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CHEMICAL VARIATIONS IN PYROCLASTIC SERIES

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ABSTRACT. — The study of pyroclastic deposits has been mainly based upon their lithological, granulometric and stratigraphic characters.

It seemed possible that chemical peculiarities have been produced in response to the physical-chemical conditions which gave rise to the different eruptive processes, and a study of pyroclastic series was undertaken to check whether the present distribution of specific elements can provide some additional information.

Samples representing the different types of pyroclastic deposits of Minoan eruption of Santorini and Pompeian eruption of Vesuvius have been investigated, as well as lavas from the same areas; sodium, potassium, iron, magnesium, fluorine and chlorine have been determined.

The distribution of Na, K, F and Cl, along with the values for leachable Na and Cl, appears of a certain interest.

Since the solubility of volatiles in magma seems to depend mainly on their concentrations in alkalies, high levels of F and Cl in pyroclastic products can be justified by the K and Na values observed at Vesuvius; for Santorini this can apply to pumices only, while a different explanation is needed for samples of surge matrix, because their low contents in alkali metals cannot account for the observed not negligible levels in Cl.

Keeping also in mind the location of the volcano an inflow of sea water into the system appears the most likely among the natural mechanisms which can produce an enrichment of Cl in the magmatic products, in spite of the lack of sufficient conditions for its solubility in the melt phase.

The explosive processes which produced the base surge deposits at Santorini seem then to be ascribed to the above mentioned inflow, while for Vesuvius the chemical evidences point out to a similar role of phreatic waters.

RIASSUNTO. — Lo studio dei depositi piroclastici si è soprattutto basato sui loro caratteri litologici, granulometrici e stratigrafici.

È sembrato possibile che si siano prodotte peculiarità chimiche in risposta alle condizioni chimico-fisiche che hanno dato luogo ai differenti processi eruttivi, ed è stato intrapreso uno studio di serie piroclastiche per verificare se l'attuale distribuzione di elementi specifici può fornire informazioni supplementari.

Sono stati considerati depositi piroclastici della eruzione Minoica di Santorino e di quella Pompeiana del Vesuvio, e lave delle stesse aree, determinando sodio, potassio, ferro, magnesio, cloro e fluoro; maggiore interesse è rappresentato dalla distribuzione di Na, K, F e Cl nelle rocce totali, e di Na e Cl nei lisciviati delle stesse rocce. Poichè la solubilità dei volatili nel magma sembra dipendere soprattutto dal suo contenuto in alcali, alti livelli di F e Cl possono essere giustificati dai valori di Na e K osservati al Vesuvio; per Santorino ciò può valere solo per le pomici, ed una diversa spiegazione è necessaria per i campioni di « surge » che hanno basso contenuto in alcali e valori significativi di Cl.

Tenendo conto anche dell'ubicazione del vulcano, un apporto di acqua marina al sistema appare il più plausibile fra i processi naturali che possono produrre un arricchimento in Cl dei prodotti magmatici, nonostante non esistano le condizioni per una sua maggiore solubilità nel fuso.

I processi esplosivi che hanno prodotto questo tipo di deposito a Santorino sembrano quindi da attribuire all'apporto suddetto, mentre per il Vesuvio le caratteristiche chimiche indicano piuttosto un ruolo simile di acque freatiche.

The explosive volcanic eruptions and their products have been largely investigated during the last ten years, and considerable results have been obtained which besides their scientific meaning have a special importance in assessing volcanic hazards in populated areas (LIRER et al., 1973; WALKER, 1974, 1977; BARBERI and GASPARINI, 1976; BOND and SPARKS, 1976; BARBERI et al., 1977; BOOTH et al., 1977; BAKER, 1979; BOOTH, 1979; DELIBRIAS et al., 1979; SHERIDAN, 1979; SHERIDAN et al., 1981).

The guideline of these researches has consisted in a careful reconstruction of past eruptive events by means of the study of pyroclastic formations, carried out following mainly lithological, granulometric and stratigraphic criteria. The chemical composition of the products involved in explosive activity is normally not taken into consideration in the frame of the above mentioned investi-

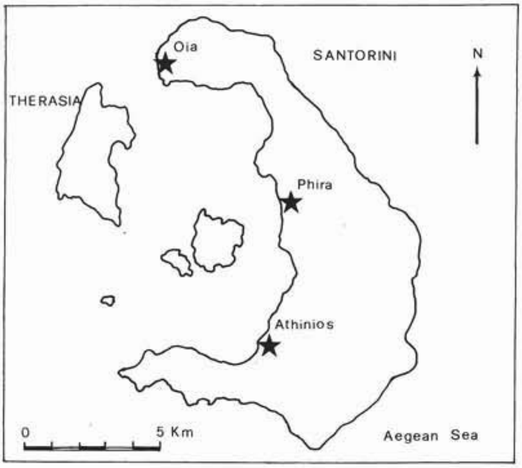

Fig. 1. — Locations of the studied samples from Santorini.

