## Alberto Bencini\*, Marino Martini\*

# HYDROGEOCHEMICAL SURVEILLANCE OF VOLCANIC AREAS: THE ISLAND OF VULCANO FROM 1977 TO 1980\*\*

RIASSUNTO. — Un programma di sorveglianza idrogeochimica dell'isola di Vulcano, che considera le variazioni nella composizione chimica della falda freatica, è in atto dal 1977. Nel corso di 8 missioni sono stati raccolti 305 campioni per i quali, oltre alla com-

posizione chimica fondamentale, sono stati determinati numerosi costituenti minori.

I risultati relativi alle prime 5 campagne avevano consentito di individuare parametri più sensibili alle variazioni chimico-fisiche del sistema vulcanico, che si sono espresse fondamentalmente in un sensibile incremento della temperatura delle fumarole della Fossa Grande con conseguente variazione del quadro chimico complessivo delle esalazioni.

Il confronto dei dati acquisiti nel corso di tre anni, tenendo conto anche delle osservazioni effettuate nel 1969, evidenzia alcune variazioni probabilmente attribuibili a fluttuazioni stagionali, ma soprattutto un incremento relativamente costante del contenuto di silice e dello ione solfato.

Viene così confermata la tendenza già segnalata nel corso delle precedenti indagini, che è interpretata come indizio di progressiva influenza termica e chimica esercitata dall'apparato vulcanico attivo attualmente in fase di evoluzione.

ABSTRACT. — A program of hydrogeochemical surveillance of the island of Vulcano, taking into consideration the variations in chemical composition of phreatic waters, is in progress since 1977.

Fundamental constituents as well as trace elements in 305 samples were determined.

Previous results allowed to recognize the most sensitive parameters to chemical-physical changes of the volcanic system, mainly expressed by a marked increase in temperatures of crater fumaroles.

By the comparison of data obtained during three years, besides seasonal fluctuations, a rather constant increase of mainly sulphate ion and silica is detected

This trend, as already pointed out, is interpreted as a consequence of the evolving volcanic activity.

#### Introduction

Under a program of the Geodynamics Project, a geochemical surveillance on the phreatic waters of the island of Vulcano is in progress since 1977, consisting mainly in the periodical check on the chemical composition of samples from wells in the area of Vulcano Porto.

Some results obtained during the first steps of this investigation were already

<sup>\*</sup> Istituto di Mineralogia, Petrografia e Geochimica dell'Università di Firenze. Centro di studio per la Mineralogia e la Geochimica dei sedimenti (C.N.R.), Firenze. \*\* Pubblicazione n. 331 del Progetto Finalizzato « Geodinamica ».

published, taking into account either the fundamental composition or the distribution of several minor constituents.

Those chemical characters possibly related to the influence of magmatic fluids are particularly studied, which could by their changes allow an inference on the evolution of the volcanic activity.

Information obtained up to february 1980 is given in this paper, along with a critical revue of the empirical validity of the parameters which in previous studies were chosen as indicators of the varying activity of the volcanic system.

### Sampling and results

More than 300 samples of phreatic waters were collected in the period june 1977 - february 1980.



Fig. 1. - Zones with different chemical characters. See text. (From MARTINI, 1979).

The present study refers to 255 samples which constitue an homogeneous set of waters, whose chemical composition was verified through all the eight sampling campaigns.

The investigated area can be divided in three different zones, on the basis of the chemical composition of waters (fig. 1).

Rock leaching with contribution of hydrothermal solution appears as the main feature of the zone A, while the chemical picture of zone B seems to be due to the influence of a shallow aquifer of brackish composition; the intermediate character of zone C is given by both the above mentioned processes, along with the alteration of rocks by superficial waters.

### TABLE 1

Mean values of concentrations of  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $Cl^-$  and  $SiO_2$ in 8 samples from zone C

Date of sampling	June 1969	June 1977	December 1977	February 1978	May 1978	November 1978	March 1979	October 1979	February 1980
нсо3	6.49	6.85	7.13	7.42	7.42	7.52	6.87	7.19	6.68
so42-	5.13	5.56	6.25	4.49	4.28	5.50	6.62	6.05	6.85
c1 <sup>-</sup>	5.71	6.29	. 8.99	6.22	6.45	6.05	7.70	6.01	6.70
sio <sub>2</sub>	1.55	1.50	1.35	1.55	1.76	1.87	1.96	1.72	1.71

Values expressed as meq/l, except for SiO2 expressed as mmoles/l.



values for SO4<sup>2-</sup>, Cl<sup>-</sup>, HCO3<sup>-</sup> (meq/l) and SiO2 (mmoles/l).

Previous studies (BENCINI and MARTINI, 1979; MARTINI, 1979) allowed to detect, on the basis of a statistical analysis, the influence of four main factors in explaining the observed chemical composition. Besides the most important one, associated with Na, Cl, Mg, which represents the influence of the brackish aquifer, well defined contributions of  $SO_4^{2-}$ ,  $HCO_a^{-}$  and  $SiO_2$  were suggested.

