

A geochemical contribution to the study of hydromagmatic process

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ABSTRACT. — The stratigraphic study of pyroclastic deposits of hydromagmatic origin, while providing useful information to understand this kind of phenomena, could not explain important features of those processes of magma/water interaction.

Geochemical investigation on the composition of soluble salts contained within pyroclastic series appears apt to clarify the nature of fluids involved in hydromagmatic processes and then their evolution during an eruptive cycle.

Data obtained for pyroclastic deposits from different episodes allowed to derive the chemical nature of soluble salts and their compositional variability in a wide spectrum of hydromagmatic products.

The preliminary study of pyroclastic samples from Fosse Cone (Vulcano island) pointed out significant variations most probably not related to secondary enrichment processes.

An interpretative model has been proposed, considering different forms of vapor phase condensation as the prevailing distribution mechanisms. An enrichment in chloride is mainly ascribed to the participation of marine-like solutions, while the cooling produced by the contribution of an important water fraction to the eruptive cloud favours the increase of sulphur species.

Key words: volcanism, hydromagmatic processes, volatiles, pyroclastic deposits, soluble salts.

Introduction

The problem of the genesis and evolution of explosive volcanism has been so far mainly investigated by taking into account stratigraphic and morphological characters of pyroclastic products.

With reference to the phenomena produced by interaction of a magmatic body and external aquifers, termed as «hydromagmatic», the ratios water/magma and the depths of interaction have been considered (SHERIDAN and WOHLTZ, 1982), as well as the degree of magma fragmentation (BARBERI, oral communication).

A different line of researches, considering the distribution of chemical species in the products of explosive phenomena has been developed by our group in the last years, along two main guidelines:

- 1) study of the distribution of volatile elements in juvenile products, in order to verify evolutive processes in the pre-eruptive stages of volcanic systems;
- 2) study of soluble salts associated to deposits of hydromagmatic nature, with the aim of obtaining evidences about the characters of the fluid phases and on the extent of their interactions with the magmatic portions.

The first topic has been already developed in recent papers (CORADOSSI and MARTINI, 1981, 1982; CAPACCIONI and MARTINI, 1986; CAPACCIONI et al., 1986); a comprehensive summary of the information obtained by considering also the soluble salts associated to pyroclastic deposits is given below.

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Results

The analytical procedures pertaining to the determination of volatiles in juvenile products have been described in previous papers; the composition of soluble salts has been obtained through a gentle washing of powdered samples (30' with deionized water, without stirring) and subsequent determination by Atomic Absorption Spectrophotometry for cations and by potentiometric procedures using specific electrodes for anions. Table I gives the concentrations of soluble sodium, potassium, calcium, chlorine and sulphate, and of total chlorine and fluorine, for pyroclastic sequences of hydromagmatic origin pertaining to the Fossa cone, Vulcano (Italy); the same information about soluble salts from Faial and S. Miguel (Azores), Santorini (Greece), Phlegrean Fields and Lipari (Italy), taken as terms of reference, is reported in Table II.

Discussion

Soluble salts associated with pyroclastic products can form as the result of different secondary processes, which substantially can be restricted to:

- alteration from fumarolic activity;
- pollution by seawater spray;
- leaching of rocks by percolating waters.

Let us consider separately each of these possibilities with reference to the results obtained.

TABLE 1
Concentrations of soluble components and of total fluorine and chlorine in the samples from Fossa cone

sample	Na	Ca	Cl	SO ₄	F _{tot}	Cl _{tot}
105/7	2355	520	3910	2160	2350	6050
105/8	260	145	1065	360	915	1540
105/9	260	100	365	155	650	1645
105/10	265	170	570	310	890	1940
89/3	1475	1010	2840	3120	1370	3530
89/4	420	200	235	515	905	1700
90/7	470	95	930	265	1020	2125
90/9	560	70	495	274	935	2025

The sample of the series 105 are from Punta Nere, the other from Palizzi

The analytical values are expressed in parts per million

a) Alteration from fumarolic activity should have produced similar distribution patterns without any substantial variation due to stratigraphic and lithological differences; significant changes are on the contrary observed.

