

LOW TEMPERATURE MANIFESTATIONS IN VOLCANIC AREAS

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ABSTRACT. — Investigations on chemical composition of gaseous flow in volcanic areas take into preferential account high temperature manifestations, which appear affected by possible surface contamination to a minor extent only.

This favourable situation, however, is only rarely available, and the possibility of obtaining useful information about the activity stage of volcanic systems depends on other types of surface evidences, like low temperature fumaroles, bubbling gases or thermal waters.

Variations in the original character of deep fluids possibly produced in a shallow environment are here considered.

The relative concentrations of hydrogen and methane for low temperature fumaroles, and of ammonium ion, boron and lithium for thermal waters, appeared useful in discriminating the genetic processes of the studied manifestations.

RIASSUNTO. — Le indagini sulla composizione chimica di gas naturali in aree vulcaniche prendono preferenzialmente in considerazione manifestazioni di alta temperatura, che appaiono meno contaminate dall'ambiente superficiale. Questa situazione favorevole però non è frequente e la possibilità di ottenere informazioni utili sullo stato di attività di sistemi vulcanici dipende da altri tipi di manifestazioni di superficie, come fumarole di bassa temperatura o acque termali. Vengono qui considerate le variazioni nel carattere originale dei fluidi prodotte dall'ambiente superficiale.

Le concentrazioni relative di idrogeno e metano in fumarole di bassa temperatura, e di ammonio, boro e litio in acque termali, sono risultate utili nella valutazione dei processi genetici delle manifestazioni studiate.

Introduction

The geochemical investigation of active volcanoes normally takes into account the gaseous emissions of highest temperature, which can provide the best information about the deep systems; it is assumed that manifestations of this kind display the lowest degree of modification by the surface environment.

This optimal condition, however, is not always fulfilled; sometimes the gaseous output is difficult or impossible to get, sometimes high temperature fumaroles cannot be found in spite of the activity stage of the volcano itself.

Because of this, it appeared interesting to investigate the lower temperature manifestations of volcanoes for which more information can derive from higher temperature fumaroles as well; we can check by this way the possibility of detecting any magmatic character in gaseous emissions of systems for which a «boiling water stage» is apparent.

This investigation has been mainly carried out at Vulcano and at Phlegrean Fields, where different kinds of manifestations are present; several samples from other volcanic areas are considered for comparison.

TABLE 1

Composition of the fumaroles of the crater of Vulcano, expressed in moles %

Fumarole	Temp.	H ₂ O	CO ₂	SO ₂	H ₂ S	HCl	HF	H ₂	B	NH ₄	Br	CO ₂ /S	H ₂ /CO ₂	H ₂ /S
F 2	255	88.9	9.52	0.45	0.35	0.81	1.44	3.6	17.8	2.9	1.49	11.9	0.38	2.75
F 5	282	89.6	8.58	0.33	0.27	0.70	0.84	6.9	16.1	0.5	0.88	14.3	0.80	11.50
F 9	185	88.4	9.58	0.42	0.34	0.83	0.50	2.2	24.0	2.4	0.88	13.0	0.23	2.9
F 11	250	89.0	9.24	0.33	0.14	0.83	0.52	2.7	18.2	1.1	1.06	19.6	0.29	5.7
F 14	102	88.2	9.64	0.40	0.24	1.08	0.07	6.0	11.3	0.04	0.33	15.1	0.62	9.2

The values for HF, H₂, B, NH₄, Br, H₂/CO₂, H₂/S, are multiplied by 10³. S indicates total sulphur species.

Sampling and analytical procedures

Gases and condensates from fumaroles, gases and waters from boiling pools have been collected according to the procedures described in previous papers, from which the analytical methods are taken as well (MARTINI et al., 1980; PICCARDI, 1982; PICCARDI and CELLINI LEGITTIMO, 1983; MARTINI et al., 1984).

Results and discussion

The analytical data for gases collected at Vulcano given in table 1 point out strong similarities for all the fumaroles collected on the crater, in spite of the temperature values which can differ substantially; it is worth noting that also for the fumarole at 102°C the observed differences refer to minor constituents only.

This situation strongly suggests the common origin for the fumaroles of the crater, with some changes introduced on their paths towards the surface; these changes appear to affect mainly the outlet temperatures while the chemical picture appears only slightly modified.

These fumaroles have been already considered as due to a boiling aquifer located at a certain depth beneath the active cone, which absorbs the convective flow of magmatic species and smooths down chemical and thermal fluctuations produced by the changing deep activity (MARTINI et al., 1980); no other better evidence is at present available to modify this general model.

The chemical composition of gases of deep origin which flow through shallow or surface aquifers can be heavily modified, because of the drop in temperature which can change equilibrium conditions and, above all, because several gaseous constituents are absorbed.

