

# The determination of deep temperatures by means of the CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermometer: an example using fumaroles in the Campi Flegrei, Italy

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**Abstract.** Chromatographic analyses of fumarolic gases, collected in sampling bottles containing an alkaline solution, have been carried out using a thermal conductivity detector and a flame ionization detector, after catalytic conversion of CO into CH<sub>4</sub>. The latter method enables the concentration of carbon monoxide to be measured with sufficient accuracy for use in a CO-CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermometer. Application of this geothermometer to fumaroles in the crater of Solfatara in the Campi Flegrei, Italy, indicates that they are fed from a steam reservoir at  $250 \pm 15$  °C and at  $10^{-36 \pm 2}$  atm of oxygen. On the other hand, the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermobarometer seems to re-equilibrate at superficial temperatures and cannot be used for inferring thermodynamic conditions at depth. Regular sampling of these fumaroles together with a geothermometric interpretation of the gas analyses provides a means of monitoring, with comparative accuracy, the chemical and thermal evolution of the hydrothermal reservoir below the Solfatara crater. Such monitoring would probably detect an increase in temperature at depth and the injection of magmatic gas into the reservoir.

In the Campi Flegrei, however, the additional possibility exists of conducting geochemical monitoring of fumarolic gases, particularly those escaping from the crater of Solfatara, the site of the most conspicuous superficial thermal anomaly in the area. If sufficiently accurate, the analysis of such gases may provide information on the conditions of temperature and pressure in the hydrothermal reservoir feeding the fumaroles, on the physico-chemical evolution of that reservoir, and on any connections between it and an underlying body of hot magma.

We have therefore collected and analysed a series of volcanic gas samples from Solfatara, obtained at intervals after October 1983. The first samples of this series were collected during a seismic crisis. We assessed the data to determine how closely they meet the conditions necessary for use as geothermometers and geobarometers. These requirements are the complete attainment of chemical equilibrium, perfect chemical quenching and the closed-system evolution of the volcanic fluids en route to the surface (Sabroux 1983).

## Introduction

Since 1982, the Campi Flegrei volcanic district, on the west coast of Italy, has experienced a period of ground uplift and sustained seismicity including several hundred felt earthquakes (Barberi et al. 1984). The events are being monitored by a permanent surveillance network, which, in common with similar systems deployed elsewhere [e. g. the Long Valley/Mono Basin volcanic complex (Hernance 1983) or the Rabaul Caldera (McKee et al. 1985)], utilizes predominantly geophysical methods (such as seismometry, microgravimetry, and ground levelling).

## Gas collection and analysis

### *Theoretical considerations*

Among the numerous chemical species which coexist in a fumarolic gas phase, carbon monoxide and, to a lesser extent, hydrogen represent the best indicators of a possible variation in temperature at depth. The equilibrium ratios  $P(\text{CO})/P(\text{CO}_2)$  and  $P(\text{H}_2)/P(\text{H}_2\text{O})$  in the gas phase range from  $10^{-6}$  to  $10^{-1}$  and from  $10^{-4}$  to ca.  $3 \times 10^{-2}$  respectively as the equilibrium temperature changes from ca. 150 °C, a value typical of the hydrothermal regime, to ca. 1150 °C, corresponding to magmatic conditions (Sabroux 1979). Both carbon monoxide and hydrogen are metastable at room temperature and are not readily oxidized under the low temperatures that may occur in the fumarolic duct, the collection tube, or the sampling flask. Nevertheless, due to

the limited availability of methods capable of analyzing carbon monoxide in the ppm range, this gas has not been used widely in hydrothermal geothermometry.

#### Sampling procedure and analysis of the gases

Because of the low carbon monoxide content of the hydrothermal gases, special procedures of sampling and analysis are necessary to obtain measurements sufficiently accurate for thermodynamic calculations for geothermometry.