TABLE 2
Concentrations of soluble components in samples from different volcanic areas

sample	Na	Ca	Cl	SO ₄
S. Miguel 39	222	15	115	445
42	140	8	120	-
44	165	20	185	-
45	150	8	240	-
46	105	8	125	-
48	255	7	210	96
49	195	8	175	72
52	425	17	210	60
53	305	12	195	24
55	195	15	95	55
56	185	13	140	-
58	145	17	220	30
64	150	12	230	42
65	2700	56	5030	615
66	260	19	250	30
68	275	11	135	72
69	205	6	255	54
Faial 1	385	63	360	200
3	450	10	470	240
4	450	12	470	240
5	1630	765	2430	1840
6	1425	770	2430	2110
Santorini 70	2090	2225	2575	9800
71	4790	1950	7110	4500
72	520	230	400	650
74	1215	1750	1405	3960
75	690	70	1010	35
Lipari 1	80	11	133	58
2	160	10	300	53
3	80	15	150	55
4	95	42	165	36
5	95	7	168	62
6	55	7	105	60
7	545	210	1045	175
9	265	7	505	58
10	125	4	215	38
11	80	12	230	36
12	380	54	460	94
14	485	4	175	100
15	340	17	255	84
16	2100	24	2560	254
18	2315	365	4695	545
19	430	2	300	94
21	500	37	255	70
23	810	42	895	155
24	155	13	222	82
25	340	16	525	58
34	1315	175	1860	68
36	970	46	1535	215
37	535	4	760	415
38	875	115	1260	350
Ph.Fields 7	1150	14	640	150
10	165	37	150	60
11	955	7	1420	335
13	625	24	530	150

b) The same could be expected by seawater spray, which can pollute to the same extent all of the exposed pyroclastic levels; sharp changes in soluble salts, however, can be easily verified.

c) Percolating waters are expected to produce concentration gradients controlled by the distribution of fractures and by the geometry of impervious levels; rock samples suitable for investigation have been thus collected by taking this into account. Even the quantitatively most significant analytical data have been obtained by a short and weak washing of the samples; if a percolation process had interested the same levels, it appears likely to have produced an almost complete depletion of their leachable components during the time elapsed since their deposition. From the section of Figure 1, which is taken as an example of a surge sequence from Fossa activity (Vulcano island), it is also possible to verify sharp changes in total soluble salts content and in Cl/SO_4 ratios between adjacent thin depositional units which can hardly be ascribed to general secondary processes. Moreover, from SEM (Scanning Electron Microscope) images, the evidence of very soluble halite fragment surrounded by gypsum crystals could be obtained (Figures 2a, 2b), which is not in favour of important percolation processes.

A process of *in-situ* depositional condensation of vapour from the eruptive cloud can be thus hypothesized as originating the soluble salts associated to the products of explosive hydromagmatic activity here investigated. We cannot say that any leaching of soluble species from pyroclastic rocks always provides consistent information about the emplacement processes; a careful sampling operation, along with an accurate chemical investigation, however, certainly allow to move ahead in the understanding of hydromagmatic activity. The following interpretation should be considered by taking all this into account.

The bulk of information about the composition of soluble salts associated to pyroclastic deposits of hydromagmatic origin, from Tables I and II, provides the evidence that approximately stoichiometric quantities of Na and Cl, and Ca and SO_4 , respectively,

can be washed away by the simple above mentioned procedure. Other components can be also detected in comparably minor concentrations.

The distribution of the samples investigated with reference to the above mentioned components (Figure 3), shows that the Na-Cl character is strongly prevailing, yet representing the most common feature of the soluble portion of pyroclastic deposits.

This circumstance had been already pointed out by ROSE (1977), who considered fresh samples from Fuego volcano eruption and explained it as a consequence of an interaction between ash particles and acid liquid droplets in the eruptive cloud; even if this processes can actually occur in volcanic plumes, however, in our opinion it cannot explain satisfactorily the observed evidence.

The near perfect stoichiometric balances between Na and Cl, and Ca and SO_4 , already noticed by ROSE, cannot result by a random reaction of particles of different composition in different eruptive events; it appears rather to obey a strict chemical rule acting everywhere similar processes occur.

Beside this general overview on chemical characters of the products of hydromagmatic activity, let us now analyse typical pyroclastic series pertaining to the island of Vulcano as described by FRAZZETTA et al (1983, 1984).