The acid gases normally dissolve in neutral solutions, and their fugacities are strongly reduced.

The permanent gases as H₂, O₂, N₂, CH₄, etc. can flow through the same aquifers more easily, with their enrichment with respect to acid species.

The compositions of gases emanating from the boiling pools and at the beach of Vulcano, reported in table 2, appear the result of this natural phenomenon. These latter manifestations, therefore, can be regarded as having the same origin as the crater fumaroles, but with different uprising paths; in this case the concentrations of permanent gases can be taken as representative of the original situation. Among these gases, nitrogen and oxygen can result also from an air pollution, while methane can be ascribed to decay of organic matter; hydrogen should be due mainly to high temperature reactions representing true magmatic conditions.

The ratio H₂/CH₄ can thus provide a good indication of the changing conditions of the investigated systems.

For a steady equilibrium situation, the well known reaction



TABLE 2

Composition of the bubbling gases at the beach of Vulcano, expressed in moles %

Location	Temp.	CO ₂	H ₂ S	H ₂	N ₂	O ₂	CH ₄	CO ₂ /S	H ₂ /CO ₂	H ₂ /S
Boiling pool	100	93.25	2.92	0.91	1.87	0.14	0.11	31.9	9.75	311
- do -	80	96.09	1.86	0.77	2.12	0.11	0.13	51.7	8.01	414
Beach	88	93.10	2.12	0.71	2.51	0.21	0.14	43.9	7.62	335

The values for H₂/CO₂ and H₂/S are multiplied by 10³. S indicates total sulphur species.

TABLE 3

Composition of the fumarole of Bocca Grande and of bubbling gases of the hot pools of Phlegrean Fields, expressed in moles %

Location	Temp.	H ₂ O	CO ₂	H ₂ S	H ₂	N ₂	CH ₄	B	NH ₄
Bocca Grande	155	84.00	15.58	0.20	0.043	0.040	0.003	0.007	0.007
(b)			97.20	1.25	0.27	0.25	0.019		
Solfatara	75		98.98	0.53	0.22	0.24	0.027		
Pisciarelli	98		98.90	0.61	0.44	0.019	0.007		

Bocca Grande (b) is recalculated on a water-free basis.

TABLE 4

Distribution of hydrogen and methane in gases from several volcanic areas

Location	Temp.	H ₂	CH ₄	H ₂ /CH ₄
Vulcano	285	0.070	n.d.	high
	100	0.91	0.11	8.3
	88	0.71	0.14	5.1
Phlegrean Fields	155	0.27	0.019	14.2
	75	0.22	0.027	8.1
	98	0.44	0.007	64
Momotombo (Nicaragua)	835	8.3	n.d.	high
	100	0.31	0.07	4.4
Tisate (Nicaragua)	98	0.52	0.26	2.0
Ambang (Indonesia)	100	n.d.	0.004	low
Makaroyen (Indonesia)	97	0.29	4.2	0.07
Lahendong (Indonesia)	98	0.08	0.003	27
Panarea	99	0.081	0.31	0.26
Lipari	95	0.030	3.58	0.008
Usu (Japan)	607	8.33	0.00005	17x10 ⁴
	100	0.74	0.011	67

N.d. indicates below the detection limit. Data for PANAREA and LIPARI are from CORAZZA et al. (written communication); those for Usu are from MATSUO et al. (1980).

can be assumed as the main natural mechanism explaining the relative concentrations of those chemical species. The rate at which this equilibrium is modified by the

increased concentrations of the reactants, however, is slow, and it is normally rather difficult to consider the changing ratios between hydrogen and methane as a rough indication of the changing equilibrium temperature of the studied systems.

Nevertheless, provided that H₂ is mainly produced by high temperature processes while CH₄ is peculiar of low temperature environments, the rise of the above mentioned ratio should indicate an increased importance of the magmatic component.