Accordingly, the sample containers chosen were evacuated glass flasks, partly filled with 4 N NaOH absorbing solution (Giggenbach 1975), which may concentrate by several hundred times the content of the so-called *uncondensable gases*, including carbon monoxide. Typically, more than one mole of fumarolic fluid (dry gas + water vapour) is introduced into the sampling volume of ca. 250 cm<sup>3</sup>. To analyse the gas composition, a flame ionization detector (FID) was used downstream from a methanizing oven, in series with a 3 m *Porapak R* column at room temperature.

In the oven, the reaction:



catalysed by Ni is almost complete at 350 °C (Fig. 1). The sensitivity of this method, which benefits from the linear response of the FID (*Varian Model 1400* gas chromatograph), lies below 1 ppm for carbon monoxide.

The other gas species were analysed with a thermal conductivity detector (microcatharometer TCD, *Varian Model 3700* gas chromatograph) downstream from a 3 m

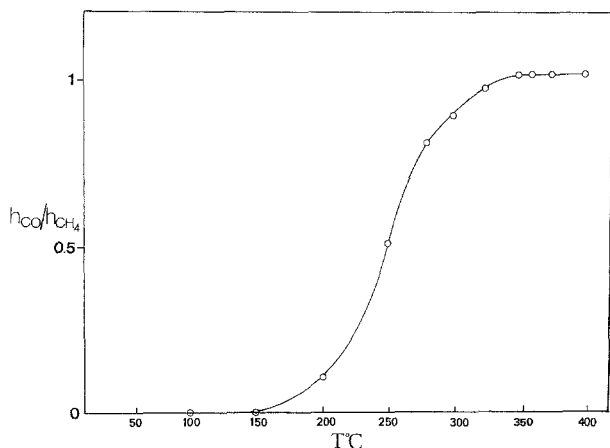


Fig. 1. Ratio of carbon monoxide to methane chromatographic peak heights, as recorded by a FID, for an equimolar ( $\pm 10\%$ ) mixture of CO and CH<sub>4</sub>, in the 100 ppm concentration range. The results are presented as a function of the temperature of the methanizer. The catalytic hydrogenation of carbon monoxide in reaction  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$  (1) is completed at ca. 350 °C

molecular sieve 5A column, either at 65 °C with helium as a carrier gas (for analysing O<sub>2</sub> + Ar, N<sub>2</sub> and CH<sub>4</sub>), or at ambient temperature with argon as a carrier gas (for analysing He and H<sub>2</sub>).

After determining the volume ratio between the liquid phase and the gas phase in the sampling bottle, the CO<sub>3</sub><sup>2-</sup> and S<sup>2-</sup> ions in the alkaline solution were analysed by the conventional methods of neutralization by HCl and titration by Pb(ClO<sub>4</sub>)<sub>2</sub>, using a *Tacussel* pH-electrode and sulphide ion-specific temperature of Soffione *Geochimica Isotopica* 1984. The mass of water vapour could then be determined as the difference between the total mass of fluid and the mass of the so-called *dry* gases (including CO<sub>2</sub> and H<sub>2</sub>S).

#### Results

Two fumaroles, Bocca Grande and Soffione, in the floor of the Solfatara crater, were chosen for the sampling programme because of their comparative permanency and accessibility. For the most part, their temperature remained at the steady value of 157 °C (Bocca Grande) and 147 °C (Soffione) during the period of investigation, although an exceptional drop of 20 °C was recorded in the temperature of Soffione after January 14, 1984

Twenty-three samples were analysed for their major component composition (apart from Cl and F in the alkaline solution) between October 1983 and February 1984. The overall composition of each sample was calculated from the corresponding results of the gas analyses, the wet analyses, and from the gas/water ratio (see Table 1, presenting sample SF01 as an example). The bulk analyses of these samples are presented in Table 2. The O<sub>2</sub> + Ar data demonstrate the particularly low degree of air contamination that is attainable with the use of a sophisticated sampling device including an iron tube, angle Dewar tube and extension Dewar tube. This sampling train is similar to the design used by other investigators on the same fumaroles (Cioni and Corazza 1981, parts 1, 2 and 3 in Fig. 1, p. 25; Piccardi 1982; Martini et al. 1984)

