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Analcimization processes in the pyroclastic rocks from Phlegraean Fields (southern Italy): compositional variations and geochemical balances

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ABSTRACT. — A series of scoriaceous fragments collected from pyroclastic fall deposits belonging to different volcanoes of the Phlegraean Fields (Neaples, Italy) shows progressive stages of analcimization. Particularly, major and trace elements and $^{87}Sr/^{86}Sr$ ratio in non-altered and altered samples from the Fondo Riccio volcano have been determined. With increasing analcimization the following geochemical balance appears: Si and K decrease, Al, Na and Fe increase, Ca and Mg remain constant. Pb is depleted whereas Rb is slightly enriched in the more analcimized samples. All rare-earth elements do not show any significant difference between non-altered and altered samples. $^{87}Sr/^{86}Sr$ ratio strongly decreases in the more altered samples. Chemical variations observed in the scoriaceous fragments from the Fondo Riccio volcano, suggest that the analcimization process occurs in an open system and that a fluid component enriched in Na is involved. Therefore in a petrogenetic modelling, Pb, Rb, and $^{87}Sr/^{86}Sr$ must be used with very caution.

RIASSUNTO. — Coni di scorie monogenici appartenenti all'attività stromboliana recente dei Campi Flegrei sono stati campionati estesamente. Le scorie sono risultate affette da diversi gradi di analcimizzazione. I bilanci geochimici, effettuati comparando scorie analcimizzate e non, hanno dato i seguenti risultati: *a*) i contenuti in silice e potassio diminuiscono con l'aumentare del grado di analcimizzazione mentre per il sodio e l'alluminio si registrano chiari incrementi; *b*) gli elementi in tracce e le terre rare non subiscono, ad eccezione del rubidio e del piombo, significative variazioni; *c*) nei campioni a più elevato contenuto in analcime si registra una perdita di stronzio radiogenico. Le variazioni geochimiche sono state attribuite a processi di interazione tra i prodotti scoriacei ed i fluidi idrotermali legati all'attività fumarolica.

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KEY WORDS: *Analcimization process, geochemical balance, latitic rocks, Phlegraean Fields.*

INTRODUCTION

Zeolitization processes are commonly observed in the potassic volcanic rocks of the Roman region although there are only few studies devoted to defining the geochemical balance (major and trace elements) during these alterations (Fornaseri and Penta, 1960; Cundari and Graziani, 1964; Barbieri *et al.*, 1977; Calderoni *et al.*, 1985; Giannetti and Masi, 1989; Giampaolo *et al.*, 1997).

The most information, moreover, is restricted to Na and K elements and to leucite into analcime transformation, whereas a large quantity of data concerning the mechanisms and the control of the zeolitization process and the fluid/solid interaction in closed and in simulated open systems on different rock-types is available (Höller and Wirsching, 1978; Hawkins, 1981; Wirsching, 1981; Barth-Wirsching and Höller, 1989; Franco *et al.*, 1989-90; Ghiara *et al.*, 1993, 1994; Ghiara and Petti, 1996).

The lack of data on geochemical variations connected to alterations is, of course, a crucial problem in petrogenetic modelling which is only based on the behaviour of major and trace elements. Moreover, it is to be noted that the glass alteration is not always easily recognizable in thin section and so apparently fresh samples may have experienced minor alteration. Therefore, accurate X-ray studies are required to find out about the presence or absence of secondary minerals.

A suitable way to define geochemical balances is to study coeval and petrographically comparable rocks with different degrees of analcimization.

A good opportunity is given by scoria cones belonging to fourth cycle of Phlegraean volcanism (Di Girolamo *et al.*, 1984). With this objective in mind, we have undertaken a detailed petrological and geochemical study of several monogenetic scoria cones which have been extensively sampled.

In this paper we report geochemical variations observed in petrographically comparable glassy and scoriaceous fragments which have experienced different analcimization degrees and coming from the recent scoria cone of Fondo Riccio.

The present study will hopefully shed a light on:

1) post-depositional alteration of the glassy matrix leading to analcime crystallization;

2) geochemical changes of major and trace elements occurring in the analcimization process.

GEOLOGICAL SETTING

The Phlegraean Fields, located in the Neapolitan Region (southern Italy), are a Quaternary and historically active volcanic area. The last eruption occurred (Monte Nuovo) in 1538 and now the area shows fumarolic and hydrothermal activity. The oldest products (Torre Franco Tuff) are about 42,000 years old (Alessio *et al.*, 1976; Cassignol and Gillot, 1982).

From a volcanological point of view, the Phlegraean Fields are mainly made up of volcanoclastic deposits, often related to phreatomagmatic eruption, minor lava flows and domes (Di Girolamo *et al.*, 1984).

Quaternary volcanic products of the Phlegraean Fields belong to the shoshonitic series of the Roman province where more or less evolved rocks (e.g. trachytes and minor phonolites) predominate over mafic or intermediate ones (shoshonitic basalts and latites) (Di Girolamo *et al.*, 1984).

