The Gas/Steam Ratio As Indicator of Heat Transfer at the Solfatara Fumaroles, Phlegraean Fields (Italy)

R. CIONI
E. CORAZZA
Istituto di Geocronologia e Geochimica Isotopica, C.N.R., Pisa, Italy

L. MARINI
Geotermica Italiana, Via C. Maffi, 5, Pisa, Italy

ABSTRACT

A simple geochemical model of Solfatara, Phlegraean Fields (Italy), is proposed on the basis of gas composition and temperature at the surface.

Data on the Solfatara fumaroles have been collected since 1979 within the framework of a geochemical monitoring for the surveillance of the Phlegraean volcanic system.

Surface manifestations of Solfatara are likely to be fed through isoenthalpic expansion of dry steam, which separates from a geothermal liquid in an intensively fractured zone at about 236°C. This value is consistent both with gas composition and surface temperature.

The gas/steam ratio appears to be the most effective parameter to detect changes of heat flow at depth.

Actually a remarkable decrease in the gas/steam ratio has been observed since 1981, while the gas composition and the temperature did not change significantly. These facts suggest increased heat flow at depth.

INTRODUCTION

Phlegraean Fields are a volcanically active fumarolic area in Southern Italy; the last volcanic eruption (Monte Nuovo) occurred in 1538.

Volcanological (ROSI *et al.*, 1983), petrological (ARMIENTI *et al.*, 1983) and geophysical (CORRADO *et al.*, 1977) evidence suggests that volcanic activity in Phlegraean Fields is fed by a cooling shallow magma chamber, centered in the proximity of the town Pozzuoli.

Since August 1982 this area has been affected by a vertical uplift (2-3 mm/day) accompanied, since March 1983, by a marked increase in seismic activity (CORRADO *et al.*, 1983). Volcano surveillance has therefore been enhanced, as an unforeseen eruption would have dramatic consequences in this very densely populated area.

Since 1979 the geochemical monitoring for the surveillance of the Phlegraean volcanic system has been carried out by the Istituto di Geocronologia e Geochimica Isotopica of Pisa, in the framework of the Italian Progetto Finalizzato Geodinamica.

Many geochemical data concerning different thermal manifestations in this area have been gathered.

Particular attention has been devoted to the sampling and the study of the fumarole discharge of the Solfatara volcano, which, on the basis of compositional and physical characteristics, can be considered as the most direct sampling point of the geothermal aquifers.

The surveillance of the Solfatara volcanic system seeks the relationship among magma chamber, hydrothermal aquifers, proved to exist (ROSI *et al.*, 1983), and surface manifestations.

The probability of forecasting a volcanic eruption depends largely on the quality of the model of the volcanic system under observation.