From the data of Figure 4 it appears that chemical information does not completely fit stratigraphic evidences. For the cycle of Punte Nere, as well as for the cycle of Palizzi, representing two subcycles separated by a magmatic fallout event (FRAZZETTA et al., 1984), the increased concentration of soluble salts at the base of the series could be also explained by the presence of underlying impermeable layers; the decreasing trend of soluble salts concentrations towards the top of the series, however, is well in accordance with the general decreasing hydromagmatic character already pointed out by the same Authors.

When a rapid condensation of vapour phase occurs, magmatic sulphur species can be captured into aqueous solution producing sulphuric acid. As the result of the interaction of this aggressive component with the solid

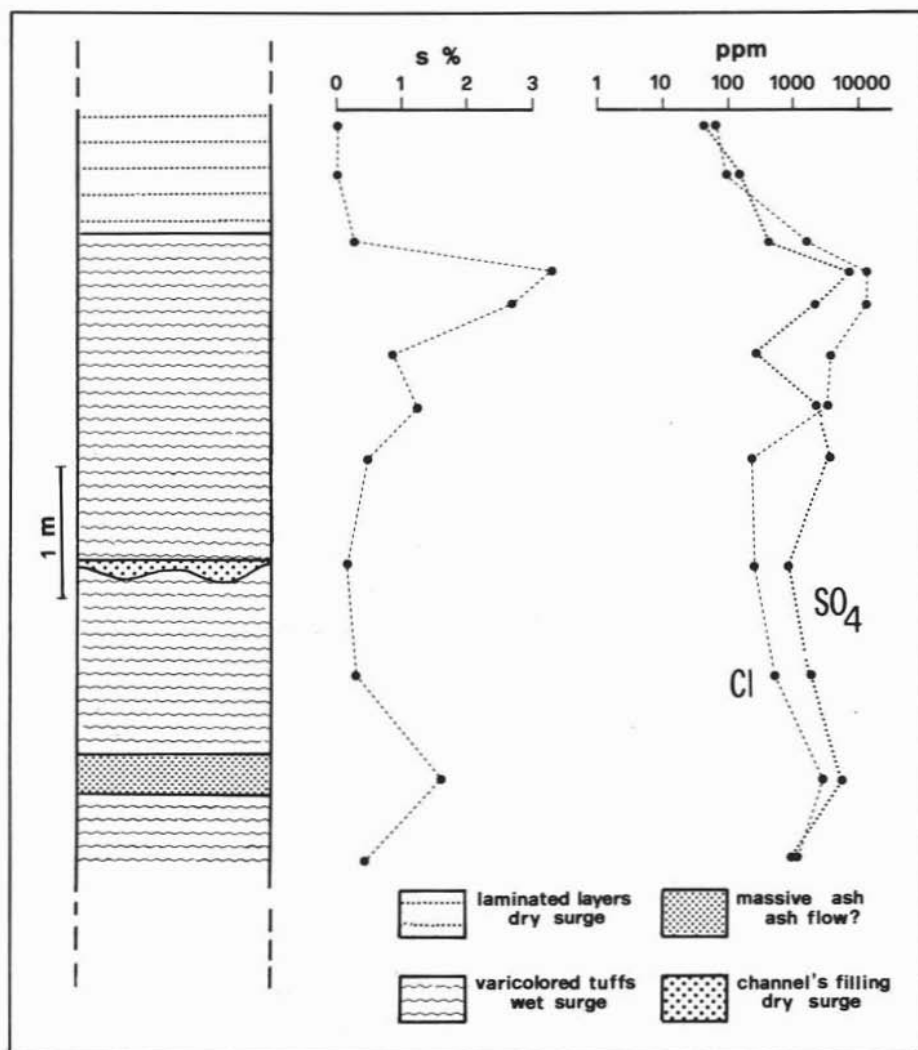
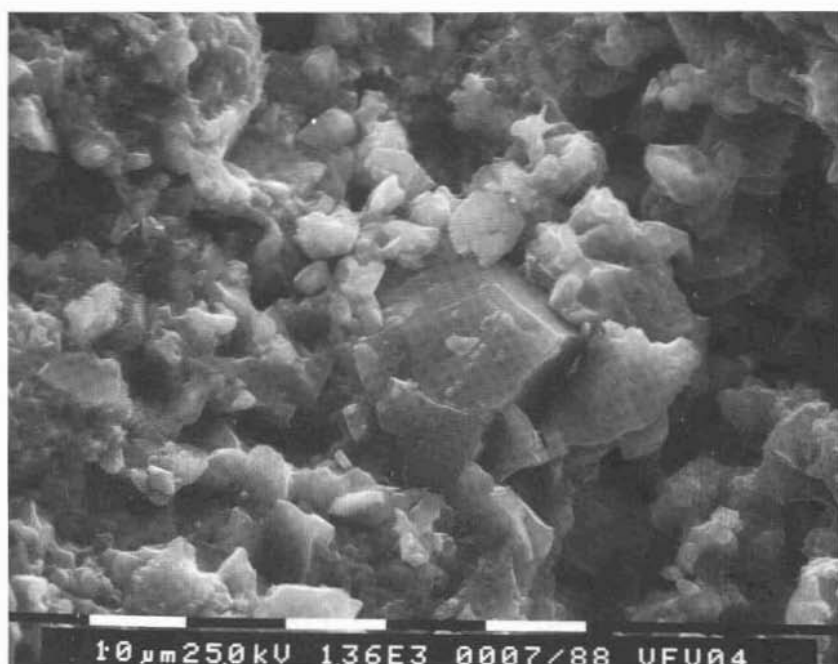