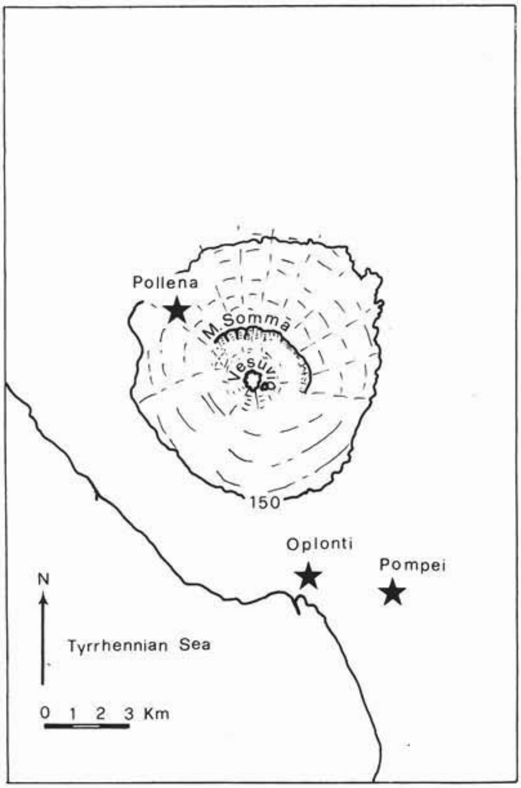

Fig. 2. — Locations of the studied samples from Vesuvius area.

gations, probably because in many instances secondary processes of alteration obliterated to a great extent the original characters.

On the contrary, if the emplacement setting allowed but a minor degree of secondary changes, it seems to us that some additional information could arise from the distribution of specific elements.

This condition can be fulfilled for pyroclastic formation of recent age, characterized by high depositional rates, considerable thickness and an early formed or contemporary impermeable cover.

To carry on a preliminar essay of this kind of investigations, samples from pyroclastic series of Pompeian eruption of Vesuvius (79 A.D.) and Minoan eruption of Santorini (1470 b.C.) are here taken into consideration, with reference to their contents in some major (Na, K, Fe, Mg) and volatile constituents (F and Cl).

Experimental

In figg. 1 and 2 are given the locations of the studied samples, described in table 1.

The analyses of Na, K, Fe, Mg have been carried out by classical procedures using absorption spectrophotometry; specific electrodes have been employed in the determination of F and Cl.

The leachate solutions have been obtained by cold extraction on 1 g of sample with 25 ml of water, without stirring.

The analytical results are shown in table 2.

Discussion

The analytical data for the series here considered allow to verify that, besides the basic differences in chemical characters, at Vesuvius significant compositional variations can be found along the different deposits, while at Santorini a substantial similarity is observed with minor exceptions.

At Vesuvius the chemical composition of cineritic and lithic components of flow deposits gradually approaches that of basal lavas of Somma; this fact has been considered as a certain degree of evidence in favour of a phreatic event which involved lavas of older age with respect to those produced in the first stages of Pompeian eruption (Martini, 1982).

Following the same logical path, the persistence of the major features in the

Table 1

Description of the studied samples

Santorini

TH 60	Fira	Pumice fall
TH 61	Fira	Pumice fall
TH 62	Fira	Pumice fall
TH 63	Fira	Matrix of base surge
TH 64	Fira	Pumice fall
TH 65	Fira	Matrix of base surge
TH 66	Fira	Matrix plus pumice, pyroclastic flow
TH 67	Fira	Pumice, pyroclastic flow
TH 68	Fira	Pumice, pyroclastic flow
TH 69	Oia	Pumice fall
TH 70	Oia	Matrix of base surge
TH 71	Oia	Matrix of base surge
TH 72	Oia	Pumice, pyroclastic flow
TH 73	Oia	Lava block, pyroclastic flow
TH 74	Oia	Pumice, pyroclastic flow
TH 75	Oia	Pumice, pyroclastic flow
TH 76	Athinios	Pumice fall
TH 77	Athinios	Pumice fall
TH 78	Athinios	Pumice, base surge
TH 79	Athinios	Matrix of base surge
TH 80	Athinios	Pumice, base surge
TH 81	Athinios	Pumice, pyroclastic flow
TH 82	Athinios	Pumice, base surge
TH 83	Athinios	Lava block, pyroclastic flow