Bull. Volcanol., Vol. 47-2, 1984

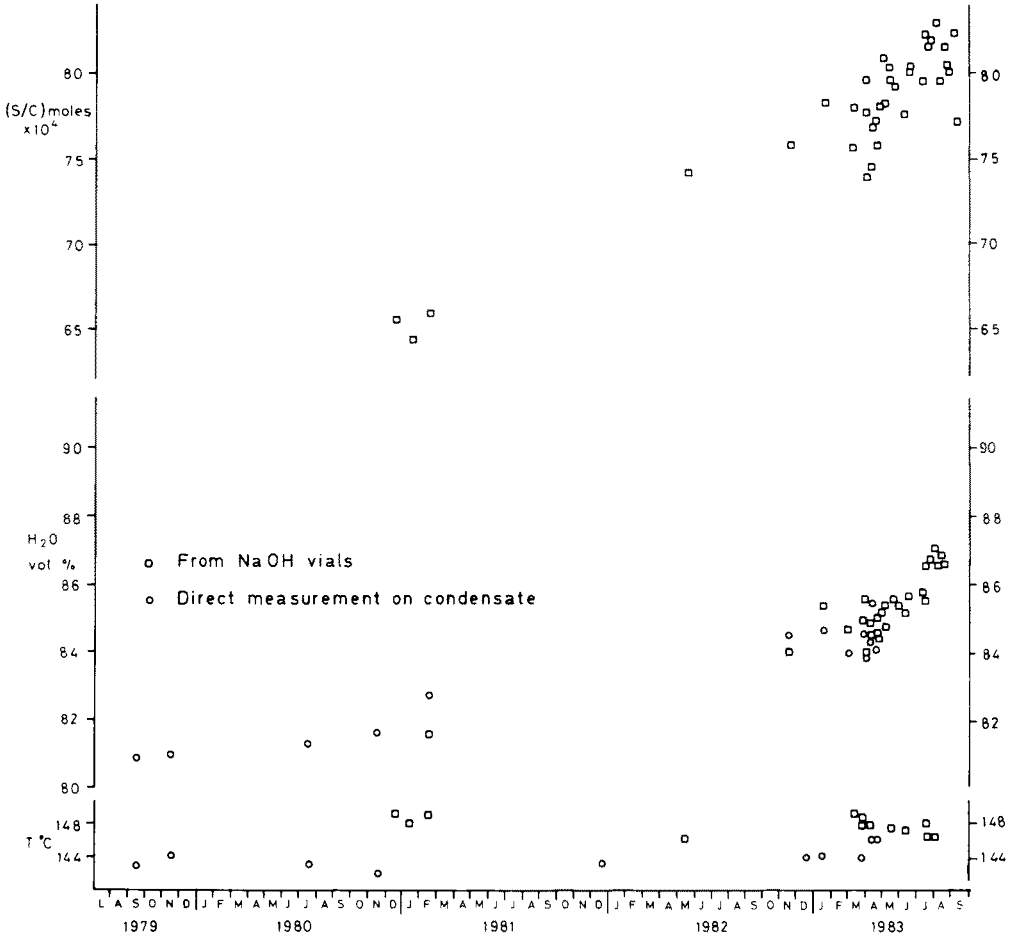

FIG. 1 – Variations of S/C ratio, H_2O and temperature versus time at a fumarole of Solfatara.

The purpose of this work is to outline:

1) The definition of a geochemical model of Solfatara which allows interpretation of changes in temperature and chemical composition observed at the fumaroles;

2) The choice of chemical parameters on which the surveillance activity has to be focused.

It will be shown that, under the specific conditions of Solfatara, the gas/steam ratio of the fumarole discharge provides relevant information on the physical changes of the underlying aquifer(s).

GEOCHEMISTRY OF SOLFATARA GASES

Variations of major and minor relevant chemical species versus time of one fumarole of Solfatara are given in Figures 1 and 2.

Analytical methods and accuracies are in Table 1.

Outlet temperature is quasi-constant. Systematic differences between measurements by mercury thermometer and those by digital thermocouple were observed.

Water percentage by volume changed from 81-82 (pre-1981 value) to 84-86 (1983). Due to the lack of data during the period 1981-1982, it is not evident when water content started to increase; anyway such a change occurred surely before the increase in seismic activity (March, 1983) and likely before the beginning of ground upwelling (August, 1982).

Carbon dioxite and hydrogen show quasi-constancy within the experimental errors (CO_2 data are not shown in diagrams).

Methane exhibits a practically constant value (around 0.025% by vol. in dry gas) since December 1982.

