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ESTIMATE OF CARBONYL SULFIDE (OCS) VOLCANIC SOURCE STRENGTH DEDUCED
FROM OCS/CO₂ RATIOS IN VOLCANIC GASES

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Abstract. Measurements of the concentration ratio of OCS and CO₂ were made in fumaroles of several volcanoes in Italy and Nicaragua. The values obtained, together with previous published data, demonstrate that the OCS/CO₂ ratio is positively correlated with the emission temperature of the gases. It ranges from $10^{-7.1}$ to $10^{-2.7}$ at the Vulcano (90°C) and Erta'Ale (1130°C) volcanoes, respectively. The global OCS volcanic source strength, deduced from SO₂ emission rates, CO₂/SO₂ and OCS/CO₂ ratios in volcanic gases, is estimated to be in the range 6-90 x10⁹ gOCS per year.

Introduction

Carbonyl sulfide (OCS) is presumed to have an important influence on the global environment, mainly by providing a steady sustained source of sulfur to the stratosphere, sufficient to maintain the sulfate aerosol layer that affects the earth's radiation balance and climate (Crutzen, 1976). For that reason, numerous efforts to quantify its sources and sinks have been conducted. The global sources, lifetime and mass balance of this species have recently been reviewed by Khalil and Rasmussen (1984). Among the natural OCS sources, volcanoes are considered of minor importance. Estimates of the OCS volcanic contribution, however, still remain uncertain (Cadle, 1980), owing to the small amount of data available on OCS concentration in volcanic gases (Giggenbach and Le Guern, 1976; Allard et al., 1979; Allard, 1980b; Delorme and Cheminée, 1981) or in plumes of erupting volcanoes. Indeed, the recent eruptions of Mt St Helens (1980) and La Soufrière in St Vincent (1979) allowed scientists to obtain the first data on OCS concentration in volcanic plumes (Bandy et al., 1982; Cronn et al., 1982a; Hobbs et al., 1982; Rasmussen et al., 1982; Cronn et al., 1982b).

In order to get a reliable estimate of the OCS volcanic production, we have determined the variability of the OCS/CO₂ concentration ratio in gases of various volcanoes. We demonstrate that this ratio closely depends on the emission temperature of the gases within the range 100-1100°C. From this relationship we can tentatively quantify the OCS volcanic flow, using available data on the CO₂/SO₂ ratios of the gases and SO₂ fluxes either estimated or measured by correlation spectrometry.

Experimental

Four volcanoes have been studied: Momotombo (Nicaragua), Vulcano, Mt Cito and Solfatara of Pouzzoles (Italy). Vulcano belongs to the Aeolian island arc, north of Sicily. Mt Cito is located

on the island of Ischia and Solfatara of Pouzzoles is located close to Naples. Gas samples were collected from fumaroles by use of dewar pipes connected with evacuated pyrex bottles (250 ml) equipped with teflon stopcocks. The sampling procedure insured complete recovery of water vapor and gaseous compounds in the bottles. From preliminary tests, sampling bottles filled with an alkaline solution, following the method of Giggenbach (1975), were found inadequate for such a study because OCS tends to react with the solution. The OCS and CO₂ stability in empty bottles was also checked. For this purpose, samples already analysed a few hours after collection were stored for several months in the laboratory and then repeatedly analysed. After nine months storage the OCS/CO₂ ratio was found to be at a maximum 50% lower than the original value. Such a decrease most probably results from the chemical reaction between OCS and SO₂ favoured by the presence of water, which leads to the formation of atomic sulfur and carbon dioxide (Fern, 1957). In the case of high temperature volcanic gases with a high SO₂ content, evacuated pyrex bottles filled with magnesium perchlorate were used for sampling in order to remove the water vapor entering the flask and to avoid this decomposition of carbonyl sulfide. The latter procedure appears to be the most suitable to maintain the integrity of the two compounds.