Apart from slight differences in sulphur and methane contents (Bocca Grande richer in H<sub>2</sub>S and Soffione richer in CH<sub>4</sub>), the fumaroles are very similar chemically. The earthquake swarm on 13 October 1983 was preceded by slightly low water content and low H<sub>2</sub>S/CO<sub>2</sub> ratio from both fumaroles (Table 2). This trend is corroborated by geochemical data collected since June 1983 by other authors (*Istituto di Geocronologia e Geochimica Isotopica* 1984). Nevertheless, fumarolic gas composition appears to have been more affected by this swarm at Bocca Grande than at Soffione. In addition, each fumarole exhibited significant variations in H<sub>2</sub>S content throughout the period of study, which was characterized by a relatively high level of seismicity.

**Table 1.** Volumetric composition of sample SF01

H <sub>2</sub> O (%)	CO <sub>2</sub> (%)	H <sub>2</sub> S (%)	N <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	He (%)	CO (%)	O <sub>2</sub> +Ar (%)
<i>Uncondensable gases</i>								
			57.9	35.8	5.38	0.253	0.0454	0.630
<i>Dry gases</i>								
	98.5	1.02	0.262	0.162	0.0243	0.00114	0.00021	0.00285
<i>Overall chemical composition</i>								
85.2	14.6	0.151	0.0387	0.0239	0.00359	0.00017	0.00003	0.00042
<i>Accuracy (%)</i>								
0.5	2	1	10	5	2	10	2	15

Added to the chromatographic analyses of the gas phase (line 1 = 100%) are the results of the wet analyses of H<sub>2</sub>S and CO<sub>2</sub> (line 2 = 100%). The overall chemical composition of the sample includes the water vapour content, determined by weighting (line 3 = 100%), although this presentation, suitable for thermodynamic calculations, leads to awkward decimals. The gas/water molar ratio equals 0.17. Note that the CO concentration in the fluids seldom exceeds 0.2 ppm, yet it has a concentration of 450 ppm when it is analysed as a constituent of the gas phase over the alkaline solution. Although accuracy can be as poor as 15% for certain gaseous species, experimental reproducibility is better than 0.5% for most components excluding water. The methanizer + FID is at least ten times more accurate for analysing carbon monoxide than the HID (Cioni et al. 1984). A 10% accuracy on the CO concentration yields a ± 7 °C uncertainty on the temperature  $T_c$  derived from thermodynamic equilibrium

**Table 2.** Volumetric composition of the samples collected from October 1983 to February 1984 at Solfatara crater

Sample no.	Date	H <sub>2</sub> O (%)	CO <sub>2</sub> (%)	H <sub>2</sub> S (%)	N <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (ppm)	He (ppm)	CO (ppm)	O <sub>2</sub> +Ar (ppm)
<i>Soffione</i>										
SF01	11/10/83	85.2	98.5	1.02	0.26	0.16	243	11.4	2.1	28.5
SF02	12/10/83	88.5	98.7	0.76	0.31	0.17	250	11.7	2.4	19.9
SF04	14/10/83	91.1	98.6	0.92	0.31	0.18	278	16.9	2.1	32.7
SF05	29/10/83	92.3	98.4	1.07	0.34	0.18	283	12.6	1.1	14.1
SF06	30/10/83	92.2	98.6	0.95	0.31	0.14	239	24.1	1.4	14.5
SF08	27/12/83	91.2	98.5	0.96	0.33	0.20	297	12.2	1.9	6.1
SF09	29/12/83	92.3	98.5	0.99	0.32	0.16	267	16.7	1.6	15.4
SF10	14/01/84	92.7	98.5	1.10	0.25	0.16	240	16.6	1.2	4.4
SF11	16/01/84	91.6	98.5	0.98	0.30	0.20	273	13.8	1.8	16.0
SF12	18/01/84	92.0	98.5	0.93	0.32	0.22	289	15.3	2.0	5.7
SF14	28/02/84	93.8	98.3	1.10	0.31	0.22	259	25.5	2.2	37.2
SF15	29/02/84	88.8	98.8	0.72	0.29	0.21	233	15.9	2.3	14.7
<i>Bocca Grande</i>										
BG01	11/10/83	n. d.	98.6	1.00	0.23	0.14	128	18.6	2.7	56.5
BG02	12/10/83	85.2	98.6	1.04	0.20	0.14	133	24.7	1.6	14.0
BG03	13/10/83	91.9	97.9	1.48	0.37	0.25	238	21.2	3.1	21.8
BG04	14/10/83	89.6	98.0	1.45	0.31	0.22	211	22.5	3.3	17.0
BG06	30/10/83	92.8	97.4	2.05	0.33	0.23	239	22.7	1.7	9.8
BG08	27/12/83	91.5	97.7	1.75	0.28	0.20	285	13.9	3.3	11.3
BG10	14/01/84	91.4	97.7	1.77	0.26	0.21	193	13.8	1.8	4.9
BG11	16/01/84	91.1	97.7	1.77	0.26	0.20	192	13.3	2.1	9.6
BG13	27/02/84	91.8	97.6	1.83	0.31	0.22	181	13.9	2.8	23.8
BG14	28/02/84	92.7	97.6	1.88	0.28	0.24	203	17.2	3.1	10.6
BG15	29/02/84	92.4	97.6	1.97	0.20	0.18	137	12.0	1.9	19.2