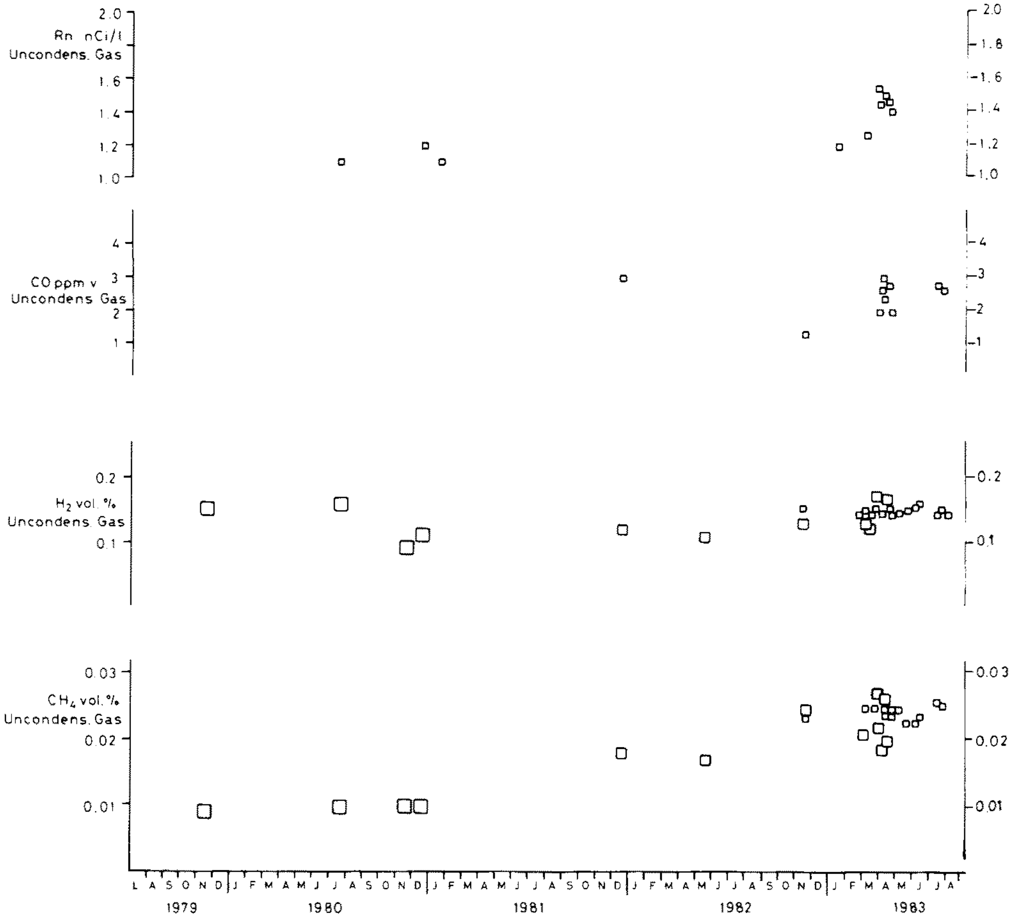

FIG. 2 – Variations of CO, H_2 and CH_4 versus time at a fumarole of Solfatara.

TABLE 1 – Composition data (molar fractions), analytical methods and accuracies.

	range	average	method	accuracy(±%)
H_2O	0.8388 ÷ 0.8542	0.8473	gravimetric	0.5
CO_2	0.144 ÷ 0.160	0.151	potentiometric titration	1-1.5
H_2	2.04E-4÷ 2.48E-4	2.24E-4	GC-TCD	10
CH_4	3.2E-5 ÷ 4.0E-5	3.73E-5	GC-HID	10
CO	2.9E-7 ÷ 4.8E-7	3.82E-7	GC-HID	30
Total S	1.07E-3÷ 1.31E-3	1.18E-3	gravimetric	2

GC-TCD = gas chromatography with thermal conductivity detector.

GC-HID = gas chromatography with helium ionization detector.

The notations E-X mean 10^{-X} multiplied by the numerical value.

Different analytical methods were utilized before 1981; their accuracies were as follows: $H_2O=\pm1\%$; $CO_2=\pm3\%$; $H_2=\pm25\%$; $CH4=\pm50\%$; Total $S=\pm20\%$.

Data are from Cioni et al. (1984).

For details on methods of sampling and analysis see Giggenbach (1975), Cioni et al. (1980) and Cioni and Corazza (1981).

Methane data previous to 1981 are lower, but their reduced accuracy does not allow to compare them with the more recent ones.

CO content ranges between 2 and 3 ppm by vol. in dry gas.

The S/C molar ratio varied 0.0065 to 0.0080; such a change mainly reflects total sulphur variations (0.735 - 0.814% by vol. in dry gas) since CO_2 content is fairly constant (around 98.8% vol. in dry gas).

The few published data (DALL'AGLIO *et al.*, 1972) suggest that the dry gas composition of the fumaroles of Solfatara did not undergo dramatic changes in the last 30-40 years.

The main conclusion that can be drawn from all available chemical data is that a significant increase of the water content in time occurred, whereas fluctuations of dry gases other than sulphur species remained within the expected analytical accuracies (see Table 1).

GEOCHEMICAL MODEL

The chemical composition of fumarolic discharge depends on the chemical and physical conditions at depth and it has been utilized for geothermometric and geobarometric applications both in volcanic and geothermal environments (ELLIS, 1957; HULSTON, 1964; LE GUERN *et al.*, 1975; D'AMORE and NUTI, 1977; GIGGENBACH, 1980; D'AMORE and PANICHI, 1980).

