

PERSISTENCE OF F AND Cl IN PRODUCTS OF PYROCLASTIC ACTIVITY

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ABSTRACT. — The products of pyroclastic activity have been normally considered as affected by secondary alteration processes, so that their present contents in several minor elements cannot be representative of the original concentration in the magma.

The volatile constituents F and Cl should pertain to those elements of easy mobility, and rarely their concentrations have been taken into account while investigating eruptive processes.

Gaseous compounds of these elements, however, play a significant role in volcanic phenomena, and this led us to verify if really any possibility of utilizing the present distribution of F and Cl in pyroclastic products should be neglected.

First of all, to check the extent of losses in gaseous form immediately after the explosions, samples of pumices have been heated up to 400, 500, 600 and 850° C; slight differences begin to appear at 500° C while at 850° C a strong depletion is observed.

The possible effects of percolating solutions have been also considered, and the same rocks have been leached at different temperatures with different solutions and at different water/rock ratios, obtaining substantially similar results.

For both elements an equilibrium situation is reached after about 30 hours, with no further extraction; the loss of F does not exceed 5%, a greater quantity of Cl is sometimes leached away.

A similar degree of depletion was observed also for the alkali metals, and it seems that for a petrographically fresh sample no significant loss in original F could occur.

This can be observed more easily in deposits of recent age, for which any natural process could have been active during a geologically very short span of time.

With reference to Cl, its distribution can be sometimes heavily affected by secondary processes.

RIASSUNTO. — La composizione chimica dei prodotti di attività piroclastica è stata normalmente ritenuta non rappresentativa di quella originale a causa di processi di alterazione secondaria.

La concentrazione di F e Cl, volatili e relativamente mobili, è stata quindi scarsamente presa in considerazione nello studio di processi eruttivi. Tuttavia, poiché composti gassosi di questi elementi

svolgono un ruolo importante nei fenomeni vulcanici, siamo stati indotti a verificare se ogni possibilità di utilizzazione del contenuto di F e Cl in prodotti piroclastici sia da scartare.

Per controllare le perdite in fase gassosa successivamente alle esplosioni vulcaniche si sono riscaldati campioni di pomice a 400, 500, 600 e 800° C; piccole differenze nel contenuto totale di F e Cl cominciano ad apparire a 500° C, mentre un forte impoverimento è osservato a 850° C.

Si sono anche considerati gli effetti possibili di soluzioni percolanti, e le stesse rocce sono state liscivate a temperature differenti, con soluzioni differenti e a rapporti acqua/roccia differenti, ottenendo risultati sostanzialmente simili.

Per entrambi gli elementi si raggiunge una situazione di equilibrio dopo circa 30 ore, senza ulteriore estrazione; la perdita di F non eccede il 5%, ma talvolta si osservano valori più alti per Cl.

Si è verificato un simile grado di impoverimento anche per i metalli alcalini, e sembra che per campioni petrograficamente freschi non si abbiano perdite significative di F, soprattutto in depositi di età recente.

La distribuzione di Cl può essere invece talvolta fortemente modificata dalla influenza di processi secondari.

Introduction

The chemical composition has been rarely taken into account in investigating pyroclastic formations, because for these products of explosive activity a certain degree of alteration normally occurs subsequently to their deposition. Secondary processes of this kind should interest mainly those volatile constituents which play a major role in eruptive volcanism, and are characterized by high mobility.

The glassy phase of eruptive products, however, could represent a quenched portion of the original magma which underwent minor losses of volatiles through secondary alteration.

TABLE 1
Variation of concentrations (ppm) of F and Cl in pumice samples after heating

Location	Original concentrations		Concentrations after heating			
			400 °C	500 °C	600 °C	850 °C
Vesuvius	F	2880	2840	2850	2820	1950
	Cl	5380	5360	5350	5350	300
Vesuvius	F	2630	2630	2570	2610	230
	Cl	5050	4960	4980	5000	250
Vulcano	F	1000	1010	980	990	60
	Cl	2300	2340	2360	2350	300
Vulcano	F	1230	1160	1200	1050	100
	Cl	3040	3050	3050	3020	1170
Lipari	F	1050	1070	1060	1070	120
	Cl	3120	3130	3120	3100	200
Lipari	F	1270	1240	1230	1130	140
	Cl	3840	3700	3150	3000	1050
Santorini	F	640	640	550	420	80
	Cl	3580	3580	3580	1550	400
Santorini	F	450	430	420	400	40
	Cl	3050	3100	3080	2360	350

The analytical procedures are from CORADOSSI and MARTINI (1981).

The investigations of ROSS and SMITH (1955) pointed out that if no hydration occurs, water and other volatiles in obsidian are pristine, while hydration has the effect of flushing CO₂, Cl and F from the system and replacing them by H₂O in the hydrated glasses.

