS HAZARD MITIGATION

While it is impossible to stop volcanoes from degassing, volcanic gases may be monitored and studied using a variety of techniques ranging from direct sampling of fumaroles (e.g., Giggenbach bottles, MultiGAS) to remote sensing techniques (e.g., FLYSPEC, mini-DOAS, OMI). Ideally, gas monitoring is carried out sufficiently frequently by volcano observatories in order to characterize the baseline or background activity for every volcano. Following the example of those working on industrial-related gas emissions, volcanologists have begun to develop and apply models of gas dispersion and deposition downwind from the volcanic source (e.g., Vulcano, Italy; Poás, Costa Rica). Based on this information, alert levels and hazard maps can then be developed and used for risk management. However, it is often the case that areas at risk lack the necessary funding and infrastructure to support such studies.

In only a few instances, such as the artificial degassing being carried out at Lake Nyos, Cameroon, is it possible to reduce or eliminate the gas hazard physically. In most cases, monitoring of the volcano and limitation of access by the public to affected areas are the only means of reducing the risk. On a short timescale, the impact of volcanic gases can be reduced by limiting exposure time, not overexerting oneself, and resting frequently. Where possible, one should remain to the windward side of the gas source and wear full- or half-face gas masks (respirators) with appropriate absorbers/filters. Where gas masks are unavailable, a wet cloth held over the face can partially reduce the amount of water-soluble gases entering the lungs (Figure 57.5).

In some cases, evacuation is necessary, but for extended long-term activity such as at Masaya or Ambrym, it is clearly not feasible. Education of the population at risk is therefore critical, and some excellent resources are now available. The International Volcanic Health Hazard Network (http://www.ivhhn.org) has prepared a comprehensive set of guidelines and pamphlets for the public and emergency managers. The International Association of Volcanology and Chemistry of the Earth’s Interior (http://www.iavcei.org) also has safety recommendations for the public online and has produced video on “Understanding Volcanic Hazards and Reducing Volcanic Hazards.”

5. SUMMARY

Volcanic gases, although a relatively minor hazard in comparison with other volcanic phenomena, can have important short- and long-term impacts on people and the environment. Gases and resulting acid rains may sometimes be detected over 1000 km from the volcanic source but are generally directly responsible for relatively few deaths. Their effects on buildings are rarely totally destructive except in the case of long-term exposure (e.g., Masaya, Ambrym). Sulfur dioxide emissions from the 1783 Laki fires were responsible in part for global temperature decreases, while CO₂ from subaerial volcanoes may contribute to global warming. Although some attempts have been made to physically reduce gas hazards (e.g., artificial degassing), gas monitoring and education of the public are the most effective means of reducing the hazard from volcanic gases.

FURTHER READING