In this specific case equilibration temperatures can be obtained from the pressure independent gas reaction:

$$CO_2 + H_2 = CO + H_2O$$

according to the equation

$$T(°K) = \frac{2053}{2.031 - \log \dfrac{X_{CO} \cdot X_{H_2O}}{X_{H_2} \cdot X_{CO_2}}} \qquad (1)$$

assuming the gas phase is representative for the equilibrium at depth. X's are molar fractions in the vapor phase.

All the fugacity coefficients are assumed to be unity. Thermodynamic data are from BARIN and KNACKE (1973).

The equilibrium temperature calculated from equation (1) with the mean values of Table 1 (which refer to a homogeneous and complete set of measurements carried out in the period February - July 1983) is 234°C.

Minimum and maximum geochemical temperatures are 220 and 246°C.

By inserting the mean temperature value, 234°C, into the pressure dependent gas reaction

$$4\ CO + 2\ H_2O = CH_4 + 3\ CO_2$$

the corresponding water pressure can be obtained according to equation

$$\log P_{H_2O} = 9.184 - \frac{8678}{T(°K)} + \frac{1}{2} \log \frac{X^3_{CO_2} \cdot X_{CH_4}}{X^4_{CO}} \quad (2)$$

on the basis of the same assumptions and considerations stated for equation (1). The calculated water pressure is 28 bar.

Such pressure and temperature values are very close to the conditions of maximum enthalpy of saturated steam (236°C, 31 bar).

An isoenthalpic expansion of the steam separated from the liquid phase under such conditions would produce dry steam with temperature of about 160°C at atmospheric pressure (KEENAN *et al.*, 1978). This temperature value is not very far from the temperature of the sampled fumarole, which ranged between 142 and 149°C, while the maximum value measured in the area was 157°C. The coincidence of observed outlet temperatures with that given for steam expanded from 236°C and 31 bar to atmospheric pressure, together with the equilibration temperature inferred from gas composition strongly suggests the existence, under Solfatara, of a zone where the above mentioned equilibrium conditions do exist.

On the basis of the previous considerations and by taking into account the geological setting of the Solfatara system, the simplified model sketched in Fig. 3 is proposed.

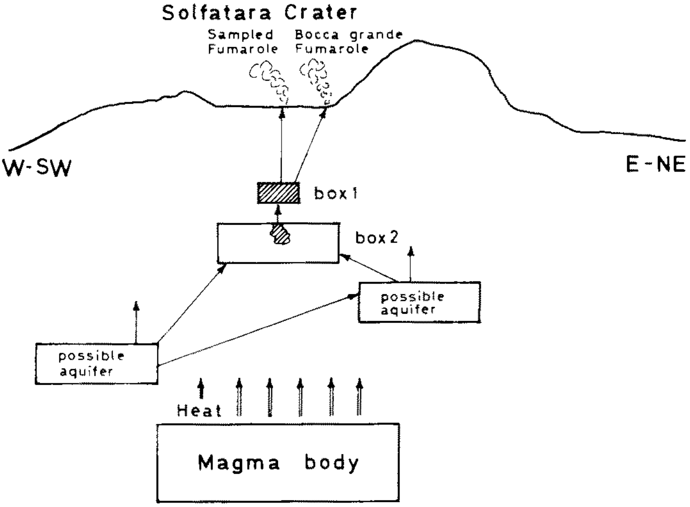

FIG. 3 – Simplified geochemical sketch of the Solfatara system. Shaded areas correspond to intensively fractured zones where the vapor phase is separated from liquid water.

A shallow magma chamber located at a depth of 3-5 km acts as heat source for the overlying hydrothermal aquifers (ARMIENTI *et al.*, 1983). The boiling of a main aquifer (box 2) located at approximately 1450 m is responsible for the origin of fumaroles fluids (MINUCCI, 1961). Complete separation of the vapor and liquid phases and gas re-equilibration at 236°C takes place within a separated intensely fractured area above it (box 1).

The possible existence of other deeper aquifers connected to the main one cannot be ruled out and would facilitate the energy transfer toward the surface.