Aphyric to subaphyric Phlegraean rocks are chiefly composed of a glassy matrix with scattered few phenocrysts (Ghiara *et al.*, 1979; Armienti *et al.*, 1983; Di Girolamo *et al.*, 1984). Post-depositional alteration, including zeolites (e.g. analcime) as alteration products of glassy matrix, adularia and albite, overgrowths on primary sanidine laths, have been frequently observed. Other secondary minerals are: fluorite and, to a lesser extent, calcite, epidote and hematite (Armienti *et al.*, 1983; Beccaluva *et al.*, 1991).

MATERIALS AND METHODS

Scoriaceous fragments from pyroclastic fall deposits belonging to Minopoli, Fondo Riccio, Concola, S. Teresa, Senga, and Monte Nuovo volcanoes (Ghiara *et al.*, 1977; Ghiara, 1989-90) were sampled along vertical sections. From a volcanological point of view, these volcanic centres are monogenetic scoria cones produced by a strombolian-like volcanic activity. Pyroclastic deposits consist of rather poorly welded and coarse-grained scoria with decimeter-sized ballistic bombs and blocks. Scoriaceous fragments are arranged in discrete and overlain layers formed during the build up of the cone. Only few beds are connected to mass-flow processes resulting from avalanching and rolling of scoria deposits.

From the Fondo Riccio cone eleven discrete layers were sampled from bottom to top (Fl-F11 samples). Nearly all the layers range from 40 to 80 cm in thickness with the exception of the seventh layer (F7) which is 4 m thick. Only one layer (F4) is mainly formed by a fine-grained vitric tuff and it shows glassy fragments with apparent differences in the vesciculation degree.

Bulk rock composition (major and trace elements) was determined by X-ray fluoroscence spectrometry (Philips PW 1400 XRF spectrometer), using pressed powder pellets, according to the method of Franzini *et al.* (1975) and Leoni and Saitta (1976). International standards were used for calibration; the precision for major elements are usually estimated to be below 3%. Mg and Na were determined by atomic absorption spectrophotometry (Perkin-Elmer model 2100) and analytical precision is within ± 1%. The analytical precision is better than 5% for Sr, Zr and Ba and better than 10 % for other trace elements. REE were determined by ICP-MS at CRPG, Nancy, France (Govindarju and Mevelle, 1987).

The analcime contents were measured, according to Parker (1978), using a Philips PW 1730 X-ray diffractometer (40 kV, 30 mA) with Ni-filtered Cukα radiation. In order to better define the analcime type, thermal analysis (DTA, TG and DTG) was performed using a Netzsch Geratebau GMBH instrument with a heating rate of 10°C/min between 20-1000°C.

Scanning electron microscope analyses were made using a Cambridge Stereoscan model 250 MK3 equipped with EDS Link model AN 10/55 S. Microprobe analyses were carried out on automated ARL SEMQ (C.N.R. Cagliari) (accelerating voltage 15 kV; beam current 20 nA). Natural silicates and oxides were used as standard materials. On-line correction for drift, dead-time and background was applied to the raw data. All data were corrected using ZAF-FLS program.

Strontium separation was carried out by dissolution of samples in HF and $HClO_4$ acids and by passage through a 50 × 8 (200-400 mesh) cation exchange resin. $^{87}Sr/^{86}Sr$ ratios were measured on a VG Isomass 54E mass spectrometer (CNR, Roma). For the NBS 987 $SrCO_3$ standard, the mean value of 0.71024 ± 0.00002 was achieved, with a standard deviation of 0.00001 (15 measurements).

Results

Classification and petrographic notes

In the present paper a classification based on CIPW normative composition is used. In the Differentiation Index (D.I.) *vs* Nepheline (Ne) classification grid (Armienti *et al.*, 1983) the investigated rocks fall into the following five main fields: 1) shoshonites, 2) latites, 3) trachytes, 4) alkali trachytes and 5) peralkaline phonolitic trachytes (fig. 1).

All the scoriaceous fragments are subrounded, dark-coloured and homogeneous in hand samples. They are aphyric to sub-

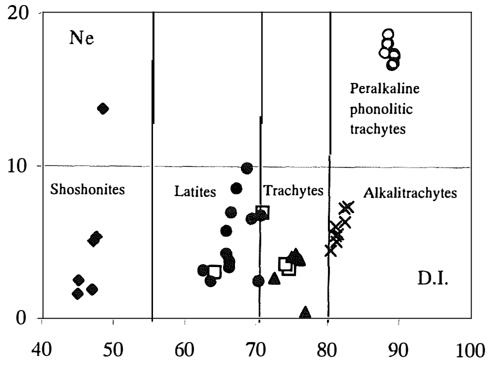

Fig. 1 – Plot of D.I. *vs* Ne (%) for Minopoli (◆), Fondo Riccio (●), Concola (□), Mt. Santa Teresa (▲), Senga (×), and Mt. Nuovo (○) scoriaceous fragments. D.I.= Ab+Or+Ne+Lc. Classification diagram modified from Armienti *et al.* (1983).

aphyric containing <5% by volume of millimeter to submillimeter size phenocrysts of plagioclase (An_{87-59}), sanidine (Or_{83-50}) and strongly zoned clinopyroxene ranging in composition from diopside (Wo_{46} En_{48} Fs_{6}) to salite (Wo_{48} En_{33} Fs_{19}). Cumulophyric aggregates of plagioclase and clinopyroxene are commonly observed. Rare olivine (Fo_{82-74}) phenocrysts occur in the shoshonites while Mg-biotite (Fe/Fe + Mg = 0.37-0.46) laths are common in latites and trachytes. Ti-magnetite and apatite are the main accessory phases. Sanidine modal abundance increases towards the trachytic rock-types while clinopyroxene phenocrysts and microphenocrysts decrease. These latter in the latites and trachytes are mainly salitic in composition.

