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THE ECOLOGICAL SIGNIFICANCE OF THE COEXISTENCE OF SULPHUR DIOXIDE AND HYDROGEN SULPHIDE IN VOLCANIC FUMAROLES

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The relative concentrations of hydrogen sulphide and sulphur dioxide in volcanic gases cannot be explained simply by the temperatures and pressures, and appear as the result of the influence of different natural factors. SO_2 is directly related to magma degassing, while H_2S can be produced by the reaction of acidic solutions on dispersed sulphide minerals.

As long as these inputs to the surface environment are of moderate extent, then readjustment of redox conditions to an equilibrium situation will occur; a permanent disequilibrium will result in increased contributions of any component.

A wide spectrum of trace elements is normally associated with the presence of sulphur compounds in volcanic areas; their importance can be estimated for any system on the basis of the quantitative relationship between the oxidized and the reduced sulphur species. Extensive polluting effects can be produced by a continuous flow from a deep magmatic source, while minor consequences are associated with a re-circulation in the surface environment of heavy metals from previous volcanic activities.

KEY WORDS Sulphur dioxide, hydrogen sulphide, fumarolic gases, environmental effects.

INTRODUCTION

A relatively wide range of chemical composition can be observed for the fluid phases emitted by volcanic fumaroles; water, carbon species and sulphur species, however, normally represent 99% of the molar components (Table 1).

Carbon dioxide is always much more important than carbon monoxide, which can only form at high temperatures; sulphur dioxide and hydrogen sulphide, on the contrary, can be present in comparable amounts. The coexistence of SO_2 and H_2S in fumarolic gases was still unknown at the beginning of the century (Mercalli, 1907), and was for the first time revealed at Vulcano in 1923 (Sicardi, 1940; 1956) mainly because of previous inadequate sampling operations, and the consequent reaction between the two species to form elemental sulphur.

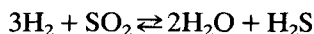
Table 1 Partial analyses of volcanic gas discharges (units μ mol/mol).

Location	Date	T °C	H ₂ O	CO ₂	SO ₂	H ₂ S	HCl	H ₂	N ₂	CH ₄	CO
Campi Flegrei	10.83	155°	845000	153000	—	1780	31	226	326	26.2	0.3
Vulcano Crater	10.80	300°	849000	134800	9100	1900	8500	6	1500	0.2	0.2
Vulcano Beach	5.80	100°	933500	63200	—	1890	30	870	450	51.0	0.03
Showashinzan	6.85	336°	998900	420	34	45	260	840	14	0.5	0.1
Mt Usu	6.85	690°	993000	3850	230	260	350	1930	120	5.3	1.6
Ngauruhoe	7.78	640°	960000	16050	10200	6800	2500	2640	1700	0.3	42.0
Ketetahi	9.79	136°	956400	37800	—	1300	—	1020	540	1070	—
White Isl. Spr.	2.84	100°	975000	22700	220	1080	16	77	260	465	0.1
White Island	2.84	106°	942000	44180	6050	7350	60	19	280	65	0.1
White Island	2.84	195°	947000	40600	3760	840	7260	21	250	44	0.1
White Island	2.84	76°	927000	52900	8150	2450	5180	3020	210	10	42.3
Erta' Ale	1.74	1130°	794000	104000	67800	6200	4200	14900	1800	—	4600
El Ruiz	9.85	82°	955000	23400	19400	1760	63	86	260	0.4	0.2
Mt St Helens	9.81	540°	985000	9130	730	1370	890	2440	470	0.2	13.0
Papandayan	12.85	400°	959000	29360	6750	2900	1250	140	550	0.6	0.3
Darajat	12.85	104°	942000	54000	—	2440	87	945	410	110	0.03
Krafla	8.78	300°	985000	13150	—	350	—	360	1180	1.9	0.8

The behaviour of SO₂ and H₂S in volcanic fluids, however, is not yet fully understood, and their reciprocal concentrations, possibly connected to different activity stages, deserve further consideration.

EQUILIBRIUM BETWEEN SO₂ AND H₂S

The couple SO₂/H₂S has been considered as the dominant buffer system in a volcanic gas phase (Giggenbach *et al.*, 1986) and a re-equilibration in response to changes in temperatures and pressures can be calculated by the simple reaction



As it can be observed in Figure 1, however, large discrepancies between the expected and the measured values of temperature are displayed by most of the fumarolic emissions investigated; observed temperatures are significantly lower than calculated. These discrepancies could be justified by a cooling subsequent to the attainment of equilibrium, but this explanation does not appear fully satisfactory when considering the huge set of observations carried out at Vulcano during the last ten years; the fluctuating differences between the equilibrium and observed temperatures do not fit a constant cooling process operating at the same site, and the possibility of a sustained permanent non-equilibrium condition seems more likely.

As can be seen in Figure 2, the values of the ratios H₂S/SO₂ appear to change to a great extent independently of temperature for fumarole F 5, but with a significant dependence on temperature for fumarole F 14; these different behaviours are difficult to explain considering their common starting point from an equilibrium condition.