For the sake of completeness it has to be noted that H_2S content (considering that hydrogen sulfide is by far the most important sulphur species present in the analyzed mixtures) is higher than expected assuming that sulphur fugacity is buffered either by the mineral assemblage proposed by GIGGENBACH (1980) or by that studied by D'AMORE and GIANELLI (1984).

DISCUSSION

The ultimate aim of the geochemical surveillance is to detect changes in the energy balance of the volcanic system under observation, particularly an increase of the heat flow from the magma body. Whatever the mechanism is, a heat flow increase produces a temperature and pressure increase in box 2, provided that the energy entering box 2 is greater than the energy leaving it.

This increase in temperature and pressure causes a decrease in the coefficients of vapor - liquid gas distribution (ELLIS, 1962; GLOVER, 1970; GIGGENBACH, 1980) and an increase in the steam fraction of the fluid leaving box 2. Both changes produce, in turn, a decrease in the gas/ steam ratio in box 1 and consequently at the surface.

Temperature changes in box 2 can be roughly estimated on the basis of:

1) the carbon dioxide mass balance,

2) the temperature dependence of the vapor - liquid CO_2 distribution coefficient, and

3) the function relating the liquid water enthalpy to the temperature of box 2.

The temperature in box 2 is assumed to be known at a certain time and the energy transfer from box 2 to box 1 is assumed to be isoenthalpic.

Isotopic geochemical evidence (NUTI *et al.*, unpublished data) suggests that the «flashing» temperature in box 2 was about 280°C in 1983 when the CO_2/steam ratio was 0.178 moles gas/ moles steam. Hence a box 2 temperature of 270°C can be calculated when the CO_2/steam ratio was 0.224 moles CO_2/moles steam (pre-1981 situation).

Moreover this variation in temperature of box 2 satisfactorily explains the observed changes in time of hydrogen sulfide and S/C ratio.

CONCLUSIONS

Theoretical considerations show that the gas/steam ratio at the Solfatara fumaroles is expected to decrease in response to an increase of the heat flow from the magma body.

A marked decrease in gas/steam ratio has actually been detected since 1981, whereas observed variations in dry gas composition were within analytical uncertainties.

Re-equilibration of the gases in response to a variation in water vapor content implies a change in relative CO_2, CO, CH_4 and H_2 contents.

Anyway expected variations in dry gases, during the period February-July 1983 (X_{H_2O} = 0.8388 to 0.8542), evaluated assuming that the oxygen fugacity is kept constant by an unknown buffer system, are well within analytical accuracies (Table 2), in agreement with observed values.

Expected variations of carbon species contents in dry gases for X_{H_2O} = 0.81 (1981 value) are negligible, while that in

TABLE 2 – Expected composition variation during re-equilibration at 236°C, evaluated assuming a constant oxygen fugacity.

X's are molar fractions in the vapor phase.
Y's are molar fractions in the uncondensable phase except atmopsheric components and H_2S.
The notations E-x mean 10^{-x} multiplied by the numerical value.

	Observed average content	Observed range of variation (%)	Expected variation for:			
X_{H_2O}	0.8473	-1/+0.8	X_{H_2O}= 0.81	= 0.8388	= 0.8542	= 0.86
Y_{CO_2}	0.9983	-0.3/+0.1	0.9986	0.9984	0.9982	0.9981
Y_{H_2}	1.48 E-3	-4.8/+4.8	1.14 E-3	1.39 E-3	1.56 E-3	1.64 E-3
Y_{CH_4}	2.46 E-4	-9.8/+2.5	2.46 E-4	2.46 E-4	2.46 E-4	2.46 E-4
Y_{CO}	2.50 E-6	-20/+20	2.50 E-6	2.50 E-6	2.50 E-6	2.50 E-6

hydrogen content is around 20 - 25%, which is the order of the analytical accuracy at that time.

Therefore the gas/steam ratio appears to be the most effective parameter to detect changes of heat flow at depth. However gas composition monitoring must be continued, in order to improve the general knowledge of the hydrothermal - volcanic system and to detect its possible dramatic changes.

ACKNOWLEDGEMENTS

The authors would like to express sincere thanks to Franco Barberi for the critical reading of the manuscript and are greatly indebted to Werner Giggenbach for his very useful comments to the first draught.

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Ms. received Sept. 1983; sent to review Sept. 1983. Revised ms. received Sept. 1984.