The glassy groundmass, in thin section, is variably coloured from coffee-brown (i.e. shoshonites) to pale brown (i.e. trachytes) and it, locally, shows irregular patches with anomalous birifrangence. Quench textures as skeletal to dendritic sanidine and pyroxene are common as well as thin films of secondary minerals filling the vescicles.

X-ray analyses

From extensive X-ray diffraction studies of scoriaceous fragments the following features emerged:

1) in addition to X-ray patterns of phenocrystic minerals most samples belonging to shoshonites, latites, and trachytes show more or less pronouced peaks at 5.6 Å and 3.43 Å which point to the presence of analcime;

TABLE 1

Chemical, normative and analcime variations of scoriaceous fragments from several scoria cones belonging to the fourth cycle of Phlegraean volcanism.

Samples	D.I.	MgO	Ne	anl	Samples	D.I.	MgO	Ne.	anl
M 1	45.0	5.19	1.6	11	T 1	72.5	1.77	2.7	-
M 2	45.1	5.22	2.5	12	T 1'	74.9	1.57	4.1	11
M 3	47.1	5.10	5.1	16	T 2	76.1	1.53	3.9	18
M 3'	48.3	6.00	13.8	27	T 3	75.5	1.67	4.3	-
M 4	47.0	4.61	1.9	13	T 4	76.9	1.35	0.5	-
M 4'	47.5	4.95	5.4	10	S 1	82.4	0.89	6.4	4
F 1	68.6	2.20	9.9	27	S 2	82.3	0.90	7.3	-
F 2	67.2	2.34	8.6	23	S 3	80.4	0.90	4.5	-
F 3	66.4	2.26	7.0	23	S 4	82.3	0.95	7.3	6
F 4	65.8	2.25	5.8	11	S 4'	82.8	0.91	7.4	-
F 4'	66.2	2.40	3.8	-	S 4''	81.1	0.87	6.1	-
F 5	66.2	2.57	3.4	12	S 5	81.2	0.82	5.1	-
F 6	69.3	2.11	6.6	20	S 5'	81.4	0.82	5.6	14
F 7	70.6	2.18	6.8	19	S 6	81.1	0.90	5.5	-
F 8	63.6	2.78	2.5	16	N 1	87.8	0.26	17.5	-
F 9	65.8	2.55	4.3	9	N 1'	89.1	0.20	17.3	-
F 10	62.5	2.54	3.2	-	N 2	88.8	0.18	16.7	-
F 11	70.3	2.11	2.5	-	N 3	89.0	0.16	16.8	-
C 1	64.1	2.39	3.1	12	N 3'	89.1	0.13	17.4	-
C 1'	70.8	2.10	7.0	20	N 4	88.1	0.13	18.1	-
C 2	74.6	1.74	3.3	9	N 5	88.2	0.14	18.1	-
C 3	74.1	1.80	3.6	11	N 6	88.2	0.12	18.7	-

M: Minopoli; F: Fondo Riccio; C: Concola; T: Santa Teresa; S: Senga; N: Monte Nuovo.
D.I.: Ab+Or+Ne+Lc; MgO is in wt%; Ne: CIPW nepheline normative amounts (%); anl: analcime contents (%); - absent.
The samples from each scoria cone refer to discrete layers and they are arranged in stratigraphic order from bottom to top. Samples coming from the same layer with different vesciculation grade have the same number (e.g. M3-M3').

TABLE 2

Microprobe analyses of analcime (1 and 2), Ti-magnetite (3), and glass (4) from sample F1.

	1		2		3		4	
	[5]	(σ)	[5]	(σ)	[7]	(σ)	[6]	(σ)
SiO_2	56.20	(1.15)	55.80	(1.28)	1.85	(0.58)	56.66	(1.32)
TiO_2					12.63	(1.30)	0.80	(0.01)
Al_2O_3	21.61	(0.45)	21.83	(0.15)	2.82	(0.50)	17.85	(0.65)
Fe_2O_3 (tot)	0.70	(0.03)	0.69	(0.01)	78.68	(1.40)	6.49	(0.30)
MgO	0.15	(0.05)	0.11	(0.05)	2.36	(0.08)	1.88	(0.07)
CaO	0.67	(0.02)	0.79	(0.03)	0.86	(0.04)	4.96	(0.03)
Na_2O	9.78	(0.35)	9.85	(0.25)			2.95	(0.53)
K_2O	1.68	(0.15)	1.82	(0.15)			7.85	(0.20)
MnO					0.60	(0.02)	0.15	(0.01)
Cr_2O_3					0.20	(0.06)		
O	96		96		32		80	
Si	33.12		32.93		0.49		26.74	
Ti					2.50		0.28	
Al	15.01		15.18		0.87		9.93	
Fe	0.31		0.31		15.57		2.31	
Mg	0.13		0.10		0.92		1.32	
Ca	0.42		0.50		0.24		2.50	
Na	11.18		11.27				2.70	
K	1.26		1.37				4.73	
Mn					0.13		0.06	
Cr					0.09			
E%	9.8		9.1					
Ulv %					36.1			