Samples were analysed by gas chromatography. The apparatus consists of a gas chromatograph (HP 5730A) equipped with a flame photometric detector (F.P.D.) and a thermal-conductivity detector (T.C.D.). Separation of OCS from the other sulfur compounds (H₂S, SO₂) was done on a 1.80m x 3.1mm O.D. FEP teflon column packed with Chromosil 310 (Supelco), operating isothermally at 40°C, with a 15 ml/min nitrogen flow rate. CO₂ was separated from the other gaseous compounds (Air, CH₄, SO₂, H₂S) on a 2m x 3.1mm O.D. stainless steel column packed with Porapak QS, maintained isothermally at 80°C and with a 30 ml/min helium flow rate. Samples were injected into the chromatographic columns via an eight port sampling valve equipped with two 0.5 ml sampling loops. Pressure in the loop was measured by using a pressure transducer. Standard concentrations of OCS and CO₂ were supplied by certified gas cylinders (Air Liquide and Matheson Union Carbide). In this configuration, the lower limit of detection using an 0.5 ml sample loop was 0.1 ppmv and 500 ppmv for OCS and CO₂, respectively. Molar OCS/CO₂ ratios are used in this paper. The accuracy of the OCS/CO₂ ratios is better than 15% in most cases.

Results.

The OCS/CO₂ ratios we have measured, and those obtained by other authors, are shown in Table 1. R represents the average molar OCS/CO₂ ratio at a given temperature for each volcano. This ratio va-

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TABLE 1. Variability of the OCS/CO₂ ratio in gases of various volcanoes

Countries	Name of the volcanoes	Sampling Year	Temp. (°C)	log $\bar{R}$	Range of log $\bar{R}$	Source
Italy	Vulcano crater	1982	290	-4.74	-(4.80-4.60)	this work
	Vulcano beach	1982	90	-7.10		"
	Solfatara of Pouzzoles	1983	150	-6.15		"
	M ^t Cito	1983	100	-6.70		"
Nicaragua	Momotombo	1983	582	-4.10	-(4.41-3.79)	"
			824	-3.23	-(3.41-3.10)	"
		1984	862	-4.06		"
		1985	862	-3.71		"
Costa Rica	Poas	1981	940	-4.00		Delorme and Cheminée, 1981
	San Cristobal	1981	525	-4.10		"
Ethiopia	Erta'ale	1976	1130	-3.04	-(3.83-2.69)	Giggenbach and Le Guern, 1976
	Ardoukoba	1979	1070	-3.88		Allard et al., 1979
Indonesia	Krakatau	1980	687	-3.40		Allard et al., 1981
	Merapi	1978	900	-2.57	-(2.66-2.54)	Allard, 1983
			819	-2.62		"
			630	-4.85		"

ries between $10^{-7.1}$ at 90°C at Vulcano (this work) and $10^{-2.7}$ at 1130°C at Erta'ale (Giggenbach and Le Guern, 1976), i.e. a range of more than four orders of magnitude. These values appear to depend closely on the temperature of the fumaroles. The decimal logarithms of our own OCS/CO₂ ratios, represented by dots, are plotted against the reciprocal of the fumarole temperatures in Figure 1. A linear relationship between log $\bar{R}$ and $1/T$ °C can be observed, the temperature dependence of $\bar{R}$ being represented by the following equation:

$$\log \bar{R} = -346.49(+31.08)/T(^{\circ}\text{C}) - 3.39(+0.19) \quad (1)$$

with a correlation coefficient $r^2 = 0.953$ for eight experimental data points. Values between brackets are the standard errors on the coefficients.

Previous published data are represented of circles in Figure 1. Except those of Merapi, the points fall close to the regression line obtained from our results and fit within its 95% confidence band limited by the two dashed lines in Figure 1. Therefore, most of the results show that the OCS/CO₂ ratio of volcanic gases is closely related to their emission temperature.

A detailed treatment of the thermodynamical significance of this trend falls beyond the scope of our article. It can be just pointed out that the experimental relationship we observe is consistent with thermodynamical calculations (Heald et al., 1963). Indeed, these show that the OCS/CO₂ ratio in a volcanic gas mixture increases with temperature (and with pressure, although less steeply).