According to FRIEDMAN and HARRIS (1961), in the first step of alteration, that is in hydration, fluorine is not lost from the glass, while a loss occurs probably during the devitrification of the hydrated glass.

Different stabilities in the presence of volatiles, one pristine and the other resulting by low-temperature hydration, were determined by ROSS (1964), who also stressed out the need of quantitative data about the concentrations of volatile compounds in interpreting volcanism.

A sharp statement, however, was then provided by NOBLE et al. (1967) on the practical impossibility of recovering useful data on halogen abundances in hydrated natural glasses, and even if a reliability* of determinations resulted for nonhydrated glasses, not many attempts followed to define the actual concentrations of F and Cl in this kind of volcanic rocks.

The further contributions of LIPMAN et

al. (1969), SHATKOV et al. (1970) and ZIE-LINSKY et al. (1977) to this problem mainly reconfirm the lower contents of halogens in felsites for comparison to perlitites and obsidians to which they are associated.

Since gaseous compounds of F and Cl are considered as important components of the volatile phase of magmas, any information on their distribution would be of great interest in studying explosive volcanism, and this led us to verify if really any possibility of utilizing the present F and Cl contents in pyroclastic products should be ruled out.

Pumices from Lipari, Vulcano, Vesuvius and Santorini have been used to check the extent of depletion in F and Cl possibly occurred after the explosion which produced them.

Analytical results and discussion

Two series of experiments have been carried out, to reproduce the loss of volatile species both in gaseous form soon after the volcanic event and as a result of post-depositional alteration by surface waters.

Different portions of the powdered samples have been heated for one hour

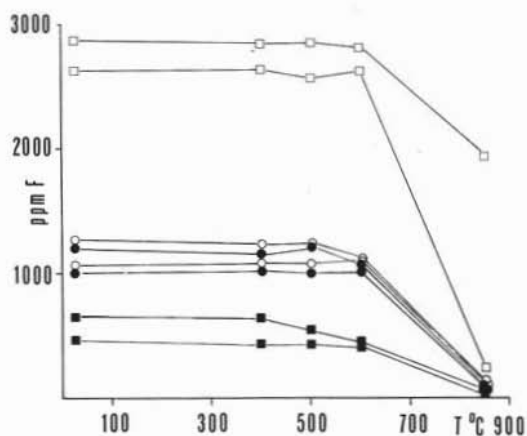


Fig. 1. — Contents of fluorine in pumice samples after heating at different temperatures. - O Lipari; ● Vulcano; □ Vesuvius; ■ Santorini.

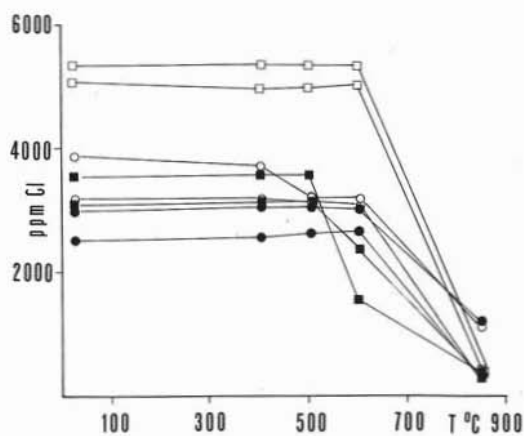


Fig. 2. — Contents of chlorine in pumice samples after heating at different temperatures. Symbols as in fig. 1.

at 400, 500, 600 and 850° C, then analyzed for their residual F and Cl contents. By table 1 and figures 1 and 2 it can be seen that no significant loss appears evident for both elements up to 500° C, while some change is observed at 600° C, and a strong depletion occurs at 850° C.

A different pattern, however, is shown by the total loss on heating, which refers mainly to the contents in water and hydroxyl groups (fig. 3).

With reference to the effect of weathering

processes, 1 g of each sample has been shaken with 25 ml of deionized water; by a series of measurements after 6 hours of treatment, it was possible to verify that an equilibrium situation was reached after about 30 hours, with no further extraction of leachable constituents.

