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# Volcanic Gases From Subaerial Volcanoes on Earth

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## 1. INTRODUCTION

There are approximately 1300 volcanoes which have been active on earth in the last 10,000 years, 627 with dated eruptions [111]. Volcanoes on other planets are not considered in this summary. Volcanoes of the World [111] is the standard reference responsible for the summarized knowledge of volcanic activity. Volcanoes are dormant or at times quiescent without gas emission. At times they degas strongly and sometimes they erupt: gas is emitted together with the solid products. Active volcanoes are those which are emitting solid products such as lava, pyroclastic flows and comminuted rock called volcanic ash. It has been estimated that 60 volcanoes erupt each year [110]. More than this number were degassing, approximately 100 each year [117]. Of the erupting volcanoes 72% were in the northern hemisphere, 20% were located 5°N.-20°N. and another 20% located 35°N.-50°N. [11]. An estimate of the total flux of any gas may be proportioned in this way to suggest its geographical distribution if one assumes that in the region the number of active volcanoes is proportional to the flux.

Volcanic emanations consist of solid and liquid particulates and true gases. These, often collectively called volcanic gases or more correctly volcanic emanations, usually consist primarily of water, carbon dioxide, sulfur dioxide and hydrochloric acid as well as other gases in smaller amounts including many different metals. Most metals are believed to be carried as chlorides though vanadium

[56] and iridium [140] are probably carried as fluorides and molybdenum and tungsten are thought to be carried as molybdic acid and tungstic acid respectively [14]. Thermodynamic modeling predicts most trace elements are transported from Augustine Volcano as simple chlorides, arsenic as a sulfide and Mo, in contrast to Bernard just cited, as  $\text{Mo}_2\text{Cl}_2$  [122].

Gas from a volcano is emitted in large part from magma underlying the volcano or volcanic rift. The process is complex. Gases may come direct from the magma or be stored in a summit reservoir [136,43]. It has been suggested [45] that at White Island, New Zealand there is a magmatic component and also, surrounding the magmatic system, a secondary hydrothermal component rising from an envelope of saline brine and vapor, a suggestion that may have wider geographical application.

Standard textbooks on volcanology [20, 23, 36, 133] summarize the many aspects of volcanic activity.

## 2. TECTONIC SETTING OF VOLCANOES

Volcanoes occur in several tectonic settings. Most volcanoes occur at converging plate margins, most commonly around the Pacific. Plate margin volcanoes often erupt at the crater with pyroclastic material thrown in the air or cascaded down the slopes as hot pyroclastic flows. Lavas are commonly among the eruptive products. There are volcanoes along rifts both in the ocean and on the continents. Prominent examples are volcanoes of the Atlantic ocean and those along the East African Rift. Etna, the largest volcano in Europe, is on a fracture where there is subduction within a continental plate. A few volcanoes occur at hot spots, for example, those that are active on Reunion Island in the Indian Ocean and those of the Hawaiian Islands in the Pacific. Lava flows are the chief products of hot spot eruptions. Volcanic activity on the

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sea floor is prominent at rifts and undersea fracture zone. Only gases from subaerial eruptions are considered in this summary. There are, however, significant amounts of volcanic gases dissolved in the submarine hydrothermal systems. Hydrothermal plumes of volcanic affiliations on the sea floor or ridges in the sea contain sulfides contributed by underwater volcanism but probably not in the form of gas.

### 3. LIMITS WITH RESPECT TO OBTAINING DATA

Gases are collected from lava lakes and fumaroles [107, 108, 109] but usually are not available for collection at active volcanoes. Much gas is emitted from very active vents where emission of solid products creates dangerous or impossible conditions for collection of gases. In rare instances gas has been collected from active vents by airplanes entering eruption clouds [17]. The advent of remote sensing spectrographic methods for detection of some gases, using a correlation spectrometer, has made gas measurements possible well away from dangerous sites. Because these measurements must be made in daylight and where the light through the volcanic plume is not obscured by volcanic ash in the plume, gas at very few active eruptions have been studied even using remote sensing equipment.