[ ]: number of analysis for each sample; (σ): Estimated standard deviations are given to the right of each number. $Fe_2O_{3(tot)}$: total iron. O: number of oxygens; E%: total balance error from Gottardi and Galli (1985). Ulv %: ulvöspinel mol. %, calculated utilizing Fe^{3+}, Fe^{2+} according to Droop (1987).

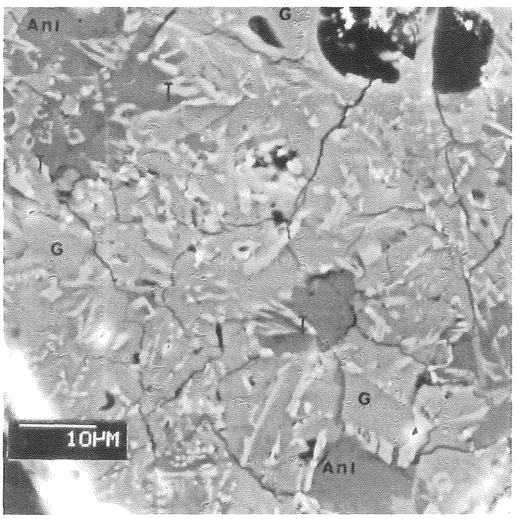

Fig. 2 – SEM images of analcimized sample (F1) from Fondo Riccio volcano: (Anl): analcime, (T): Ti-magnetite, (G): unaltered glass.

2) only few samples of alkalitrachytes show analcime peaks which are absent in the samples of peralkaline phonolitic trachytes;

3) the analcime amount of fragments coming from a single volcano varies as follows: Minopoli 10 – 27%, Fondo Riccio 0 – 27%, Concola 9 – 20%, Santa Teresa 0 – 18% and Senga 0 –14 % by volume (Table 1);

4) the analcime amount of fragments coming from a single layer is strongly variable [e.g. M3 - M3' (16 – 2%), C1 - C1' (12 – 20 %) and F4 - F4' (0 – 11%)] (Table 1).

Thermal analyses

Simultaneous DTA-TG-DTG analyses were carried out on analcime-rich samples (e.g. F1 and M3'). The samples show a dehydration band between 235 and 320°C; according to Giampaolo and Lombardi (1994) this

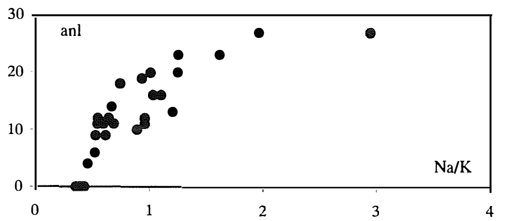

Fig. 3 – Analcime (anl) contents *vs* Na/K ratios of all samples from Table 1.

behaviour is typical of X-type analcime which is mainly formed by leucite alteration whereas hydrothermal analcime, displays a strong sharp endothermic peak between 350 and 370°C.

Microprobe analyses and scanning electron microscope

The electron microscope coupled with microprobe analyses on the glassy matrix of F1 sample indicate the following main textures produced by devetrification processes:

1) spherulitic-like textures consisting of radiating aggregates of warm-shaped Fe-Ti opaques (Table 2; fig. 2);

2) patchy textures following a sharp boundary between very fine-grained analcimized and unaltered regions (Table 2; fig. 2)

The analcime compositions are comparable to that of literature. The ulvöspinel content of newly formed opaques is 36.1 wt%. Microprobe analyses on unaltered parts of glass are strictly comparable to whole-rock analyses obtained for fresh sample (e.g. F11, Table 3*a*).

Major and trace elements variations

Scoriaceous fragments of each volcanic centre display narrow variations in their MgO content (e.g. MgO from 2.11 to 2.78 wt% in the Fondo Riccio volcano); this matches the monogenetic character of scoria cones. However, wide variations of the Na/K ratios and consequently of normative nepheline amounts at same D.I. value occur (Table 1; fig. 3). The Na/K ratios are positively correlated to analcime contents evaluated on the basis of X-ray diffraction and they can be roughly used to estimate the degree of analcimization (fig. 3).