Discussion

The OCS/CO₂ values gathered in Table 1 cover nearly the whole range of volcanic gas temperatures (100-1100°C) and, moreover, encompass the two main types of terrestrial volcanism, i.e. basaltic volcanism in rift zones (Erta'ale, Ardoukoba) and andesitic-type volcanism in orogenic areas (e.g. Momotombo, Vulcano, Krakatau). Knowing the variability of the OCS/CO₂ ratio with temperature and the respective CO₂/SO₂ gas ratio and SO₂ fluxes for basaltic and andesitic volcanoes, we can thus evaluate the volcanic contribution to the atmospheric OCS budget. According to Simkin et al. (1981) and Berresheim and

Jaeschke (1983) there are about 520 active volcanoes. 55 volcanoes showed a yearly average of one or more eruptive events for the period 1961-1979 (Berresheim and Jaeschke, 1983), the 465 others remaining in a non eruptive state (Table 2-column 8).

Calculation of the Eruptive OCS Emissions.

Most erupting volcanoes (≈ 50) are andesitic-type volcanoes located in orogenic areas. The

Fig. 1. Logarithm of the average of the OCS/CO₂ ratios (log $\bar{R}$) plotted against the reciprocal of the emission temperature of the gases ($1/T^{\circ}\text{C}$). Dots refer to our analytical data. Circles refer to previously published data.

TABLE 2. Estimate of the OCS volcanic source strength.

(*) Molar ratio.

Activity classes	Categories	Temperature range (°C)	OCS/CO ₂ * range	SO ₂ flux range(10 ⁶ g/d)	CO ₂ /SO ₂ * range	CO ₂ flux range(10 ⁶ g/d)	Number of volcanoes	OCS flux range(10 ⁶ g/y)
Eruptive	Basaltic	900-1100	1.7x10 ⁻⁴ -2.0x10 ⁻⁴	1000-4000	1.2-1.8	825- 5000	5	350- 2500
	Andesitic	800-1000	1.5x10 ⁻⁴ -1.8x10 ⁻⁴	300-2000	4-10	830-14000	50	3000-63000
							55	3350-65500
Non eruptive	extra-eruptive	100- 400	1.4x10 ⁻⁷ -5.5x10 ⁻⁵	10	10-20	70- 140	100	0- 400
	post-eruptive	400- 800	5.5x10 ⁻⁵ -1.5x10 ⁻⁴	50	4-10	140- 340	265	1000- 7000
	"	"	"	275	"	760- 1900	100	2000-14000
Global							465	3000-21400
							520	± 6500-87000

emission temperature of their gases is usually in the range 800-1000°C (Table 2- column 3). The remaining 5 volcanoes are of the basaltic-type and are located in regions of most intense basaltic volcanism (Hawaii, Iceland, East Africa, Sicily and Reunion). Their typical emission temperature is in the range 900-1100°C (column 3), slightly higher than the former. The corresponding OCS/CO₂ ratios deduced from equation (1) are shown in Table 2- column 4. Therefore, eruptive OCS emission rates can be assessed from these ratios, from ranges of SO₂ fluxes (column 5) and representative CO₂/SO₂ ratios in the corresponding gases (column 6). The sulfur dioxide flux from these two classes of volcanoes have been reviewed by Berresheim and Jaeschke (1983) and Stoiber et al. (1983). Measured SO₂ emissions from andesitic-type volcanoes range from about 200 x10⁶ g/d (e.g. Pacaya) to about 10000 x10⁶ g/d (e.g. San Cristobal), but commonly lie between 300 and 2000 x10⁶ g/d (e.g. Fuego, Santiaguito, Mt St Helens, Merapi). There are comparatively few measured SO₂ flow data for erupting basaltic volcanoes; most are measurements of the continuous activity of Mt Etna, Sicily. Its SO₂ discharge over the period 1975-1985 ranged from 1000 to 12000 x10⁶ g/d, depending on the level of activity, with an average value of about 4000 x10⁶ g/d (Carbonnelle et al., 1985). This value is taken as an upper limit for the yearly SO₂ emission from basaltic volcanoes. It is likely that there are other continental basaltic volcanoes (e.g. Niragongo (East Africa)) that have a SO₂ production as high as that of Mt Etna, although measured fluxes are not yet available. A lower limit of about 1000 x10⁶ g SO₂/d is considered representative of the SO₂ production from oceanic basaltic volcanoes according to the recent estimate of Gerlach and Graeber (1985) for sustained summit eruptions of Kilauea, Hawaii. Consequently, our calculation of the global SO₂ flux from erupting volcanoes leads to values ranging between 7 and 44 x10¹² g per year. Such values are higher than those reported by Berresheim and Jaeschke (1983), about 1 x10¹² g/y, but are considered realistic since they are based on recent SO₂ determinations. The CO₂/SO₂ molar ratio in high temperature basaltic gases is typically about 1.5 ± 0.3 (Giggenbach and Le Guern, 1976). In these gases nearly all sulfur is in the form of SO₂ (Table 2- column 6). The C/S ratio in gases from andesitic-type volcanoes tends to be higher, between 2 and 5 (Allard, 1980a; Matsuo et al., 1982; Allard, 1983). In such gases, at 800-900°C, sulfur is present in the form of both SO₂ and H₂S in nearly equal proportions (e.g. Allard, 1980b; Gerlach and Nordlie, 1975).