For each sample, the composition of the dry gases is recalculated to 100%, in order to enhance the legibility of the table

**Discussion**

To illustrate the thermodynamic approach used to evaluate the maximum temperature above the inferred aquifer, which by boiling feeds the fumaroles, the geothermometry

and the geobarometry as applied to the data will be shown hereinafter in some detail, using sample SF01 as an example.

The validity of this approach, together with the relevance of the analytic method chosen (metha-

nation + FID) was first thoroughly checked on fluids sampled in 1978 from 11 wells of the Larderello geothermal field (Mestrel 1983). They were then applied to samples from Soufrière of Guadeloupe volcano (Dajlevic and Sabroux, unpublished results; Allard 1983, p. 383).

#### The CO-CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermometer

Before discussing the implications of the results, we consider the assumptions inherent in the geothermometric and geobarometric interpretation of the geochemical data. These are: (1) that the sampled gases were in equilibrium in their geological environment, at the calculated temperature and pressure conditions; (2) that each of the gas samples had evolved as a closed system en route to the surface; (3) that complete and fast chemical quenching was achieved when collecting the gases; and (4) that the gases, including water vapour, behave ideally.

The fluids discharged from the fumaroles were mixtures of dry steam and gas, but liquid water was undoubtedly present in the source region, as in most geothermal systems (Marinelli 1976). Nevertheless, it is justified to consider that chemical equilibrium is attained within a gaseous phase at depth, bearing in mind the water-vapour pressure

at any temperature below the critical point to fit the steam saturation curve.

The fundamental equilibrium condition is described by the so-called conversion (or water-gas-shift) reaction, which has the advantage of being independent of total pressure:



The required values of the free energy change of the reactions as a function of temperature,  $\Delta G^0(T^0\text{K})$ , are determined by linear interpolation within the 100<sup>0</sup>K intervals of the tabulated thermodynamic functions given by Barin and Knacke (1973) for pure substances excluding H<sub>2</sub>O, and by Barin and Knacke (1977) for H<sub>2</sub>O.

According to reaction (2), the equilibrium temperature of sample SF01, for example, is  $T_c = 228^\circ\text{C}$ . At this temperature the saturation pressure of water vapour is  $P_s = 26.6$  atm, while the partial pressure of oxygen can be calculated from either of the following reactions:



both leading, of course, to the same value. For sample

**Table 3.** Results of the thermodynamic calculations

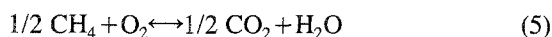
Sample no.	Date	Temperature (°C)	$T_c$ (°C)	$\log P(\text{O}_2)_c$	$P_s$ (atm)	$P(\text{H}_2\text{O})$ (atm)	$T_{\text{FT}}$ (°C)	$\log P(\text{O}_2)_{\text{FT}}$
<i>Soffione</i>								
SF01	11/10/83	147 ± 2	228	-38.6	26.62	22	159	-46.6
SF02	12/10/83	147 ± 2	251	-36.1	39.93	94	151	-47.6
SF04	14/10/83	147 ± 2	255	-35.6	42.69	179	143	-48.5
SF05	29/10/83	147 ± 2	230	-37.8	26.62	93	138	-49.1
SF06	30/10/83	147 ± 2	255	-35.2	42.69	371	132	-49.8
SF08	27/12/83	147 ± 2	243	-36.7	34.83	99	146	-48.2
SF09	29/12/83	147 ± 2	253	-35.6	41.30	255	136	-49.3
SF10	14/01/84	127 ± 2	239	-36.8	32.47	168	135	-49.5
SF11	16/01/84	127 ± 2	245	-36.6	36.05	108	145	-48.3
SF12	18/01/84	127 ± 2	250	-36.1	39.26	135	145	-48.3
SF14	28/02/84	127 ± 2	268	-34.2	52.66	404	138	-49.0
SF15	29/02/84	127 ± 2	237	-37.6	31.34	37	158	-46.7
<i>Bocca Grande</i>								
BG02	12/10/83	157 ± 2	223	-38.9	24.25	19	159	-46.5
BG03	13/10/83	157 ± 2	265	-34.8	50.21	155	153	-47.3
BG04	14/10/83	157 ± 2	260	-35.4	46.43	94	158	-46.7
BG06	30/10/83	157 ± 2	243	-36.7	34.83	103	145	-48.2
BG08	27/12/83	157 ± 2	259	-35.5	45.58	97	157	-46.9
BG10	14/01/84	157 ± 2	241	-36.9	33.63	71	150	-47.6
BG11	16/01/84	157 ± 2	250	-36.1	39.26	100	150	-47.5
BG13	27/02/84	157 ± 2	267	-34.6	51.83	185	150	-47.5
BG14	28/02/84	157 ± 2	274	-33.9	57.82	261	149	-47.7
BG15	29/02/84	157 ± 2	262	-34.8	47.85	243	143	-48.4

Results of the thermodynamic calculations. For each sample, the temperature  $T_c$ , determined from the conversion reaction (2), is given together with the equilibrium value of  $\log P(\text{O}_2)_c$  at  $T_c$ . When  $P(\text{H}_2\text{O})$ , calculated from reaction (5) by inserting known values of  $P(\text{CH}_4)/P(\text{CO}_2)$ ,  $P(\text{O}_2)_c$  and  $T_c$ , is greater than the saturation pressure  $P_s$  of water vapour at the same temperature, the lowest possible Fischer-Tropsch equilibrium (6) temperature  $T_{\text{FT}}$  and its corresponding  $\log P(\text{O}_2)_{\text{FT}}$  are calculated assuming a total pressure of 1 atm (sampling pressure). The values of  $P_s$  (in atm) are calculated from the steam tables (in S.I. units) compiled by Irvine and Hartnett (1976).

SF01, the equilibrium partial pressure of oxygen  $P(O_2)_c$ , is calculated as  $10^{-38.6}$  atm.

*The CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermometer*

The calculated equilibrium values of  $T_c$  and  $P(O_2)_c$ , together with the measured ratio  $P(CH_4)/P(CO_2)$ , may be used to determine the equilibrium  $P(H_2O)$  of sample SF01 from the reaction:



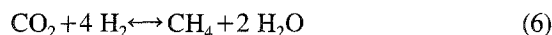
which depends on temperature but not on total pressure.

The resulting value of  $P(H_2O)$ , 22.5 atm, is lower than the saturation pressure and indicates that equilibrium (5) was possibly attained by the sampled gases en route to the surface, at a level where the fumarolic fluid is already a mixture of dry steam and gas. For sample SF01, therefore, initial assumption (1) is justified at temperature  $T_c = 228^\circ C$  and total pressure  $P = [100 \times P(H_2O)]/85.2 = 26.4$  atm. Taken as a whole, these conclusions are similar to those of Cioni et al. (1984) for a homogeneous set of samples taken from February to July 1983 at the same fumarole.