The variation diagrams reveal that some elements (e.g. K_2O and Na_2O) are more or less

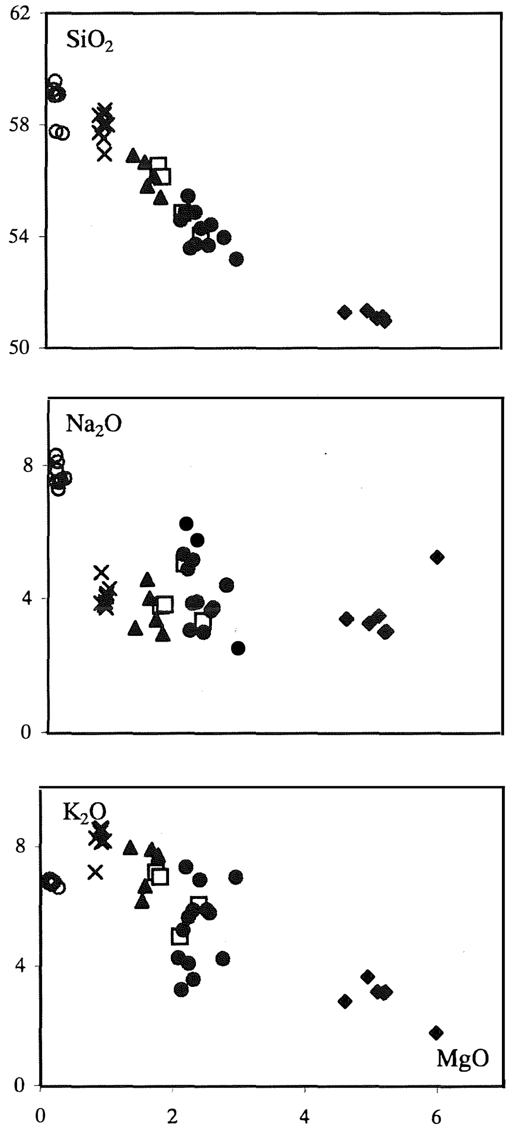

Fig. 4 – SiO_2, Na_2O and K_2O (wt%) variations of scoriaceous fragments plotted against MgO (wt%). For symbols see fig. 1

scattered. This scattering is more evident in samples coming from Fondo Riccio, Minopoli and Concola volcanoes which, on the basis of X-ray patterns, show wide variations in the analcime content (see Table 1). Particularly, in the products of Fondo Riccio volcano, the Na_2O and K_2O define a «*within-trend*» which does not overlap with the general trend (fig. 4).

Major and trace element compositions of latitic scoriaceous fragments from the Fondo Riccio volcano are given in Tables 3*a* and 3*b*. The samples show wide variations in Na_2O and K_2O contents (from 3.11 to 6.26 wt % and from 3.26 to 7.40 wt% respectively) which, moreover, are negatively correlated; in addition to the K_2O decrease is coupled with a slight Al_2O_3 increase. The other major elements are nearly constant. The Fondo Riccio samples display trends (in the plots K_2O *vs* Al_2O_3 and Na_2O) moving towards the analcime field (fig. 5*a*). The loss of K_2O is roughly balanced by increases of Na_2O and Al_2O_3.

As for trace elements, only Pb is depleted whereas Rb is slightly enriched in the strongly analcimized samples (e.g. F1) (fig. 5*b*). Rb increase has been previously observed by Fornaseri and Penta (1960) and by Giannetti and Masi (1989) in the analcime from leucite alteration. Other trace elements do not show significant variations in the Fondo Riccio rock suites (Table 3*b*).

The patterns of chondrite-normalized REE are shown in figure 6*a*. Like for most trace elements, no significant difference between non-altered and altered rocks samples is found. In addition, no REE fractionation occurs during analcimization processes as clearly suggested by K/Na *vs* La/Yb diagram (fig. 6*b*).

Sr isotope ratios of several rock samples from the Fondo Riccio volcano are given in

TABLE 3*a*

Bulk-rock chemical analyses and C.I.P.W. norms of latitic scories from Fondo Riccio volcano. The samples are arranged in stratigraphic order from bottom to top.

	F 1	F 2	F 3	F 4	F 4'	F 5	F 6	F 7	F 8	F 9	F 10	F 11
SiO_2	54.63	54.45	54.35	54.57	55.49	54.87	55.34	55.61	54.57	54.56	55.27	55.78
TiO_2	0.94	0.98	0.98	0.99	0.92	1.01	0.92	0.91	0.95	0.98	0.91	0.90
Al_2O_3	18.27	18.11	18.19	17.66	17.39	17.41	18.05	17.94	18.33	17.55	17.82	17.37
Fe_2O_3	7.89	8.12	8.10	8.29	7.49	8.15	7.66	7.25	8.12	8.16	7.43	7.07
MnO	0.14	0.14	0.14	0.14	0.16	0.14	0.14	0.14	0.15	0.15	0.14	0.15
MgO	2.20	2.34	2.26	2.25	2.40	2.57	2.11	2.18	2.78	2.55	2.54	2.11
CaO	5.78	5.96	6.05	5.98	5.85	5.83	5.55	5.31	5.94	5.92	5.80	5.80
Na_2O	6.26	5.83	5.20	3.87	3.00	3.76	5.42	4.95	4.45	3.71	2.52	3.11
K_2O	3.26	3.61	4.20	5.68	6.90	5.83	4.34	5.29	4.31	5.97	6.99	7.40
P_2O_5	0.51	0.46	0.53	0.53	0.40	0.43	0.47	0.42	0.40	0.44	0.58	0.31
Or	19.0	21.1	24.4	33.6	41.4	34.6	25.4	31.0	25.4	35.4	41.7	44.0
Ab	39.7	37.5	35.0	26.4	21.0	28.2	37.3	32.8	35.7	26.1	17.6	23.8
An	11.6	12.4	13.9	14.8	13.8	13.5	12.1	11.0	17.3	13.7	16.9	11.7
Ne	9.9	8.6	7.0	5.8	3.8	3.4	6.6	6.8	2.5	4.3	3.2	2.5
Di	11.0	11.0	10.1	9.2	10.4	10.1	9.8	9.9	7.6	10.2	8.2	9.0
Ol	3.8	4.3	4.5	5.1	5	5.3	4.0	3.7	6.7	5.2	6.9	4.4
Mt	2.5	2.6	2.6	2.6	2.5	2.6	2.5	2.5	2.6	2.6	2.7	2.5
Il	1.3	1.4	1.4	1.4	1.2	1.4	1.3	1.3	1.3	1.4	1.5	1.3
Ap	1.1	1.0	1.1	1.1	0.9	0.9	1.0	0.9	0.8	0.9	1.2	0.8