### 4. METHODS OF COLLECTION AND ANALYSIS OF VOLCANIC GAS

#### 4.1. Collection and Evaluation of Analytical Data

There are several means in common used for finding the composition of volcanic gas. They include collection of gas in evacuated vessels, collecting condensates, allowing gas to pass through filters, as well as the use of spectroscopic detectors and sensors designed for analysis of a specific gas. Evaluation of the quality of the analytical data from St. Helens indicates that highest quality data are obtained by field chromatographic measurements and caustic soda bottle samples as compared with those collected in evacuated bottles or pumped through double stopcock tubes [44]. Errors inherent in the use of the correlation spectrometer for determining  $\text{SO}_2$  flux have been evaluated [114]. Evaluation of the techniques and the errors in results of volcanic gas analysis has been the purpose of several field workshops [47]. Some investigators dispute the basic assumption that all species were in equilibrium

under one set of conditions [45].

#### 4.2. Collection of Volcanic Gas in Evacuated Vessels

Samples of gas may be collected in evacuated containers. They are analysed by the usual laboratory methods or in some instances by a gas chromatograph designed for use in the field [69]. Air content is accounted for by the nitrogen and argon content in the sample. Because of the change in species after collection, resort has been made to recalculation of analyses based on thermodynamic considerations. The result is the probable composition of the gas before emission when it was in thermodynamic equilibrium. Disequilibrium modification results from atmospheric oxidation of  $\text{H}_2$  and to a lesser extent of  $\text{CO}$ . The resulting analyses are characterized as "improved compositions" or "restored analyses" [40].

Lava lakes are the safest sites for such collections. A variant on collecting gas from fumaroles is the collection of gases from pyroclastic flows [82]. Beneath the fine compact crust on the ash deposit on the surface of the flows two weeks after the eruption the pyroclastic material was saturated with gases which were collected in an evacuated vessel. The gases were very largely juvenile as indicated by isotopic analysis.

#### 4.3. Condensates

The major constituent of volcanic gases, water vapor, is condensed, often in an alkaline solution. Condensates are usually collected safely from volcanic fumaroles. Analysis of condensate includes the gases which dissolve in it. Gas collected in an evacuated tube at the fumarole may be used to supplement the analyses of condensates so as to include insoluble gases in the total analysis [81].

A modified collection technique is to allow volcanic gas to pass for periods of many days over an alkaline solution and subsequently analyze the solution thus integrating the amount and kind of soluble constituents in the gas over the time of collection [89]. The amount of gas is dependent on the part of the gas cloud sampled as well as wind conditions during sampling. This technique does, however, provide data as to the ratio of these gases in the plume.

#### 4.4. Filters

Allowing volcanic gas to pass through treated filters and subsequent analysis of the filters is used to analyze the acid gases, aerosols and particulates in the gas stream [35, 67, 97, 124].

#### 4.5. Sensors Designed for Analysis of Specific Gases

Sensors through which volcanic gas is pumped have been devised and used in the field to analyze for H [103], He [93], Hg [129], Rn [38], Oxygen [104], HCl, SO<sub>2</sub> [116] and reduced gases [78].

#### 4.6. Spectral Analysis

Flames at volcanic vents as the source of emission spectra and absorption spectra using glowing lava as the light source [86] have indicated the presence of several constituents in volcanic gas, most often Na, Cu, H<sub>2</sub> and water, but have not provided much significant quantitative information. A spectrometer, Miran, in which a sample of gas is analysed in the field [51] has enlarged our data base providing the direct measurements of CO<sub>2</sub> [51, 77].

A spectroscopic method produces quantitative data is the portable correlation spectrometer known as a COSPEC. The blue sky is used as a light source for the SO<sub>2</sub> spectrum to be analysed. This has allowed SO<sub>2</sub> in volcanic clouds to be measured remotely [114]. The concentration-pathlength product multiplied by the wind speed at which the SO<sub>2</sub> is moving is the flux.