Fig. 1. — Variations of soluble salts content, chlorine and sulphate along a pyroclastic sequence from Forgia Vecchia parasitic crater (recent activity of Fossa cone, Vulcano); «s» represents the sum of leachable Ca, Na, K, Cl and SO_4 . Note that at higher values of «s» Cl/ SO_4 ratios increase above the unity (from CAPACCIONI et al., 1988, modified).

particles, sulphates are expected to precipitate preferentially with respect to chlorides; beside CaSO_4 also Na-sulphate can form instead of NaCl, given the respective solubilities.

If the condensation process is slower, magmatic contribution can become subordinate with respect to that of shallow or surface water bodies, the sharp sulphate character of the resulting solutions does not occur, and no significant sulphate phase will

form accordingly. In this case, minor quantities of soluble salts will result from the interaction of pyroclastic deposits with waters of low salinities; chloride precipitations will prevail, on the contrary, if salty or marine waters are involved in the eruptive event. On this basis, the diagram of Figure 5 appears apt to provide some information about the characters of different explosive episodes. The star represents the ratios of soluble species



a)



b)

Fig. 2. — SEM images of wet surge deposits from recent Fossa activity (Vulcano island).

- a) Halite crystal surrounded by gypsum crystals, precipitated on its surface, and silicatic fragments.
- b) Gypsum crystals with silicatic glass and crystal fragments.

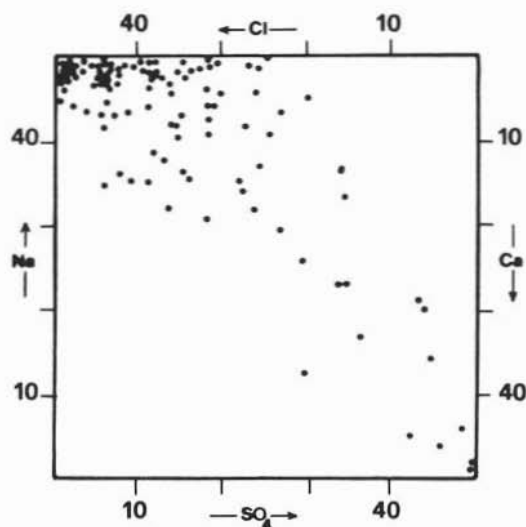


Fig. 3. — Main leachable components of hydromagmatic products from Santorini (Greece), Faial and S. Miguel (Azores), Lipari, Vulcano and Phlegrean Fields (Italy), expressed as molar ratios.

which can be expected if solutions of marine-like composition participated to the emplacement of pyroclastic formations without any important fluid/rock reaction; the trend towards sulphate corner should be due to the increasing importance of magmatic components, while the trend towards sodium corner should indicate the increasing extent of *sin-* or *post-*depositional reactions between solid particles and fluids.

It is worth noting the absence of a trend pointing out an enrichment in chlorine, which can only actually occur in a natural environment through the contribution of NaCl solutions.