Major elements (wt%) normalized to H_2O-free basis; H_2O content ranges from 0.75 to 1.34 wt%. F4' from the same layer of F4.

TABLE 3*b*

Trace element contents (ppm) in latitic scories from the Fondo Riccio volcano.

	F 1	F 2	F 3	F 4	F 4'	F 5	F 6	F 7	F 8	F 9	F 10	F 11
Li	17	21	18	21	21	19	23	24	16	19	18	25
Rb	370	355	305	258	270	270	278	260	327	293	305	300
Pb	14	21	23	33	35	36	31	37	31	36	43	43
Sr	880	890	900	920	853	855	845	835	876	880	905	835
Ba	1760	1765	1690	1695	2037	1700	1727	1730	2275	1710	1850	1740
Y	28	28	28	30	29	27	31	29	29	39	28	29
Zr	215	210	220	215	292	215	215	220	272	225	245	240
V	210	220	215	217	160	206	198	131	177	202	195	171
Nb	32	30	30	33	40	32	32	34	42	34	36	36
Cr	23	22	28	19	11	27	16	31	14	23	24	24
Co	17	18	18	17	17	18	15	14	41	16	17	14
Ni	10	8	10	10	15	8	7	10	16	10	11	11
Zn	89	94	92	94	90	93	90	92	53	96	96	95
La	56.7	57.8	56.0	56.9	59.2	54.0	61.3	61.9	58.5	63.0	56.1	59.9
Ce	114.1	114.6	113.5	110.6	116.2	110.6	118.3	116.2	114.1	119.0	109.1	119.5
Nd	50.1	50.8	49.1	51.8	51.2	47.4	52.7	52.3	52.3	n.d.	51.1	50.0
Sm	10.3	10.2	10.3	10.6	10.2	10.1	10.9	10.5	10.3	n.d.	10.1	10.1
Eu	2.40	2.40	2.40	2.40	2.40	2.30	2.50	2.40	2.40	n.d.	2.50	2.40
Gd	7.40	7.40	7.40	7.90	7.50	7.30	8.30	8.00	7.80	n.d.	7.60	7.10
Dy	5.45	5.65	5.34	5.54	5.37	5.46	5.73	5.65	5.64	n.d.	5.51	5.38
Er	2.59	2.58	2.55	2.66	2.60	2.53	2.72	2.68	2.59	n.d.	2.61	2.56
Yb	2.43	2.40	2.36	2.62	2.54	2.42	2.67	2.55	2.56	n.d.	2.43	2.50
Lu	0.39	0.37	0.39	0.37	0.40	0.37	0.38	0.37	0.40	n.d.	0.38	0.41

n.d.: not detected

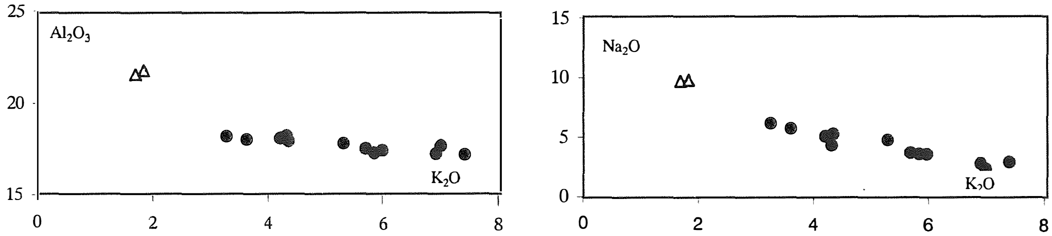

Fig. 5*a* - Variation diagrams [Al_2O_3 and Na_2O (wt%) *vs* K_2O (wt%)] of the scoriaceous fragments from Fondo Riccio (●), analcime this work (Δ)