Vesuvius

PFSV 290 A	Oplonti	Pumice fall
PFSV 290 B	Oplonti	Pumice fall
PFSV 291	Oplonti	Pumice fall
PFSV 292	Oplonti	Pumice fall
PFSV 293	Oplonti	Pumice fall
PFSV 294	Oplonti	Pumice fall
Porta a Nola	Pompei	Base surge
PFSV 286	Pollena	Pumice, pyroclastic flow
PFSV 287	Pollena	Pumice, pyroclastic flow
PFSV 288	Pollena	Pumice, pyroclastic flow
PFSV 289	Pollena	Pumice, pyroclastic flow
Φ_0	Pollena	Same level as PFSV 286
Φ_1	Pollena	Same level as PFSV 287
Φ_2	Pollena	Same level as PFSV 288
Φ_3	Pollena	Same level as PFSV 289
Φ_4	Pollena	Pyroclastic flow

(C = grain size less than 0.063 mm
L = grain size between 0.50 and 0.71 mm)

Table 2

Analytical data of the studied samples

sample	Na_2O %	K_2O %	FeO^+ %	MgO %	F ppm	Cl ppm	Na_e ppm	Cl_e ppm
TH 60	4.45	2.67	3.09	0.91	315	3530	905	1510
TH 61	4.49	2.81	2.57	0.59	500	3625	870	1110
TH 62	4.49	2.88	2.57	0.58	415	2660	325	165
TH 63	4.41	2.67	2.83	0.99	540	3110	460	790
TH 64	4.45	2.93	2.51	0.60	365	2660	175	220
TH 65	4.26	2.59	3.09	1.14	465	6200	135	2020
TH 66	4.38	2.61	2.96	1.06	485	6025	010	1760
TH 67	4.53	2.82	2.57	0.63	510	2450	240	445
TH 68	4.64	2.83	2.57	0.60	380	2545	165	215
TH 69	4.64	2.94	2.44	0.56	445	3100	625	935
TH 70	4.64	2.67	2.66	0.83	435	4760	090	2575
TH 71	4.75	2.66	2.89	0.92	525	0100	790	7110
TH 72	4.45	2.99	2.38	0.61	340	2500	520	400
TH 73	5.03	2.04	4.08	1.25	400	1640	197	115
TH 74	4.53	2.93	2.44	0.66	430	3530	215	1400
TH 75	4.64	2.63	2.83	0.74	410	3100	690	1005
TH 76	4.80	3.01	2.92	0.63	435	2540	122	106
TH 77	4.82	2.95	2.70	0.56	415	2480	155	115
TH 78	4.70	2.93	2.78	0.59	470	2480	105	50
TH 79	4.64	2.91	2.74	0.34	465	2130	240	115
TH 80	4.64	2.72	3.07	0.80	440	2185	210	275
TH 81	5.00	3.04	2.49	0.50	390	3080	575	775
TH 82	4.70	2.47	2.95	0.83	385	2130	430	970
TH 83	5.26	2.37	3.67	0.78	450	1730	110	25

sample		Na_2O %	K_2O %	FeO^+ %	MgO %	F ppm	Cl ppm	Na_e ppm	Cl_e ppm
PFSV	290 A	5.81	9.48	2.85	0.65	2890	4525	590	215
PFSV	290 B	4.78	8.60	4.08	2.35	2360	4190	170	150
PFSV	291	4.99	8.76	4.28	2.90	2415	5065	370	260
PFSV	292	4.92	8.70	4.13	3.13	2260	5065	335	215
PFSV	293	5.05	8.70	3.86	2.67	2330	5075	440	220
PFSV	294	5.01	8.24	4.33	3.48	2320	5050	425	260
Porta a Nola		4.11	5.22	4.95	2.64	1740	1960	135	25
PFSV	286	5.01	7.94	4.12	1.92	2300	4420	315	220
PFSV	287	5.01	8.70	4.05	1.69	2340	5240	125	185
PFSV	288	5.59	9.00	3.28	1.33	2400	5305	190	195
PFSV	289	6.21	9.42	2.10	0.31	3895	5970	665	365
Φ_0	C	3.13	7.58	4.44	4.59	1870	2900	175	20
Φ_1	C	3.06	4.64	5.92	5.29	1630	2140	175	20
Φ_2	C	2.86	4.34	5.08	5.47	1815	1920	125	20
Φ_3	C	1.78	4.34	4.50	4.74	1255	1060	700	535
Φ_4	C	2.45	4.38	5.02	4.10	1480	810	445	260
Φ_0	L	3.93	7.46	4.33	2.49	1625	1345	70	80
Φ_1	L	3.17	5.88	4.50	4.29	1455	1450	85	95
Φ_2	L	3.33	5.58	4.95	4.33	1575	1320	125	95
Φ_3	L	1.81	4.04	3.56	4.51	1235	1270	310	275
Φ_4	L	2.18	4.46	4.14	3.60	1645	1060	295	140