For most of the other samples, however, the  $P(H_2O)$  calculated at  $T_c$  and  $P(O_2)_c$ , using reaction (5), is higher than that the saturation pressure of water vapour at the same temperature, thus invalidating the assumption that an equilibrium gas phase and a liquid phase coexisted in the source region. This precludes deriving a geobarometer from gas-phase chemical reactions involving methane (Carapezza et al. 1984).

In a volcanic gas phase at thermodynamic equilibrium, higher methane concentrations are favoured by both lower temperature and higher total pressure (Sabroux 1979). Therefore, to account for the contradictory values calculat-

ed for the pressure [ $P(H_2O) > P_s$ ], we suggest that the sampled gases contained a slight excess of methane with respect to the equilibrium conditions at depth defined by the conversion reaction (2) and the characteristics of saturated steam. Accordingly, reaction (6) would yield equilibrium temperatures significantly lower than  $T_c$  if it were used as a geothermometer at  $P(H_2O) = P_s$ . Such excess methane is frequently observed in low temperature fumarolic gas samples and is interpreted as deriving from organic matter interbedded within the volcanic pile (e. g. Matsuo 1961). Indeed, the extremely slow rates of reaction of the Fischer-Tropsch syntheses without catalyst generally rule out the hypothesis of significant methanation of carbon dioxide during subterranean gas transfer to the surface. Nevertheless, the presence of active catalysts in the fumarolic gases and sublimates is conceivable, so this hypothesis deserves re-examination. Accordingly, we have calculated the lowest temperature,  $T_{FT}$ , at which methane could eventually equilibrate with the bulk gas sample by means of the Fischer-Tropsch reaction:



at 1 atm total pressure (outlet pressure).

The results of the thermodynamic calculations for the 22 available complete analyses are displayed in Table 3 and Figs. 2 and 3. For samples SF01 and BG02, in which no excess methane can be detected by our computational procedure, the CO-CO<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O geothermometer indicates that the equilibrium temperature at depth is ca. 225 °C and the total pressure is intermediate between the saturation + dry gases pressure at  $T_c$  and the outlet pressure (1 atm). On the other hand, the conversion geothermometer is biased toward high temperatures (up to 274 °C) for those samples with excess methane [ $P(H_2O) > P_s$ ], and no estimate of