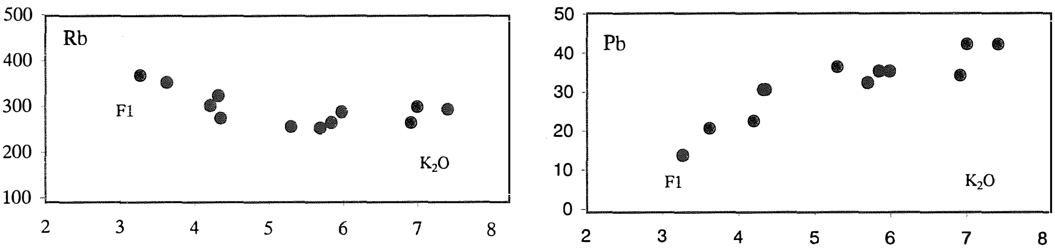

Fig. 5*b* – Variation diagrams [Rb and Pb (ppm) *vs* K_2O (wt%)] of the scoriaceous fragments from Fondo Riccio.

TABLE 4

Sr isotope compositions of representative scoriaceous fragments of Fondo Riccio volcano

	$^{87}Sr/^{86}Sr$
F 10	0.70785±0.00002
F 11	0.70790±0.00003
F 4’	0.70786±0.00002
F 4	0.70786±0.00003
F 8	0.70776±0.00002
F 3	0.70743±0.00002
F 1	0.70745±0.00002

F4’ from the same layer of F4.

Table 4. $^{87}Sr/^{86}Sr$ ratios remain quite constant in the non-altered or relatively altered samples but with increasing analcimization (i.e. samples with 23-27 % in analcime) $^{87}Sr/^{86}Sr$ abruptly decrease (fig. 7).

DISCUSSION

X-ray data and re-equilibration textures observed in SEM investigations clearly reveal that the glassy matrix of scoriaceous fragments coming from Phlegraean Fields volcanic products has experienced an alteration process leading to very fine-grained analcime aggregates.

On the whole, the analcimization process progressively decreases towards the evolved rocks (i.e. alkalitrachytes and peralkaline phonolitic trachytes). This is conform to the lower reactivity of felsic glass compared with basic glass reactivity as clearly shown by Ghiara and Petti (1996) in fluid/rock interaction experiments.

The study of geochemical modifications produced by analcimization processes on glassy fragments is the main goal of the present paper and consequently we have chosen the Fondo Riccio samples because they show *a)* wider data scattering in variation diagrams; *b)* low differences in the MgO content; *c)* wider variations in the analcime content.

In order to explain the Fondo Riccio trends the most relevant textural, mineralogical and chemical features of the scoriaceous fragments are:

a) all the investigated juvenile fragments are aphyric to sub-aphyric and so the scattered chemical trends cannot be related to accumulation processes of phenocrysts;

b) X-ray and microprobe analyses indicate that the re-equilibration product of metastable glass is mainly represented by analcime;

c) X-ray quantitative analyses clearly indicate that the glassy matrix of scoriaceous fragments have experienced different degrees of subsolidus re-equilibration;

d) K_2O and Na_2O are negatively correlated and tend, as expected, towards the analcime field (fig. 5*a*).

In order to compare unaltered and altered rocks, the major elements are usually normalized to the least mobile element during alteration processes. Titanium is often used for normalization owing to its low solubility and mobility during alteration processes (Nesbitt,

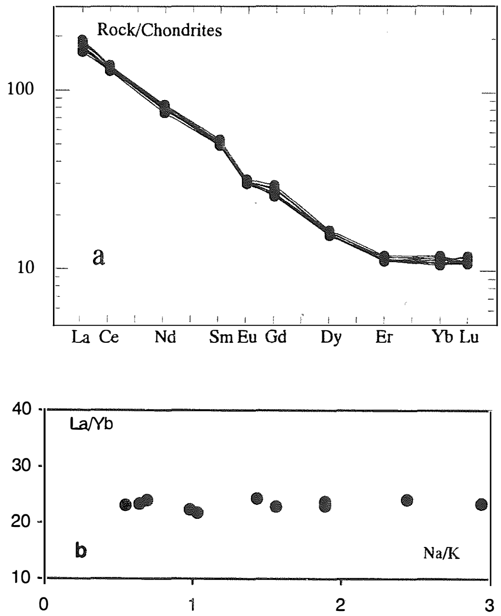

Fig. 6 – Chondrite-normalized REE patterns (a) and La/Yb *vs* Na/K atomic ratio (b) of representative scoriaceous fragments of Fondo Riccio volcano. Normalizing values from Boynton (1984).

TABLE 5*a*

Half-anhydrous Barth's standard cell contents (on the basis of 80 oxygens) of bulk rock; the samples are ordered according to the increasing of the analcimization process.