1977

1978

1979

1980

These should correspond to the input into the phreatic waters of gaseous species as  $H_2S$  and  $CO_2$  which through oxidation processes and neutralization by the confining rocks of the resulting acidity, give rise to sulphate and hydrogencarbonate

### TABLE 2

Mean values of concentrations of  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $Cl^-$  and  $SiO_2$ in samples pertaining to zones A and C

Date of sampling	June 1977	December 1977	February 1978	May 1978	November 1978	March 1979	October 1979	February 1980
нсо3	5.57	5.67	5.75	5.88	6.31	5.41	6.39	6.25
so <sub>4</sub> <sup>2-</sup>	11.99	12,24	12.71	13.08	13.85	13.77	15.37	15.91
c1 <sup>-</sup>	6.38	7.96	5.76	5.85	5.68	6.10	5.72	6.10
sio <sub>2</sub>	1.56	1.46	1.63	1.76	1.96	1.93	1.87	1.91

Values expressed as meq/l, except for SiO2 expressed as mmoles/l.

# TABLE 3 Maximum temperatures recorded in Vulcano fumaroles



Fig. 4. — Zone C: variation in time of mean values for  $SO_4^{a-}$ ,  $Cl^-$ ,  $HCO_{B^-}$  (meq/l) and  $SiO_2$  (mmoles/l).

Fig. 5. — Zones A + C: variation in time of mean values for  $SO_4^{2-}$ ,  $Cl^-$ ,  $HCO_8^-$  (meq/l) and  $SiO_2$  (mmoles/l).

SO2

HCO3

SiO,

1980

ions, while silica concentrations could follow the fluctuations in environment temperature.

Because of this, even if a complete chemical analysis is available for all collected samples,  $SO_4^{2-}$ ,  $HCO_3^{-}$  and  $SiO_2$  concentrations only are here considered. Cl<sup>-</sup> concentrations representing the global composition of the brackish aquifer without any connection with magmatic phenomena are taken as reference, in order to verify the actual seasonal fluctuations of the investigated natural system.

Since some data from a previous investigation are available (MARTINI and TONANI, 1970) the extent or the variations occurred from 1969 to 1977 was also verified.

The comparison is possible for 8 samples from the zone C only (table 1), but in spite of the reduced number of data it is possible to observe that no important change intervened, and that the mean values for the 8 samples here considered substantially agree with those for the whole zone C.

In figures 2, 3 and 4 the variations of the considered species for the different zones are shown. A gradual increase of  $SO_4^{2^-}$  values is observed, along with a similar but less pronounced behaviour of  $HCO_4^{-}$  and  $SiO_2$ .

Those features appear stronger for zone A, the nearest to the active cone, then gradually diminishing to the zone B; if we take also into account the values for  $Cl^-$ , we can observe a similar extent of variation for zones A and C, while samples from zone B do not show any significant change.

It seems thus better to consider the samples pertaining to zones A and C as a whole, for which table 2 and figure 5 can be obtained.

All the factors for which a magmatic influence was postulated show an increase with the time in the phreatic waters of Vulcano, and a continuous positive evolution of the volcanic activity should be derived accordingly. This evolution could simply consist in an increased permeability which allows the fulfilment of conditions for a stronger input of gaseous species of magmatic nature and a raised temperature in the lower layers of the phreatic body.

However, as already pointed out, natural waters change with some delay in response to changes in physical-chemical conditions of the environment, so that it is possible that we are still observing the late results of a short-lived modification of the volcanic system, wich already stopped.

As a matter of fact we can say that a gradual variation is observed in chemical composition of waters collected in the last three years; if we extend the comparison to the data of 1969, the chemical changes occurred after eight years of substantially constant composition.

The temperatures of the fumaroles of the active crater after a marked increase are still at the highest values recorded since forty years (table 3).

The observed changes could be attributed to a defined trend in the evolution of the volcanic system, but the evidence available at present does not allow much more than a working hypothesis.

#### Conclusions

A gradual increase in concentrations of  $SO_4^{2-}$ ,  $HCO_3^-$  and  $SiO_2$  is observed for phreatic waters of Vulcano up to february 1980.

Earlier investigations interpreted those changes as a hint of increased input of chemical species sensitive to modifications in physical-chemical conditions of the volcanic system, and the new observations can only confirm the empirical validity of this assumption.

No previous information is available referring to chemical changes in water composition at the same time of a marked increase in temperatures of fumaroles of the active cone, as observed at present.

It is however possible to hypothesize that either the varying chemical composition or the raising temperatures of fumaroles are due to a general evolution of the system, which could mainly consist in an increased permeability.

Those phenomena should not be simply interpreted as forerunners of a new eruptive activity, but the social connections of this possibility recommend a careful management of the situation.

#### REFERENCES

BENCINI A., MARTINI M. (1979) - Variazioni del contenuto di silice nelle acque freatiche di Vulcano. Rend. Soc. It. Min. Petr., 35, 639-646.

 MARTINI M. (1979) - Chemical survey on the phreatic waters of Vulcano (Aeolian Islands, Italy). Bull. Volc., 43, I, 265-274.
MARTINI M., TONANI F. (1969) - Rilevamento idrogeochimico di Vulcano. Palermo, pagg. 18.

MARTINI M., TONANI F. (1969) - Rilevamento idrogeochimico di Vulcano. Palermo, pagg. 18. SICARDI L. (1973) - The thermal oscillations of the fumaroles of the Island of Vulcano from 1913 to 1970. Stromboli, 13, 65-68.