An important quantitative application of spectroscopy to gas analysis is the use of TOMS, the total ozone mapping spectrometer, [27, 60, 61, 62, 131]. Sulfur dioxide is detectable from space, if the emission is large enough or if the plume rises high enough, using the near ultraviolet

absorption bands of this compound. TOMS produces global images of the atmospheric ozone distribution and can also observe volcanic clouds. From the spectral data the SO<sub>2</sub> content of the cloud can be calculated. Although the TOMS data are not cited directly in Table 1 with respect to the annual SO<sub>2</sub> flux, they are of great significance in this regard.

### 5. SOURCES WHICH PROVIDE LIMITED QUANTITATIVE INFORMATION

#### 5.1. Leachates

Volcanic ash is a product of many eruptions. If collected before it has been rained on, the water soluble components can be washed from the ash and are known as leachates [8]. Condensed water soluble volatile compounds and aerosols in the cloud of gas are adsorbed on the ash surface. It has been suggested that some of the soluble chemicals in the leachates are the result of adsorbed acid gases reacting with the glass or minerals of the ash fragments [100]. The several hypotheses have been summarized [53]. Many elements have been detected in leachates but all are found in volcanic gas by some other more direct method [85, 112].

#### 5.2. Melt Inclusions

Analysis of gas content of melt inclusions and volcanic glass in rocks is an indirect method by which one may

TABLE 1. Volcanic Gases: Estimates of Annual Subaerial Flux

Gas	Class of volcanoes	Annual Flux Tg.yr <sup>-1</sup>	Reference
CO <sub>2</sub>	All subaerial	65	[135]
	Erupting	31	[135]
	Passive degassing	34	[135]
SO <sub>2</sub>	All subaerial	18.7	[117]
	Erupting	11.9	[117]
	Not erupting	6.8	[117]
HCl	All subaerial	0.4-11	[120]
	Small explosions and degassing	0.3-10	[120]
HF	All subaerial	0.06-6	[120]
	Small explosions and degassing	0.05-5	[120]

learn the quantity of the analysed gases which may have escaped from a body of rock [5, 26]. The quantitative estimates when applied to gas discharge depend on the amount of magma degassed which is not easily estimated. To the extent that a greater volume of magma has been degassed than has been erupted the estimates of the volume of gas erupted calculated from melt inclusion data are minimal [7].

### 5.3. Vapor phase minerals

Minerals entrapped in vesicles or in miarolitic cavities indicate the presence of some elements (Cu, Mn, Ti, Fe, Sn) in volcanic gas but do not provide quantitative estimates of the amount [28, 29, 55, 71, 72].

### 5.4. Wallrock Alteration

The composition of altered wallrock around volcanic gas vents is a clue to the chemical composition of the gas. [70, 94].

### 5.5. Sublimates

Elements derived from volcanic gas are major elements, or less often trace elements in minerals deposited as sublimates at fumaroles. Artificially formed sublimates are deposited in silica glass tubes inserted into fumaroles. These sublimates form without the intervention of the air [68, 13, 119], resulting in the deposition of many elements before they escape into the atmosphere. Elements in sublimates are not present in amounts related to the quantitative amount in the gas [87]. A compilation of sublimate minerals [118] refers to the earlier classical studies [84, 139, 137, 138]. Additional elements found in sublimates are recorded in more recent papers [9, 14, 32, 59, 95, 98, 105, 128]. All elements in sublimates have been detected in volcanic gas by other more direct methods.

## 6. NON-VOLCANIC MATERIAL WHICH ARE INDICATORS OF VOLCANIC GAS COMPOSITION

Analysis of non-volcanic natural products may be indicative of volcanic gas composition but frequently leads only to qualitative information as to the gas species or elemental composition of volcanic gas and chemical fallout. These inferential sources of information include composition of lakes [1], seawater, (an unusual amount of some elements such as B, Fe, Mn, Si, P are in the sea water near Santorin [99]), rainwater downwind from a degassing volcano [57], ice, in antarctica [25] and the Greenland Ice Sheet [50, 52], snow [2] and vegetation growing in a volcanic environment, Mt. Etna [90]. The volcanic con-

stituents have been found to occur in volcanic gases by other more direct procedures.