The increased water/magma ratio within the eruptive column will produce a decrease in temperature, and an easier condensation of gaseous phases; according to this, the displacement of the samples towards the sulphate corner should indicate a progressive hydromagmatic character of the eruptive event as observed for the *surtseyan* eruption of Capelinhos, in which seawater was involved to a significant extent (MACHADO and FORJAZ, 1968). The points clustered around the star indicating a seawater composition should also pertain to hydromagmatic events through magma/seawater interactions, but without a

sufficiently rapid condensation of gaseous phases to capture magmatic components: e.g. phreatoplinian events of Faial and S. Miguel (WOLFF and STOREY, 1983) and Santorini (BOND and SPARKS, 1976).

The condensation of the eruptive cloud because of an important water contribution, however, cannot explain the extent of fluorine concentrations in surge deposits from Vulcano (Fig. 4); fluorine content of volcanic gases is always very low with respect to chlorine and sulphur, and a *pre-eruptive* enrichment process is needed to justify this circumstance.

Because of its strong affinity with OH-group, fluorine tends to be enriched wherever aqueous phases come in equilibrium-contact with melt; actually, not-explosive interaction of shallow aquifers with magma bodies can produce such concentration in the upper portions of the uprising magma columns.

According to this, the strong hydromagmatic character of the initial eruptive phases of *Punte Nere* and *Palizzi* cycles (Fig. 4) should have been prepared by a magma/water not-explosive interaction at shallow depth.

Conclusions

Beside the evidences provided by the classical stratigraphic study on the products of eruptive episodes, the investigation of soluble salts entrapped in pyroclastic series belonging to different eruptive centres allows to characterize their common chemical features.

On the basis of different evidences an interpretative model has been proposed. In particular, a chloride composition of those salts has been referred to the participation of marine-like solutions to the eruptive mechanisms, while higher water/magma ratios pertaining to the same processes should produce cooler eruptive clouds, easier condensation of sulphur gaseous species and consequent prevailing sulphate composition. The information available for the eruptive events of Faial and S. Miguel (Azores), Vulcano, Lipari and Phlegrean Fields (Italy), Santorini (Greece) here considered, and the chemical data obtained by the study of their