If we take different origins for the different sulphur species into account, we can easily justify both equilibrium and non-equilibrium conditions; the buffer

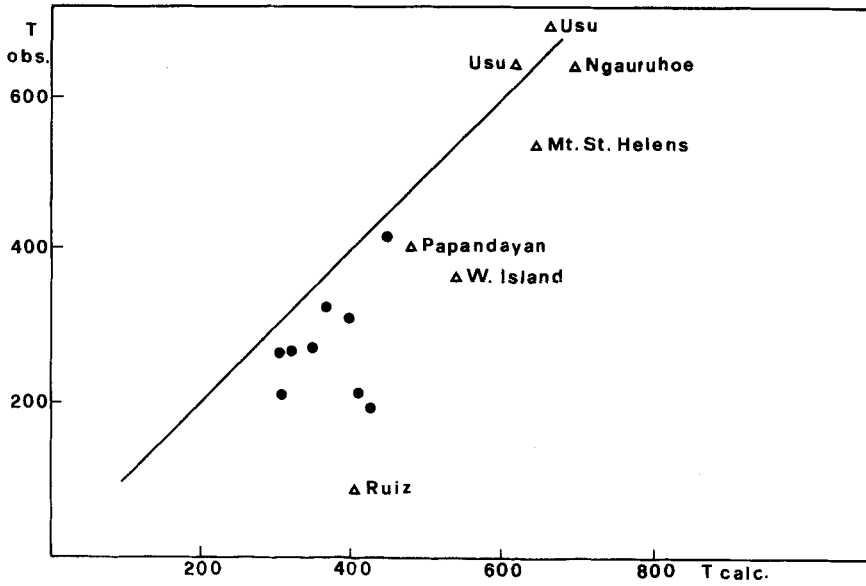


Figure 1 Correlation between observed and calculated temperatures for fumaroles from different volcanic systems.

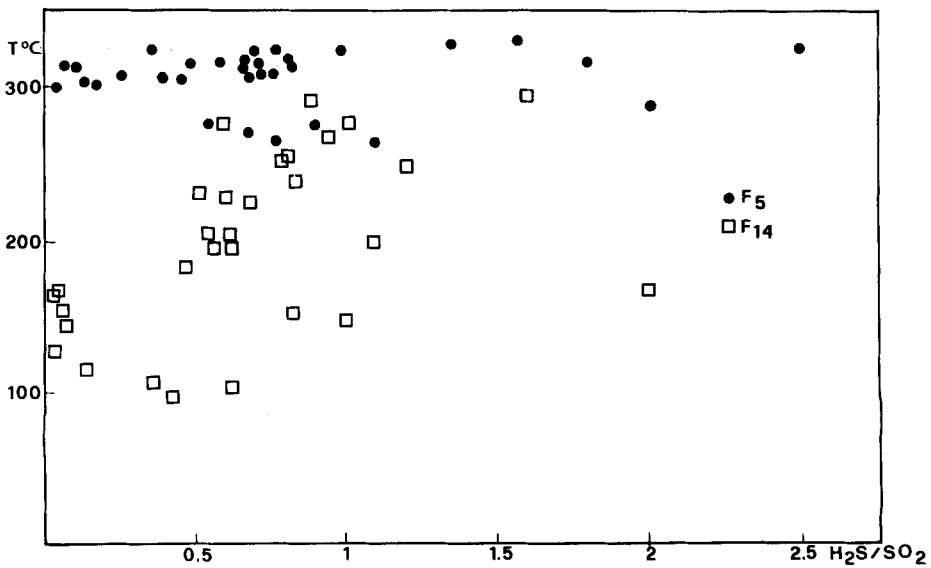


Figure 2 Correlation between observed temperatures at two crater fumaroles of Vulcano and the values of the ratio H₂S/SO₂.

system can allow the attainment of equilibrium if the input rate of the different species does not exceed the re-equilibration rate, while a permanent disequilibrium will predominate for input rates above this threshold.

Sulphur dioxide can be produced only at magmatic conditions, but a different possibility can be suggested for hydrogen sulphide. Dispersed metal sulphides are normally present in any volcanic environment, and their reactions with acidic solutions could produce significant concentrations of hydrogen sulphide. This process can occur even for weakly acidic CO_2 -charged ground waters, and will be much more effective if solutions of stronger acidity are involved.

Both situations are easily encountered in areas of active volcanism, so that the possible generation of hydrogen sulphide at shallow depth as the result of an interaction of dispersed sulphide minerals and circulating solutions appears quite likely.

A similar input of hydrogen sulphide into the volcanic system can produce a readjustment of redox conditions, but without perturbation of equilibrium, in so far as its rate remains below the above mentioned threshold; a permanent disequilibrium condition will prevail, however, for the more important contributions of H_2S .

Figure 3 gives the analytical data for water content and the ratio $\text{H}_2\text{S}/\text{CO}_2$ obtained at Vulcano subsequently to a seismic crisis which occurred at the beginning of 1984.