## 7. VARIATIONS IN THE COMPOSITION OF VOLCANIC GAS

### 7.1. Overview

Variations in volcanic gas in time and place emphasize the uncertainties in quantitative estimates of gas flux. Emission, even from one volcano, is episodic, making it extremely difficult to calibrate the accuracy of estimates. The variability in the total amount of gas emitted, the kinds of gases and the relative amounts of constituents in emissions require a large data base if the overall composition of volcanic gas is to be properly evaluated. Data are getting better each year as more volcanic emissions are being monitored, new instruments are being used to measure gas and better analytical methods are employed.

Many things contribute to the variability in volcanic gas data including the original abundance of each volatile component in the magma, the specific magmatic product from which the gas is evolving, the temperature of collection, the temperature at which it is evolved from the magma, the length of time gas has been evolving which is a function of the stage of the volcanic eruptive activity, the possible reactions within the gas after evolution but before collection, the degree to which the gases are derived from a non-magmatic source such as ground water, the reaction of gas with wallrock as it exits from the magma. There are also variations due to conditions of collection. The distance down-wind from the volcano or below the gas plume at which gas is sampled determines the amount of fallout by dry deposition. Inappropriate collection methods such as those which allow the possibility of reaction of gas with the collection apparatus may result in variations in the data.

Some volcanoes have emitted gas unusually rich in one or another component and the reason is unexplained. The eruption at the Valley of Ten Thousand Smokes emitted large amounts of fluorine. Etna erupts unusually large amounts of CO<sub>2</sub>. Observers of Etna and Vesuvius have considered that Cu is the characteristic element of Etna and Pb of Vesuvius [33]. St. Augustine and Sakurajima are Cl rich relative to SO<sub>2</sub> [58]. Differences in the SO<sub>2</sub> flux are highlighted by the contrast of the very large flux at Bagana and that at Arenal. The later is very much smaller though many other volcanic features of the two volcanoes are very similar [134].

### 7.2. Variation related to the type of volcanic deposit from which the gases are derived

A noteworthy variation depends on the type of volcanic

setting from which the gases are derived, whether the gases are from the main vent or from associated lava flows or pyroclastic deposits. Long ago it was noted [25] that HCl was preferentially emitted from flows and SO<sub>2</sub> from main vents. Ratios of two gases are most often shown to vary rather than absolute amounts of one.

### 7.3 Variation related to magma type

Gases differ because of the composition of the magma from which gases are generated. The type of magma is related to the tectonic setting and to the stage of differentiation or assimilation the magma has undergone. The kind and amount of volcanic gases are related to the magmatic products from which they are derived. The composition of glass inclusions in phenocrysts in tephra indicates strikingly different yields of S, Cl and F are to be expected from basaltic, intermediate and silicic eruptions: S, 600; Cl, 65 and F, 100 ppm from eruptions of basaltic magma; S, 560; Cl, 900 and F, 520 ppm from eruptions of intermediate magma; S, 70; Cl, 135; F, 160 ppm from eruptions of silicic magma [108]. More alkaline magmas are distinctly richer in CO<sub>2</sub>. Those from less alkaline or tholeiitic lava are richer in water.

There is an increase in CO<sub>2</sub>/SO<sub>2</sub> ratio with increasing magmatic alkalinity and tholeiitic magmas are richer in water [41]. Icelandic rift zone tholeiitic volcanism is distinguished [92] by low halogen contents and very low F/Cl ratios. Off-rift volcanism (alkaline) is associated with high halogen content and high F/Cl ratios. In incrustations in Cl rich system alkali metals dominate, and trace metals are Fe, Cu and Zn. In F rich systems major cations are Ca, Al, Na and Si and trace metals Ti, Mg, Mo and Sr are abundant. Mo is more prominent in the fumarolic incrustations at dacitic domes than in fumaroles in other locations and Cu more prevalent at fumaroles of volcanoes with lavas of andesitic or basaltic composition [Stoiber, unpublished data, 1983].