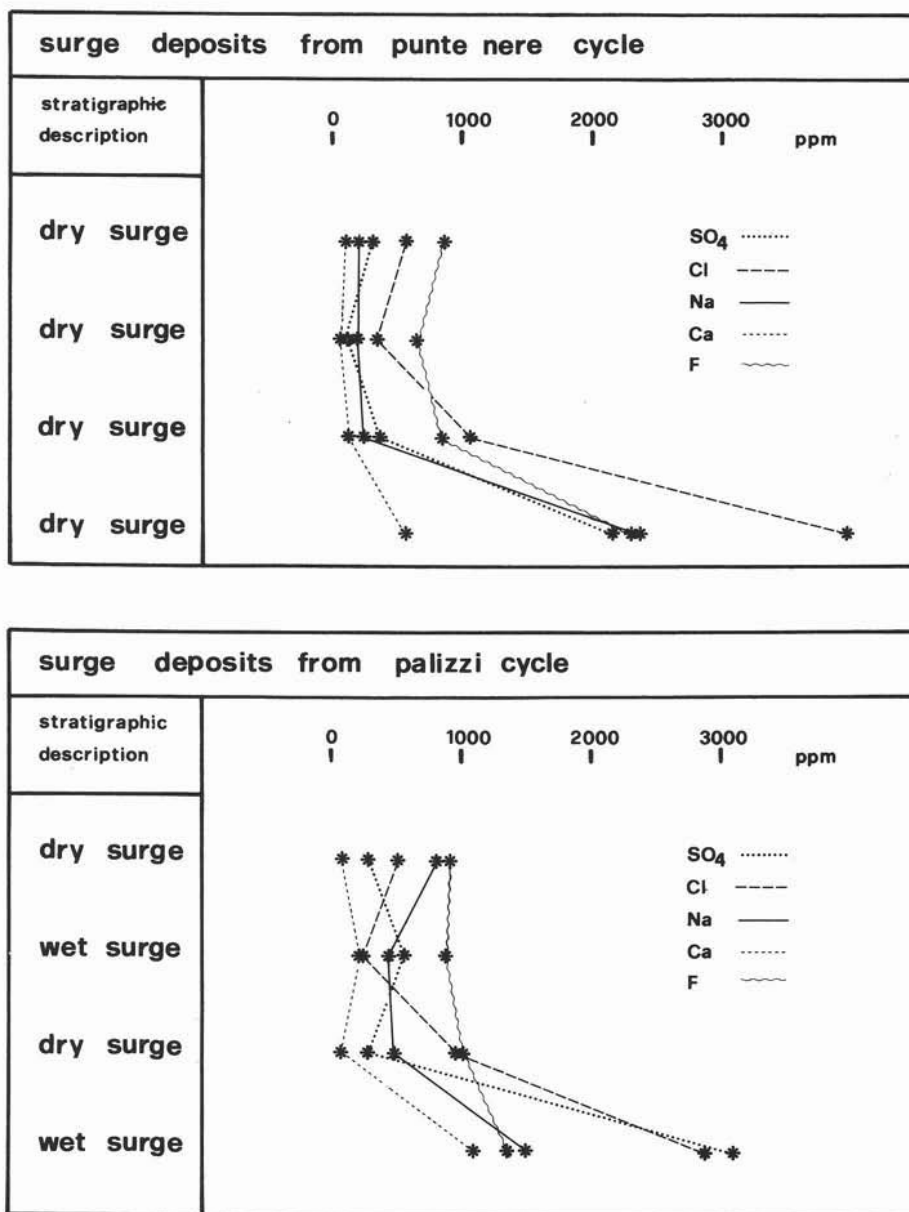


Fig. 4. — Variations of leachable species and total fluorine concentrations along Palizzi «a» and «b» subcycles and Punte Nere cycle (Vulcano).

deposits, appear in sufficient accordance with these assumptions. With reference to base surge deposits from recent eruptive cycles at Vulcano, by also taking into account fluorine distribution which is interpreted as the result of not-explosive water / magma interaction

at shallow depths, a decreasing trend in hydromagmatic character can be derived accordingly.

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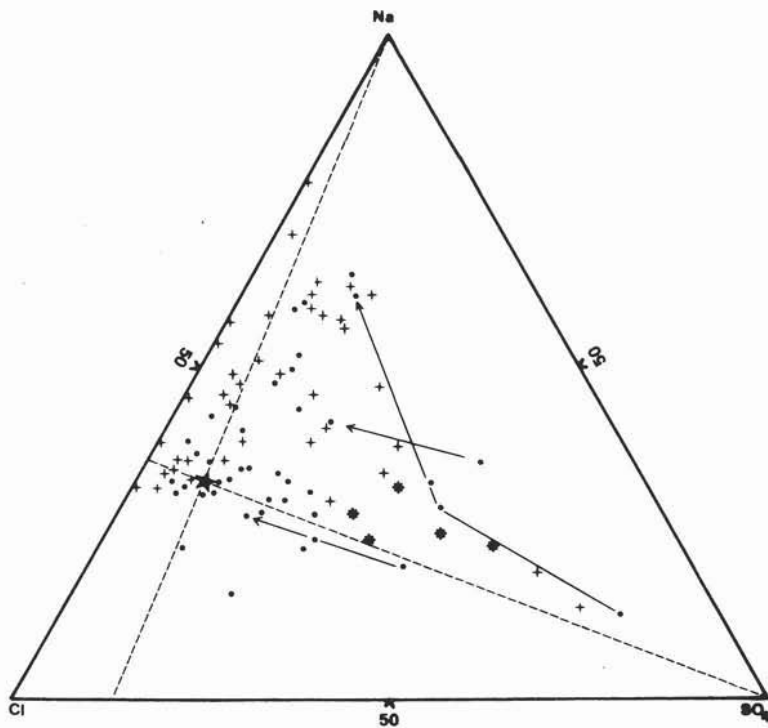


Fig. 5 — Distributions of leachable sodium, chlorine and sulphate. Star: seawater composition; points: base surge deposits from Lipari, Vulcano and Phlegrean Fields; crosses: pyroclastic flows and surge deposits from Faial, S. Miguel and Santorini; diamonds: base surge deposits from surtseyan eruption of Capelinhos (1957-58). The arrows indicate the chemical changes along the pyroclastic sequences from Vulcano here investigated.

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