The procedure was then modified, by treating 1 g of powder with 50 ml of sulphuric solutions at pH = 2 and pH = 4 at room temperature for 12 hours, and with 50 ml of deionized water at 90° C for 6

TABLE 2
Variation of concentrations of F, Cl, Na and K in pumice samples after leaching

		Vesuvius				Vulcano		Lipari		Santorini	
F	A	2880	2630	3950	5450	1000	1230	1050	1270	640	450
	B	45	40	34	96	11	6	6	5	-	-
	C	83	83	71	180	23	8	12	14	-	-
Cl	A	5380	5020	6075	6850	2300	3040	3120	3840	3550	3050
	B	160	187	206	112	290	190	44	98	790	965
	C	230	235	235	267	285	220	89	120	810	1135
Na	A	3.73	3.66	4.54	6.03	2.86	3.22	2.87	2.88	3.32	3.46
	B	267	295	225	760	225	105	125	180	440	375
	C	560	550	455	1325	375	235	250	400	835	810
K	A	4.53	7.01	7.75	6.06	4.00	4.33	4.20	4.17	2.25	2.42
	B	430	615	425	130	200	35	22	26	24	41
	C	860	1260	775	305	340	52	42	50	90	80

A = original content in the rock (ppm for F and Cl; percent for Na and K); B = concentrations (ppm) of the solutions after 30 hours of treatment of 1 g of sample with 25 ml of water; C = concentrations (ppm) of the solutions after 12 hours of treatment at 90° C of 1 g of sample with 50 ml of water.

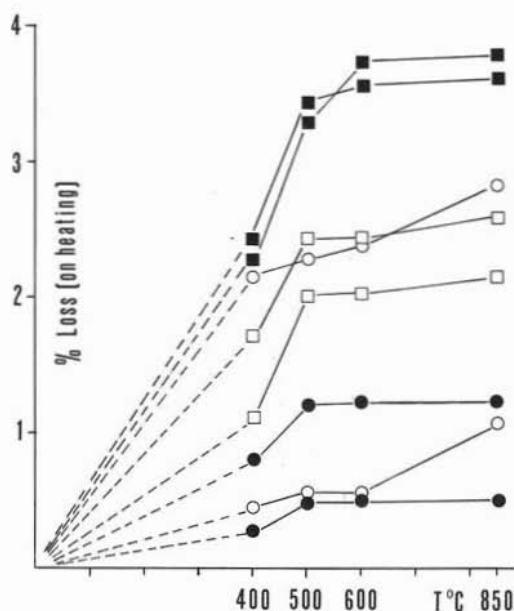


Fig. 3. — Total loss on heating of pumice samples. Symbols as in fig. 1.

hours. We did not carry out any experiments at higher temperatures, because it is well known that hydrothermal solutions can extract significant quantities of leachable elements from any kind of rocks (ELLIS and MAHON, 1964, 1967).

The extent of F and Cl leached away by means of the different experiments is given in tables II and III, along with the values for Na and K which can represent a standard of reference for the general degree of

TABLE 3

Concentrations (ppm) of F, Cl, Na and K in sulphuric solutions after treatment of 1 g of sample

		Vesuvius	Vulcano	Lipari	Santorini
F	pH = 2	240	16	10	2
	pH = 4	50	6	10	2
Cl	pH = 2	1025	158	170	219
	pH = 4	233	138	25	35
Na	pH = 2	2350	840	2160	515
	pH = 4	380	840	2070	85
K	pH = 2	8500	470	1550	140
	pH = 4	950	380	1040	20

(water/rock = 50 : 1)

alteration of the studied rocks.

The total amount of F extracted by neutral solutions never exceeds 5% of the original content, while values above 30% can be observed for Cl. The acid character of the leaching solutions appears to be more effective in the extraction of the alkaline metals than of F and Cl.

The obtained values seem to point out different forms of stability for the investigated elements F and Cl, which are leached away to a certain extent with no further significant extraction.

This situation should correspond to actual differences in bond energies mainly due to the structural position of the elements in the investigated volcanic glasses.

On the basis of experimental data, KOGARKO et al. (1968) suggested that in alkali-rich melts F is present as NaF, while in acid melts the same element acts as depolymerizer forming Si-F bonds and substantially similar views are expressed by BAILEY (1977); according to MANNING et al. (1980) in aluminosilicate melts F may be present as complex aluminofluoride or silico-fluoride anions, and as free fluoride ions.

A low proportion of Cl extractable by water has been noticed previously (ZIES, 1960; MURAMATSU and WEDEPOHL, 1979) and the occurrence of Cl in granitic rocks in the form of fluid or soluble-solid inclusions and in lattice-bound state has been proposed (FUGE, 1979).

Not much information has been subsequently provided on this subject, but the deepening of the problem of the correct structural position of F and Cl in volcanic glasses, though very interesting, is beyond the objectives of this research.

The percentages of the extracted elements with respect to their original amounts are reported in figures 4 and 5. It is easy to verify that in spite of the different absolute quantities a very similar extent of depletion occurs for the sum of the alkali metals and fluorine; for chlorine some exceptions are observed.