### 7.4. Variation related to tectonic setting

Variability in gas composition depending upon tectonic type has been noted in a few instances. The Hawaiian hot spot volcanoes have less HCl relative to sulfur gases when compared to volcanoes in other tectonic settings [73]. It is found at hot spot volcanoes in the particulates and in deposits in silica tubes inserted in fumaroles. It is not limited to hot spot volcanoes for it has been reported from a Russian converging plate margin volcano [31].

### 7.5. Variations related to the stage of activity

The most prominent variations in gases or gas ratios are related to the stage of activity of the volcano [88].

The stage in the eruptive cycle influences the composition of the gas, the least soluble being evolved from the magma earliest. SO<sub>2</sub> variations have been studied more than any others. The flux of SO<sub>2</sub> has been shown to vary between quiet times and times of active eruptions [74, 79], and over periods of years or days [7, 22, 116]. Hg is said to increase at times of greater activity. Radon increased more than four times before the commencement of a new eruption during the 1970 activity of Karynsky volcano [21].

### 7.6. Variation in gas composition indicated by variations in ratios of component gases

Changes in ratios such as S/Cl, Cl/F, <sup>3</sup>He/<sup>20</sup>Ne and CO<sub>2</sub>/CO<sub>2</sub>+H<sub>2</sub> have been examined because they may be useful precursors of change in eruptive activity of a volcano [54, 79, 89, 101, 123]. Large As/Se ratios [97] may be associated with volcanoes that have recently had large eruptions. Concentrations of SO<sub>4</sub>, Ti, Al, K, Na, Sn, Zn and Cr tend to decrease in Central American fumarolic condensates as the mean temperatures of the fumaroles decreases [39]. At White Island gas composition has been related to cyclic variations in outlet temperature [45]. There were variations in trace metal and halogen ratios in magmatic gases through an eruptive cycle of the Pu'u O'o vent, Kilauea, Hawaii, July-August 1985 [34].

## 8. COMPOSITION OF VOLCANIC EMANATIONS

### 8.1. Overview

Almost all the elements have been detected in volcanic gas, condensates or aerosols and many are found in ash leachates and in fumarolic incrustations. Estimates of gas flux or the percent of each of the gas constituents made in more recent years are an improvement on estimates in classical accounts of volcanic gas [4, 6, 132].

The concentration of an element in a volcanic plume is of little significance relative to the volcanic flux of the element. Measured concentrations depend on where in the plume the sample was taken and how much air had been admixed [30]. Estimates of volcanic gas flux have many shortcomings. Many are based on a published estimate of total SO<sub>2</sub> flux, but all are not from the same estimate. In many instances the flux for degassing volcanoes is estimated separately from that for active volcanoes and the definition of these may differ from author to author. There may be specific caveats in the estimates made for each gas. For CO<sub>2</sub>, for example [135], diffusive gas through flanks of volcanoes [3, 19] is not included. The amount of CO<sub>2</sub> gas from such localities as Lake Nyos and other similar localities [46] is unknown.

## 8.2. Water

Water, believed by most investigators to be the most abundant constituent of volcanic gas, is estimated to vary from 87-98% by volume [6], most often 95% or more. Menyailov [personal communication 1992] believes that the average water in the gas from circumpacific volcanoes is 95-97 volume per cent. There has been some disagreement. Not over 50% has been suggested as the appropriate value [26]. A recent compilation of 18 analyses [48, 125] contains none from the main vent eruptions of subduction zone volcanoes but does include much of the best data available. The median for  $H_2O$  is 78.5 mole per cent. An equal number of data are between 69-79% and 81-98%. A few estimates have been made for water flux at individual volcanoes: 1300 tons per day at Parícutin and 39,000 tons during its period of activity [37], 3.2 million tons from St. Helens [33] and 8500 tons per day (equivalent to  $3 \text{ Tg} \cdot \text{y}^{-1}$ ) at White Island [101] where it was estimated that the  $SO_2$  discharge was about 1% of the total world discharge of  $18.7 \text{ Tg} \cdot \text{y}^{-1}$  [76]. Information relative to the abundance of water has never been completely assembled. Indirect methods of estimation of the water flux as a percent of solid products erupted give estimates of the annual flux of water of the same order of magnitude despite the uncertainty in the figures on which such estimates are based [5, 16].