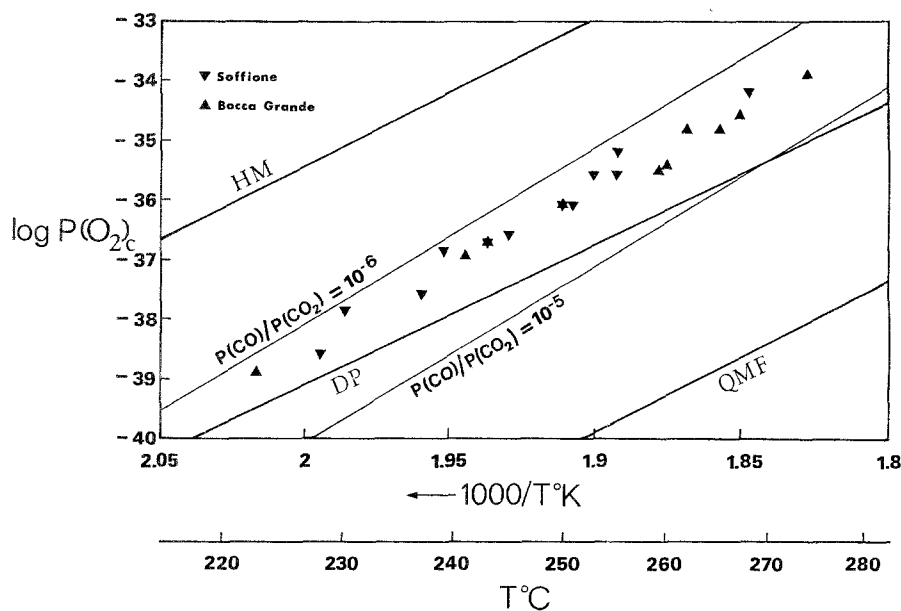


Fig. 2. Calculated by means of reactions (2),  $H_2 + CO_2 \leftrightarrow H_2O + CO$ , and (3),  $2 CO + O_2 \leftrightarrow 2 CO_2$ , the partial pressure of oxygen of 22 samples yields a linear plot against the reciprocal of the absolute temperature. For hydrothermal and volcanic gases, this trend is typical of either a closed system or a buffered thermal evolution; in this particular case it reveals the narrow range of variation of the  $P(CO)/P(CO_2)$  ratio for each of the 22 samples. The  $\log P(O_2)$  vs  $1/T$  °K linear plot labelled "DP" is the least-squares straight line fit calculated from the gas composition of 34 widespread geothermal systems (D'Amore and Panichi 1980). Two geological buffer lines are provided for visual reference: "HM" for Haematite/Magnetite (Eugster and Wones 1962) and "QMF" for Quartz-Magnetite/Fayalite (Wones and Gilbert 1969)

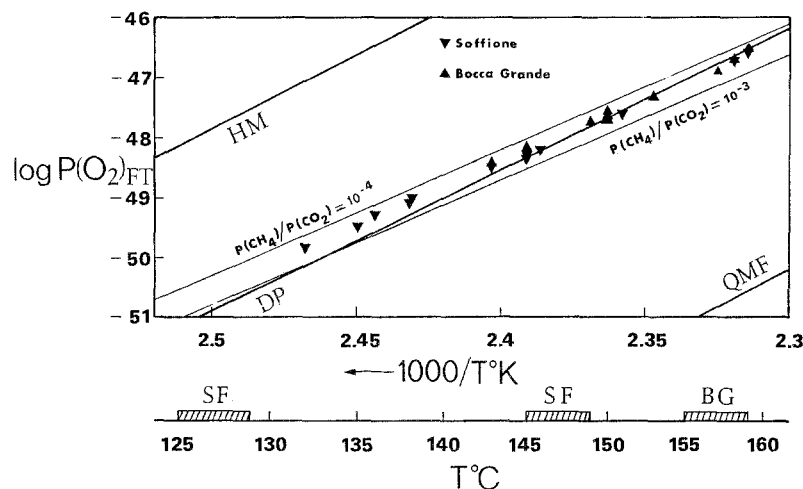


Fig. 3. The Fischer-Tropsch reaction (7),  $\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ , at 1 atm total pressure leads to an equilibrium  $T_{\text{FT}}$ , which, combined with reaction (6),  $1/2 \text{CH}_4 + \text{O}_2 \leftrightarrow 1/2 \text{CO}_2 + \text{H}_2\text{O}$ , yields an equilibrium value of  $P(\text{O}_2)_{\text{FT}}$ . The plot of  $P(\text{O}_2)$  vs  $1/T_{\text{FT}}$  K is also linear, according to the small variation of methane content in the sample. The linear plots  $P(\text{CH}_4)/P(\text{CO}_2) = \text{constant}$ , are calculated from reaction (6) by assuming  $P(\text{H}_2\text{O}) = 0.9$  atm.

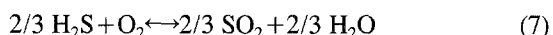
“BG”: temperature of fumarole Bocca Grande ( $157 \pm 2$  °C). “SF”: temperature of fumarole Soffione before and after mid-January 1984 ( $147 \pm 2$  °C and  $127 \pm 2$  °C, respectively)

equilibrium pressure can be given within the framework of the simple thermodynamic model proposed here. In both cases, the oxygen fugacities are consistent with the redox state of most geothermal reservoirs (D’Amore and Panichi 1980), although slightly higher.