Total iron is expressed as FeO^+; Na_e and Cl_e represent the results of cold extraction.

chemical picture should allow to infer for Santorini a true phreatomagmatic episode, producing poorly differentiated materials from the same magma chamber. If we extend the observation to the studied volatile constituents, however, a good uniformity is still present for fluorine distribution, but two strong peaks are shown by chlorine concentrations (fig. 3).

The abundance of volatile constituents in magmas are normally limited by their solubility, which in turn seems to depend on the alkali metals content (Kogarko et al., 1968; Kogarko, 1974).

The substantial uniformity of sodium and potassium content in the whole series of pyroclastic products at Santorini appears to infer that the variations observed for chlorine cannot depend on different conditions for its solubility in the magma.

The results obtained by simple leaching show that significant quantities of extractable chlorine correspond to the « highs » in total concentration of this element. Sodium is another important constituent of the same

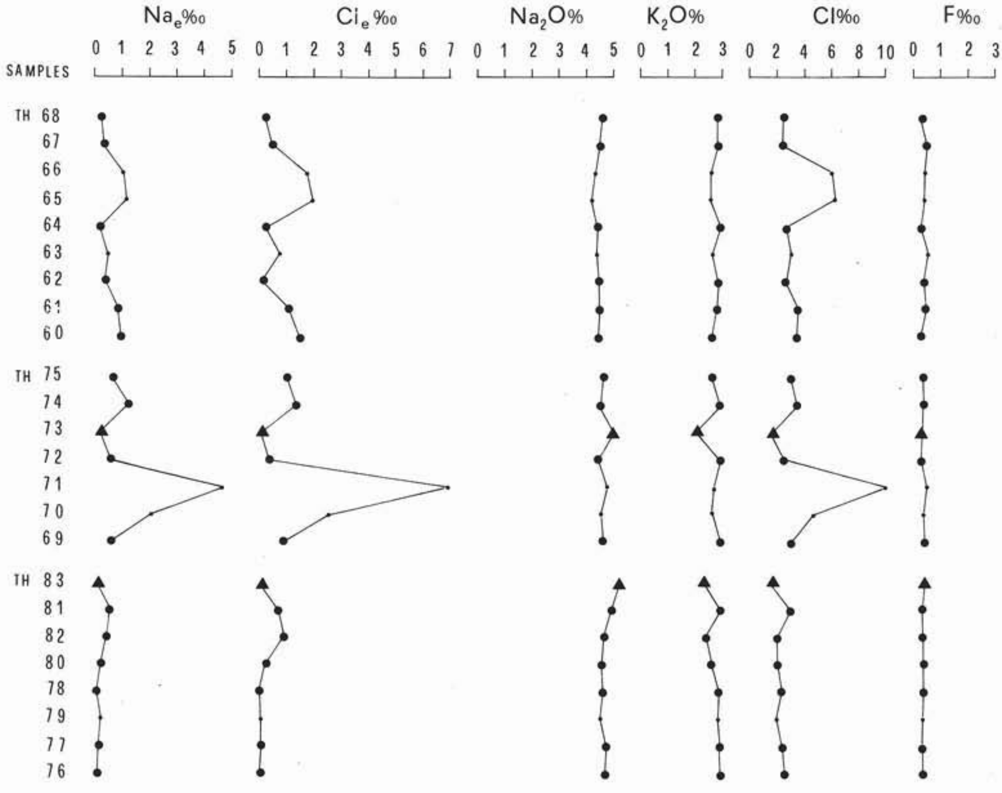

Fig. 3. — Chemical variationin series from Santorini. - • surge matrix; ● pumice; ▲ lava.