The amount of water in volcanic plumes that is magmatic is the subject of debate. In some fumaroles it seems to be very large, based on isotopic evidence [125]. Ground water may supply the gas for eruptions which are then called phreatic. Large volcanic plumes erupted by St. Helens a month before the May 1980 eruption, were largely meteoric, the eruptions phreatic. The ash was not new magmatic material. Only very small amounts of  $SO_2$  were detected by COSPEC [113]. Lava which enters the sea may heat and react with the sea water to create acid-bearing aerosols [102].

## 8.3. Major Constituents $CO_2$ , $SO_2$ , $HCl$ , $HF$

The annual subaerial flux of several of the major constituents of volcanic gas,  $CO_2$ ,  $SO_2$ ,  $HCl$  and  $HF$  has been estimated (Table 1).

## 8.5. Less Common Constituents: $CO$ , $COS$ , $HBr$ , $H_2$ , $He$ , $H_2S$

Both the concentration of  $CO$ ,  $COS$ ,  $HBr$ ,  $He$ ,  $H_2S$  and  $H_2$  and their volcanic gas flux are poorly known. Estimates are in Table 2. In a compendium of basaltic volcanism [10] it has been concluded that  $H_2$ ,  $H_2S$  and the noble gases are all present in minor concentrations, less than 0.1 mole per cent in gases from basaltic mag-

mas. In a table of basaltic gas analyses by Taran and others [125], the median values for  $CO$  and  $H_2S$  are respectively 0.57, and 1.72 mole per cent. Oxygen fugacity ranges from Ni-NiO to a half order of magnitude below quartz-magnetite-fayalite. Concentrations of minor species in volcanic gas are extremely sensitive to temperature and oxygen fugacity within the NNO-QMF bounded region. Calculations of limiting compositions of volcanic gas indicates that  $SO_2$  is favored by temperature above  $800^\circ$ ,  $O_2$  fugacities above QMF and relatively anhydrous conditions.  $H_2S$  is favored by low temperature, low oxygen fugacities and higher water concentrations [41].

The use of sulfur dioxide COSPEC measurements are the key to the estimates of the annual flux of  $Cl$ ,  $CO_2$ ,  $HCl$  and  $HF$ . The COSPEC allows the flux of  $SO_2$  to be measured but without measurement of any other constituent simultaneously. If however the ratio of a constituent with sulfur can be measured by some other method in a plume for which COSPEC information is available, the output of the ratioed element in the plume may be ascertained. The more common procedure is to estimate the ratio of an element with sulfur in as many volcanic plumes or hot fumaroles at sites of volcano degassing as possible. The average ratio is then applied to the latest COSPEC estimate of the annual flux of sulfur from all volcanoes to arrive at an annual flux from all volcanoes for the ratioed element.

## 8.6. Metallic elements

Annual flux data available for some metallic elements in volcanic gas (Table 3) are estimates usually derived from ratios with  $SO_2$  the flux of which has been measured. All estimates except for  $Hg$  are from few data. Patterson and Settle have data from two sites and four volcanoes. Phelan's data in Table 3 is from six non-erupting volcanoes. Nriagu writes that his values are a good order of magnitude [91]. These annual fluxes of the metals for which estimates have been made (excluding  $Mn$  and  $Al$ ) are all small, 7 to 15000 Megagrams (Tonnes) per year. The flux estimates in  $Mg$  per year of the 26 elements in Table 3 vary from less than 100 to 250,000. For two of the elements the flux is less than 100, for seven the flux is 100-1000 for nine elements the flux is 1000-10,000 and for eight elements the flux is over 10,000.

The world  $Pb$  flux and  $Po$ /element ratios have also been used to estimate gas flux in a few instances [66]. The  $C/3He$  ratio, a best estimate being  $2 \times 10^9$  is believed to be unfractionated during degassing. It has been used with the  $^3He$  flux of the solid earth to estimate carbon flux per year [75], (but see discussion [42]).