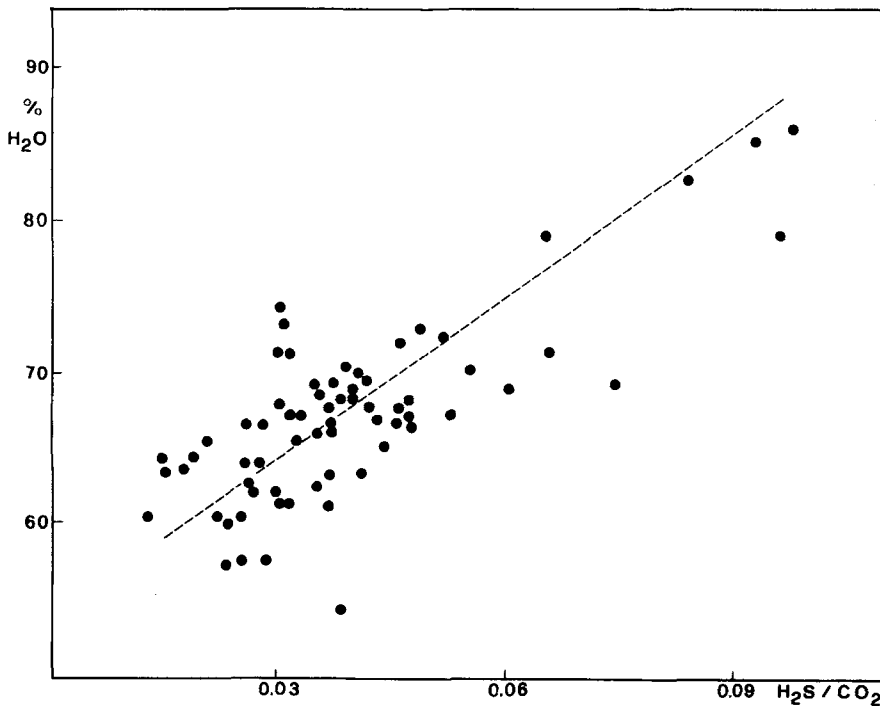


Figure 3 Correlation between water content in different fumaroles at the crater of Vulcano and the values of the ratio $\text{H}_2\text{S}/\text{CO}_2$.

A well defined increase of hydrogen sulphide with respect to carbon dioxide occurs at the same time as increased water content can be observed. For any contribution of water to the system, the more soluble H₂S would dissolve more easily than the less soluble CO₂; a decreasing trend of H₂S/CO₂ ratios with increasing water content should be observed accordingly.

The opposite trend displayed by the fumaroles of Vulcano implies an additional input of H₂S which can overwhelm the effects of its higher solubility. The production of this constituent as the result of an interaction of acidic solutions with dispersed sulphides appears to be the simplest mechanism which can justify the situation observed.

The significant increase in the H₂S/CO₂ ratio should also correspond to an increasing rate of the process itself, so that the buffer system is not able to readjust to equilibrium conditions.

ENVIRONMENTAL EFFECTS

An input of volatiles of deep origin into the surface environment is a very polluting process; sulphur compounds and trace metals can strongly affect the composition of soils, and, consequently, of groundwaters, with effects on plants and livestock (Cellini Legittimo *et al.*, 1986, 1988; Piccardi *et al.*, 1988). It is not easy to provide a quantitative measure of these polluting effects, but it is possible, however, to give a broad idea of the extent of the same phenomena on the basis of the relative abundance of the sulphur species considered.

By taking into account the above mentioned processes, as long as substantially similar concentrations of SO₂ and H₂S can be found in fumarolic gases, then a continuous degassing from the underlying magma can be inferred. Shallow and surface aquifers are not able to neutralize the acidity produced by the partial dissolution of SO₂, which can persist in gaseous phase; a concentration of H₂S approximately corresponding to the acidity due to SO₂ can form accordingly. When a limited magma degassing flows towards the surface, an increased fraction of the total SO₂ can be dissolved by groundwaters, so that a minor concentration of this component can persist in gaseous form.

For a still further decreased output of volatile species from the deep magmatic system, the shallow and surface environments can neutralize the total acidity produced by dissolution of SO₂, which can no longer persist in gaseous form. H₂S-fumaroles will result, characterizing the low-temperature solfataric stage of quiescent volcanic systems.

Different degrees of environmental impact can be predicted according to the different relative concentrations of the two sulphur species. The highest contribution of pollutants can be associated with the highest levels of SO₂ and, consequently, of the ratio SO₂/H₂S; a rather limited extent of a deep contribution to the surface environment pertains, in contrast, to SO₂-depleted fumaroles.

Sometimes the measured temperatures can provide a similar indication; this circumstance, however, is not always verified, and it is much more appropriate to rely on chemical evidence of fumarolic emissions. As a matter of fact, a SO₂-depleted solfataric stage can be observed at Phlegrean Fields at temperatures above 150°C, while SO₂-rich fumaroles have persisted inside the crater of Vulcano at temperatures around 100°C.

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