TABLE 5

Distribution of NH₄, B and Li in thermal pools from volcanic areas

Location	NH ₄	B	Li	Ref.
Vulcano	1.05	0.26	0.011	1
Phlegrean Fields	31.5	0.04	0.006	2
	24.8	0.02	0.003	3
	1.0	0.0001	0.0001	4
Momotombo (Nicaragua)	1.0	0.0001	0.0001	4
S.Jacinto (Nicaragua)	2.8	0.015	0.0006	5
Ambang (Indonesia)	0.06	0.30	0.010	6
Makaroyen (Indonesia)	14	0.007	0.004	7
Lahendong (Indonesia)	1.6	16	0.004	8
Nysiros (Greece)	0.009	0.006	0.0001	9
Furnas (Azores)	0.55	0.001	0.009	10
Esguicho (Azores)	0.018	1.1	0.035	11
Ribeira Grande (Azores)	0.13	0.046	0.002	12
Caldeira Velha (Azores)	0.62	0.066	0.003	13
Wairakei (New Zealand)	0.032	0.032	0.014	14
Rotorua (New Zealand)	0.080	0.56	0.47	15
Ohaki (New Zealand)	0.25	2.8	1.4	16
Tongonan (Philippines)	0.13	3.2	1.0	17
Inan Maharang (Philippines)	0.66	0.001	0.0001	18
Noboribetsu (Japan)	5.2	7.0	0.0001	19
Iwo Yama (Japan)	0.35	3.0	0.002	20
Hakone (Japan)	0.93	0.0001	0.0001	21
Seltun (Iceland)	0.07	0.0001	0.001	22
Krafla (Iceland)	0.05	0.0001	0.001	23

The values are expressed in millimoles/liter.

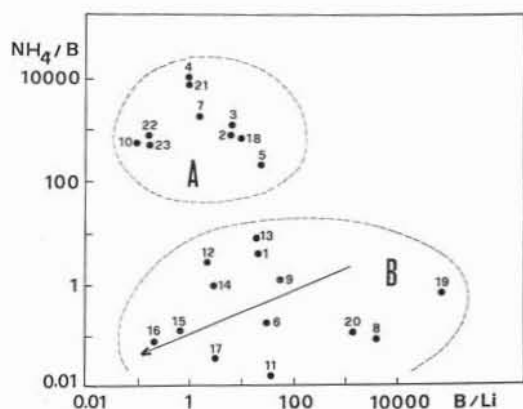


Fig. 1. — Correlation between the ratios NH_4/B and B/Li , referred to molar concentrations. See text.

All this can apply to the gases of Phlegrean Fields as well, according to the analytical data reported in table 3. We can also verify the strong differences in chemical composition with respect to the crater fumaroles of Vulcano, even when similar temperatures have been observed; the absence of acid gases at Phlegrean Fields points out the above mentioned influence of shallow or surface aquifers.

Referring to the ratios H_2/CH_4 which can be considered as an indication of the relative contribution of deep systems and the surface environments, we can see from table 4 that both at Vulcano and at Phlegrean Fields the same evidence of prevailing magmatic conditions can be obtained either from the fumaroles or from the boiling pools.

The same information could derive from these latter manifestations even if higher temperature fumaroles were absent.

The other values reported in the same table 4 appear to fit rather well these findings when high and low temperature fumaroles are available; if only boiling pools or weak steaming are the visible manifestations, the indication of the ratios H_2/CH_4 is not against the recorded activities in the different areas.

It is also possible that no gaseous emissions are detectable, and the only indication of an anomalous thermal output is given by the temperatures of springs and pools.

It that case it appeared useful to consider the ratios between ammonium ion, boron and lithium concentrations in the studied solutions.

Because of the chemical characters on the above mentioned constituents, if the heat supply to surface is provided by a gaseous flow, ammonium will predominate, while relatively high boron contents pertain to a steam inflow into shallow aquifers; significant lithium concentrations are normally associated to a prolonged leaching of country rocks.

The values for NH_4 , B and Li observed in boiling pools from different areas and tectonic settings are reported in table 5. The ratios NH_4/B and B/Li are considered in fig. 1, where the group A discriminates the representative points of natural manifestations whose thermal character should be due mainly to gaseous input into surface aquifers; for group B a steam contribution appears more likely, with an increasing extent of rock leaching according to the direction of the arrow.

It is possible that all the considered processes are operating in the investigated areas, but the predominance of a specific factor is often observed.

At present it does not seem possible to establish firm correlations between the observed chemical characters and the activity stages of volcanic systems; however, the minor constituents here considered appear to provide further information on the genetic processes of surface thermal manifestations.

Conclusions

The geochemical investigation in volcanic areas, in order to get information on their activity stages, should mainly take into account high temperature gas vents, which can provide the best evidence on the chemical equilibria pertaining to the deep systems; these manifestations, however, are rarely available and the volcanic fluids uprising to surface must be regarded as the result of an interaction of magmatic species with aquifers at intermediate and shallow depths.

This process can produce different degrees of dissolution of acid species, with a relative enrichment of permanent gases, so that the chemical evidence of surface manifestations cannot be anymore considered as representative of the deep conditions.

For a given system an indication of the

relative importance of a deep contribution and of shallow modification, can be provided by the variation in the values of the ratio H_2/CH_4 .

When no gaseous manifestation is available, the distribution of ammonium ion, boron and lithium in thermal waters can represent an

useful tool in investigating their genetic processes.

If the heat supply to surface is provided by a gaseous flow, ammonium will predominate, while relatively high boron contents pertain to steam inflow and lithium is associated to leaching of country rocks.

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