TABLE 2. Flux Estimates of Gases Exclusive of Major Constituents in Table 1 and Metals and Rock-Forming Elements in Table 3

Gas	Annual Flux	Comments	Reference
CO	0.02 Tg·y <sup>-1</sup>	(approximate)	[18]
COS (all volcanoes)	0.006-0.09 Tg·y <sup>-1</sup>		[12]
COS (erupting volcanoes)	3500-40,000 Mg·y <sup>-1</sup>		[12]
H <sub>2</sub>	0.24 Tg·y <sup>-1</sup>	(said to be a poor estimate)	[18]
H <sub>2</sub> S	<1% of S gas	(exceptions cited)	[117]
HBr	0.0033 Tg·y <sup>-1</sup>		[115]
CH <sub>4</sub>	0.34 Tg·y <sup>-1</sup>	(most common organic)	[18]
<sup>210</sup> Po	50,000 Ci·y <sup>-1</sup>		[64]

TABLE 3. Mineral and Rock-forming Elements: Subaerial Flux

Element	Mg·y <sup>-1</sup>	Reference	Element	Mg·y <sup>-1</sup>	Reference	Element	Mg·y <sup>-1</sup>	Reference
As	3800	[91]	Cu	9400	[91]	Ni	14000	[91]
Al	88000	[66]	Cu	15000	[66]	Pb	400	[91]
Au	8	[97]	Hg	880	[130]	Pb	2500	[66]
Bi	1200	[96]	K	250000	[66]	Sb	710	[91]
Bi	1500	[66]	Mg	1000	[91]	Se	240	[97]
Cd	820	[91]	Mg	45000	[66]	Tl	200	[96]
Cd	1000	[66]	Mn	42000	[91]	W	53	[97]
Cr	15000	[91]	Mo	400	[91]	Zn	9600	[91]
Na	194000	[66]	Zn	5000	[66]			

The daily flux for many elements for which annual flux estimates are not available have been estimated at each of four volcanoes: Erebus [63], White Island [127], Etna [15] and Merapi [119]. Symonds [121] has used Augustine data and equilibrium calculations to estimate the emission rates of many species. There is wide variation in flux at the different localities.

There are analyses of elements in volcanic gas from diverse locations without estimation of any flux values. Many elements, for which there are no estimates of flux, were detected at Tolbachik [80]: Ce, Eu, Ga, Hf, La, Lu, Pt, Sm, Sn, Ti, Ba. In Hawaii Os and Re and Ir [140] have been detected. Information regarding the radioactive elements <sup>210</sup>Pb, <sup>210</sup>Bi and <sup>210</sup>Po, daughter products of <sup>222</sup>Rn is derived from the work of Lambert, Andouin and Polisan [65].

## 9. ESTIMATE OF SUBAERIAL VOLCANIC GAS COMPOSITION AND FLUX

Variation in volcanic gas data emphasizes the difficulty in arriving at estimates of annual subaerial volcanic gas flux. Quantitative information in Table 1 suggests that the annual flux of the major constituents excluding water, CO<sub>2</sub>, SO<sub>2</sub>, HCl, HF, is 84-100 Tg·y<sup>-1</sup>. The constituents, weight percent, calculated water free, are 65-77% CO<sub>2</sub>, 19-22% SO<sub>2</sub>, 0.5-11% HCl, 0.01%-6% HF. If we assume that H<sub>2</sub>O is 95% volume percent in volcanic gas, an assumption open to question, the weight percent of water is approximately 88%. If 88% by weight of the annual gas flux from subaerial volcanoes is H<sub>2</sub>O, the weight of volcanic gas emitted annually is approximately 800 Tg·y<sup>-1</sup>. This gas, calculated from the annual flux esti-

mates, is composed, by weight, of CO<sub>2</sub>, 8%; SO<sub>2</sub>, 3%; HCl, 1%; HF, less than 0.1%; and H<sub>2</sub>O, 88%. together with at most a very few percent of gases for which there is

inadequate quantitative information. These include H<sub>2</sub>, CO, H<sub>2</sub>S, COS, CH<sub>4</sub> and HBr. There is also very small amounts of the metals.

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