Therefore, their CO₂/SO₂ molar ratio can be considered to range from about 4 to 10.

From these different values, the respective CO₂ and consequently the OCS fluxes can be calculated (Table 2- columns 7 & 9). Estimate of the eruptive OCS emissions ranges from about 3.5 to 65 x10⁹ g per year, the mean being about 30 x10⁹ g per year.

Calculation of the Non Eruptive OCS Emissions.

Following the classification of Berresheim and Jaeschke (1983), the non-eruptive volcanic activity can be divided into post- and extra-eruptive activity, the corresponding number of volcanoes being 365 and 100 respectively. Post-eruptive activity can last for weeks to years and is characterized by permanent fuming or fumarolic activity at temperatures that remain high, between 400°C and 800°C. Extra-eruptive activity shows exclusively fumarolic and solfataric activity for years to centuries, with low temperature gases (100-400°C). The corresponding OCS/CO₂ ratios are shown in Table 2- column 4. Measured SO₂ fluxes from extra-eruptive volcanoes (e.g. Vulcano) are generally around 10 x10⁶ g/d (Sabroux, 1980). The CO₂/SO₂ ratio in such gases tends to be higher than 10 and can reach 20 (Cioni et al., 1980). About 265 volcanoes in post-eruptive states release an average daily emission of 50 x10⁶ g, and 275 x10⁶ g for the other hundred volcanoes. The CO₂/SO₂ ratio in post-eruptive high temperature gases has been taken as similar to that in andesitic-type eruptive gases because of the difficulties is estimating the H₂S weight in the C/S ratio. This tends to rather underestimate the CO₂/SO₂ ratio and the OCS flow also.

The results of the calculation show that the OCS extra-eruptive contribution (0-400 x10⁶ g/y) is negligible compared with the post-eruptive one (3-21 x10⁹ g/y).

Hence, one can see from Table 2 that the intensity of the eruptive OCS flow is higher than the non eruptive one. Thus, the global volcanic OCS emission appears to be in the range 6-90 x10⁹ g per year, the mean being 40 x10⁹ g/y. There are few reliable data on the global OCS emissions from volcanoes, since only few measurements have been performed so far (Cadle, 1980). Khalil and Rasmussen (1984) estimated a global volcanic source strength in the range of 10-50 x10⁹ gOCS/year based on recent studies of Mt St Helens eruptions. Our own estimate is in accordance with Cadle's (1980: 20 x10⁹ g/y) and with the range proposed by Khalil and Rasmussen (1984) in their global mass balance of carbonyl sulfide in the earth's atmosphere.

Conclusion

Measurements of the OCS/CO₂ ratio in gases from various volcanoes have shown that this ratio varies between $10^{-7.1}$ and $10^{-2.7}$ and is positively correlated with the emission temperature of the volcanic gases. Calculation of the global volcanic OCS source strength based on this relationship, and on CO₂ flows deduced mainly from measured SO₂ fluxes and CO₂/SO₂ ratios, leads to the estimate of 6 to 90 $\times 10^9$ g/y. Although our evaluation is based on many assumptions and extrapolations, and needs further development and correction, it confirms the order of magnitude of the OCS volcanic source strength, which is useful for the statement of the atmospheric OCS budget. The OCS volcanic flux represents less than 10% of the flux of OCS from the oceans to the atmosphere reported by Khalil and Rasmussen (1984).

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