It is thus possible to infer that if any kind of change in the original content of fluorine is produced by natural solutions, the same should be observed also for the alkali metals. If this is true, since the alkali metals

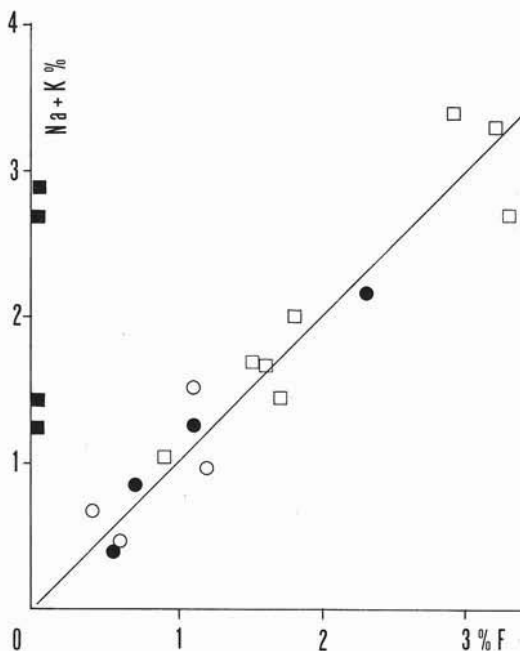


Fig. 4. — Correlation between the losses after leaching of sodium plus potassium and fluorine, expressed as percentages of the original contents. Symbols as in fig. 1.

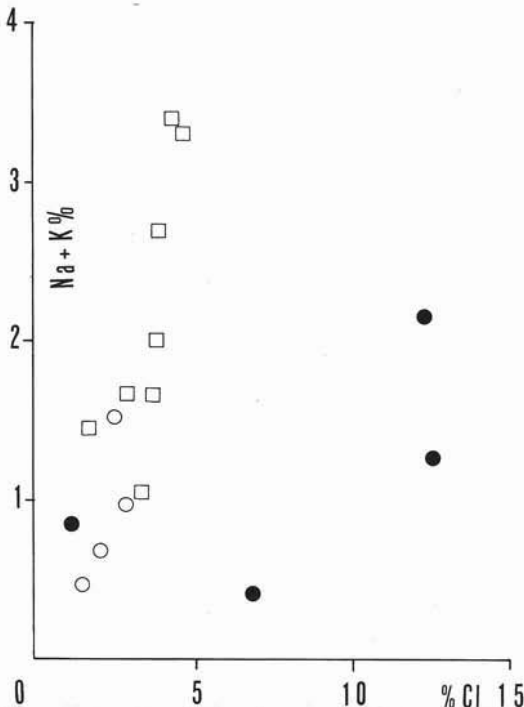


Fig. 5. — Correlation between the losses after leaching of sodium plus potassium and chlorine, expressed as percentages of the original contents. Symbols as in fig. 1.

are major constituents of rock forming minerals, no significant leaching of F by secondary processes can be derived when petrographic analyses in thin section do not show any degree of alteration.

Conclusions

The studied pumice samples represent portions of molten magma quenched immediately after the explosion; no actual data can be obtained for the thermal changes pertaining to this process, but it seems reasonable that a very short time was sufficient to reach temperatures below 600° C. Since no important loss in gaseous form has been observed for F and Cl by heating the samples up to 600° C, we think that it can be derived that a negligible quantity of those volatiles, if any, was lost subsequently to the very first phases of the volcanic explosions.

The leaching of the rocks, resembling weathering processes in the surface environment, appears to introduce slight changes for F, and sometimes variations of greater extent for Cl.

Even if we used in our experiments powdered samples instead of massive pumices, and the leaching was operated by shaking, it is obvious that we cannot reproduce the effect of percolating waters during a time comparable with that elapsed since the deposition of the pyroclastic formations; because of this we do not have a real proof that processes which were not effective in the laboratory have not been active during some thousands of years.

The alkali metals, however, are leached away roughly in a same proportion as F, and natural processes which cause a depletion in F are expected to produce a similar effect for Na and K, with an appreciable degree of alteration of the whole rock sample; because of this, if no significant alteration is observed, we can infer that the freshness of the samples can account for a substantial similarity between the original and the present contents of fluorine.

This could apply with some exceptions for Cl as well, but the possible influence of seawater on eruptive processes can introduce some chemical modifications whose extent has not been completely evaluated yet.

The data we present in support of our findings refer to pumices only, but the verified situation should be true for any glassy fraction of magmatic rocks, while in considering the slow cooling of lavas we have to take into account also the chemical conditions for the solubility of the volatiles in magmas.

The persistence of the original contents of F can be thus assumed for quenched phases when no appreciable extent of alteration is observed by petrographic investigations; the available evidence, however, is not sufficient for a defined statement about Cl distribution, as well as for other components of pyroclastic formations.

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