As high values of  $T_c$  roughly correlate with low values of  $T_{\text{FT}}$ , at least for Soffione ( $r=0.5$ ), it is inferred that the additional methane is more likely to have been derived from inorganic (Fischer-Tropsch) synthesis at a temperature close to the sampling temperature – a process which consumes hydrogen (6) and consequently increases the equilibrium temperature  $T_c$  (if reaction (2) does not re-equilibrate at low temperature) – than from the decomposition of organic matter close to the surface (Matsuo et al. 1982).

#### The redox equilibrium among sulphur species

Determination of  $T_c$  and  $P_s$  has another important consequence. Setting  $P(\text{H}_2\text{O}) = P_s$ , the equilibrium ratio  $P(\text{H}_2\text{S})/P(\text{SO}_2)$  may be determined using the reaction:



For sample SF01, the calculation yields  $P(\text{H}_2\text{S})/P(\text{SO}_2) = 1.8 \times 10^9$ , a result which justifies treating the total sulphur content as S in the alkaline solution, provided any oxidation of the sample before and during analysis is avoided.

Under superficial conditions ( $T = T_{\text{FT}}$  and  $P = 1$  atm), the ratio  $P(\text{H}_2\text{S})/P(\text{SO}_2)$  remains within the same order of magnitude. This is expected, because lowering of both temperature and pressure on a closed volcanic system has a competing effect on the sulphur redox ratio.

#### Conclusions

Being sufficiently resistant to re-equilibration at low temperatures,  $P(\text{CO})/P(\text{CO}_2)$  and to a lesser extent

$P(\text{H}_2)/P(\text{H}_2\text{O})$  ratios in a volcanic gas phase are suitable for constructing a geothermometer, even at hydrothermal temperatures, provided that besides the major components, accurate analyses of carbon monoxide are available. Application of the technique to samples collected in the Campi Flegrei fumaroles from October 1983 to February 1984 suggests that the fumarolic fluids originated from a steam reservoir at a temperature close to that of maximum enthalpy of saturated steam (Cioni et al. 1984), and at a depth of 300 m or so. This situation of thermal equilibrium is frequently encountered in geothermal reservoir. The drop in temperature of approximately 100 °C between the reservoir and the surface can readily be attributed to the isenthalpic decompression of the fluid as it ascended. This observation, however, is not consistent with the earlier assumption that the gases may be considered as ideal; the present model, therefore, will have to be refined to take into account the non-ideal behaviour of the gas mixture, or at least of the water-vapour.

However, the drop of calculated temperature  $T_c$ , using fugacities of water vapour instead of partial pressures (Hass 1970), will be less than 10 degrees. An additional problem to be solved is that of clarifying the origin of the excess methane measured in most of the gas samples, and correcting the geothermometric calculation accordingly. We assumed that methane was produced at low temperature through catalytic hydrogenation of carbon dioxide; but again, if this is valid, the drop of calculated temperature  $T_c$  due to the increase in hydrogen content of the equilibrium gas mixture will not amount to more than 10 °C or so. An attempt to use the methane content as a geobarometer within the framework of a simplified thermodynamic model (homogeneous gas phase) is bound to fail, especially if the steam saturation curve has to be extrapolated beyond the critical point (Carapezza et al. 1984). On the other hand the calculated temperatures  $T_{\text{FT}}$  are consistent with an inorganic origin of methane at superficial temperatures. Nevertheless, the mere fact that our model is invalidated at

pressure higher than saturation pressures does not preclude the possibility of methane being produced at deeper levels, and accordingly at higher temperatures. The  $^{13}\text{C}/^{12}\text{C}$  and D/H ratios in  $\text{CH}_4$  from Solfatara support this hypothesis (Nuti et al. 1985).

Despite these difficulties, the simplified thermodynamic procedures adopted here are satisfactory provided that relative thermal variations at depth, instead of perfectly accurate values of temperatures, are required. Hence it is possible to use the  $\text{CO}-\text{CO}_2-\text{H}_2-\text{H}_2\text{O}$  geothermometer, on carefully collected and analysed gas samples, to monitor the thermal evolution of the steam reservoir being tapped by the fumarolic vents in the crater of Solfatara.

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