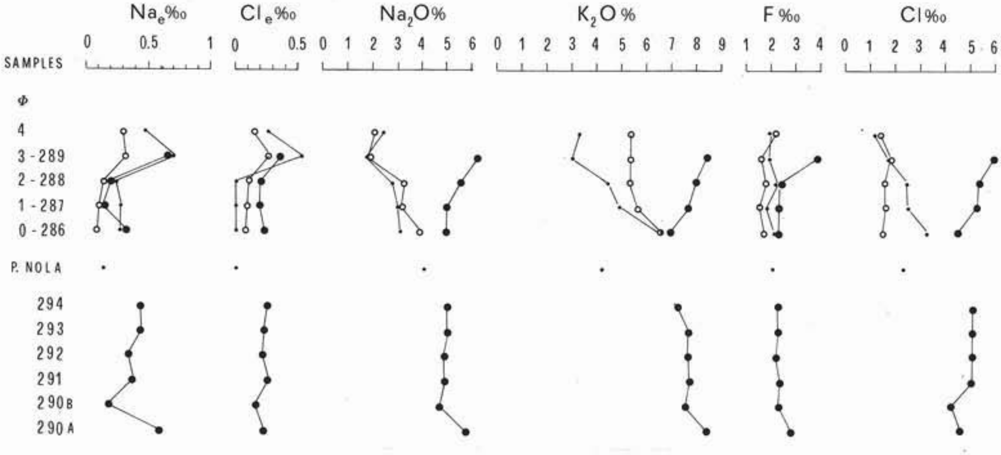

Fig. 4. — Chemical variations in the series from Vesuvius area. - • surge matrix or pyroclastic flow (size less than 0.063 mm); ○ pyroclastic flow (size between 0.50 and 0.71 mm); ● pumice.

solutions, with a distribution similar to that of chlorine, but its absolute quantities represent only a small fraction of the total sodium content of the samples.

For Vesuvius the situation is quite different, because in spite of the significant concentrations of chlorine in the rocks, very minor concentrations are observed in leachates (fig. 4).

The extent of leachable chlorine does not appear as depending on the pyroclastic nature of the rocks nor on the total content, and must be accounted for by a different process among the natural ones which substantially can be restricted to:

1) leaching of rocks by percolating waters, with accumulation in levels of slight permeability;

2) alteration by secondary fumaroles, with enrichment in volatiles;

moreover, taking into account the sodium chloride character of the solutions obtained by leaching, we can consider

3) pollution by seawater spray;

4) contribution of seawater to the eruptive mechanism which determined the emplacement of the studied pyroclastics.

The freshness of the samples, collected on the front of quarries under exploitation, seems to rule out any alteration by fumarolic activity, while modifications by percolating waters cannot be completely excluded.

The observed concentrations in leachates, however, result from a very short and weak treatment of samples with cold water, and we think that during the time elapsed since their deposition even a reduced rate of percolation through the studied formations would have produced an almost complete depletion in their leachable components; any extent of heavier alteration should have introduced also modifications in the uniformity of the chemical picture, expecially between levels of different granulometry.

Besides this, no significant concentrations in leachates are observed for samples collected at Athinios, which also should have been interested by a general process of secondary chemical changes.

If we consider the possibility of seawater as providing the excess of chlorine, we think that any pollution by marine spray should have interested to a similar extent all of the exposed formations; moreover, our investigation on deposits of the same nature located on a cliff near the seaside in the island of Vulcano has demonstrated that a very minor quantity of sodium chloride, if any, can be provided through a process of that kind.

The contribution of seawater to eruptive mechanism has therefore, in our opinion, the best probability among the processes here considered, and the location of the volcanic system of Santorini seems to allow such an hypothesis (Bond and Sparks, 1976).

Significant concentrations of sodium and chlorine in well defined levels in the studied series could be thus considered as witnesses of an inflow of seawater into the volcanic conduit, and should pertain to those deposits more directly associated to phreatomagmatic activity triggered by such contribution.

As a matter of fact, the highest peaks in chlorine and sodium occur in base surge deposits, which are thought to be produced by the above mentioned type of eruption.

Nothing similar is observed at Vesuvius, for which an inflow of phreatic waters has been proposed (Sheridan et al., 1981).

At present, no further general explanation can be provided, keeping in mind the preliminary character of this research, but we think that the obtained results stress out that a deepening of the studies is needed in order to verify possibilities and limits of a chemical approach in the investigation on recent pyroclastic formations.

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