	F 11	F 9	F 5	F 4	F 7	F 8	F6	F 3	F2	F1
Si	26.33	25.81	25.86	25.74	25.98	25.70	25.92	25.54	25.56	25.58
Ti	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
Al	9.66	9.76	9.78	9.84	9.93	10.12	9.96	10.07	10.02	10.13
Fe^{3+}	2.51	2.90	2.89	2.94	2.63	2.86	2.70	2.86	2.87	2.78
Mg	1.55	1.72	1.67	1.58	1.53	1.73	1.47	1.58	1.64	1.54
Ca	2.87	2.98	2.93	3.01	2.71	2.97	2.77	3.03	2.98	2.89
Na	2.85	3.40	3.44	3.54	4.50	4.04	4.92	4.74	5.31	5.70
K	4.46	3.60	3.51	3.42	3.17	2.58	2.59	2.52	2.16	1.96
Mn	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
P	0.12	0.18	0.17	0.21	0.17	0.16	0.19	0.21	0.18	0.20
Na/K	0.64	0.94	0.98	1.03	1.43	1.56	1.89	1.89	2.44	2.94

TABLE 5*b*

Atomic differences observed in the main elements involved during the analcimization process, with respect to an unaltered sample (F 11).

	Si-Si	Al-Al	Mg-Mg	Ca-Ca	Na-Na	K-K	Na/K
F 11							0.64
F 9	-0.52	0.10	0.17	0.11	0.55	-0.86	0.94
F 5	-0.41	0.12	0.12	0.06	0.59	-0.95	0.98
F 4	-0.60	0.18	0.03	0.14	0.69	-1.04	1.03
F 7	-0.35	0.27	-0.02	-0.16	1.65	-1.29	1.43
F 8	-0.63	0.46	-0.18	0.10	1.20	-1.88	1.56
F 6	-0.42	0.30	-0.08	-0.10	2.07	-1.86	1.89
F 3	-0.80	0.41	0.03	0.16	1.89	-1.94	1.89
F 2	-0.78	0.36	0.09	0.11	2.46	-2.30	2.44
F 1	-0.75	0.47	-0.01	0.02	2.86	-2.50	2.94

Na/K atomic ratio

1979; Middelburg *et al.*, 1988). In the Fondo Riccio rock-suite Ti-value of F11 sample have been used to normalize all the altered samples.

Moreover, assuming that alteration process takes place without appreciable change in volume and in order to have a better comparison between Fondo Riccio rocks, all the major elements have been normalized using half of Barth's anhydrous standard cell (Barth, 1952) (Table 5*a*). This procedure allows the comparison of values unaffected by molecular weight and the reproduction of a more realistic feature of chemical variations occurring in the analcimization processes.

The results of a quantitative comparison between unaltered sample (F11) and altered samples are given for each major element in Table 5*b* and plotted in figure 8.

From the overall data set the following geochemical balance appears:

1) Si and K decrease whereas Al and Na increase clearly suggesting an open system during devitrification and ensuing alteration;

2) Ca and Mg, however scattered, can be

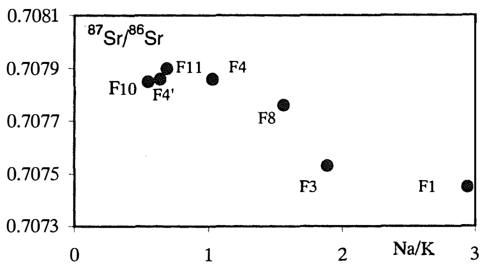

Fig. 7 – $^{87}Sr/^{86}Sr$ *vs* Na/K atomic diagram for representative samples from the Fondo Riccio volcano.

considered quite constant;

3) the lack of Fe^{2+}/Fe^{3+} ratios preclude to understand the iron behaviour;

4) in the less altered rocks (e.g. F9 and F5) the K loss is mainly balanced by Na increase;

5) in the more analcimized rocks (e.g. F1 and F2) the Na increase is higher than K decrease;

6) Na/K and Si/Al atomic ratios progressively increase (from 0.64 to 2.94) and decrease (from 2.73 to 2.52), respectively and they can be used as index of the degree of analcimization.

As to 4 and 5 points this behaviour is like due to different glass/interaction fluids ratios. It has to be remarked that, respect to unaltered rocks, K concentrations are depleted up to 56% and Na contents are enriched up to 100% in the strongly analcimized rocks.

Chemical variations observed in the Phlegraean glassy rocks defer from those detected by Giampaolo *et al.,* (1997) in leucite-bearing lava flow; in the latter in addition to K, a Ca and Mg loss is also observed.

Most trace elements, including REE concentrations, are essentially conservative, even at significant degrees of analcimization of glassy products of Phlegraean Fields volcanism. Conversely, only Pb is clearly removed ($Pb_{(F1)}/Pb_{(F11)}$ = 0.33), and Rb is slightly enriched ($Rb_{(F1)}/Rb_{(F11)}$ = 1.23).

This geochemical scenario is compatible with fluid-glass interaction processes in an open system and requires fluids enriched in sodium. These fluids are likely connected to hydrothermal and fumarolic activity of Phlegraean Fields. Indeed, the fluids spreading out from Phlegraean fumaroles, solfataras and thermal springs display a high salinity mainly of the sodium-chloride type (Cortecci *et al.*, 1977; Ghiara *et al.*, 1988). Moreover, an alteration model involving trapped hydrothermal fluids is in good agreement with spatial distribution of analcimization degrees which are more elevated in the lower portion of scoria cones.

The important role played by interacting fluids is confirmed also by $^{87}Sr/^{86}Sr$ ratios

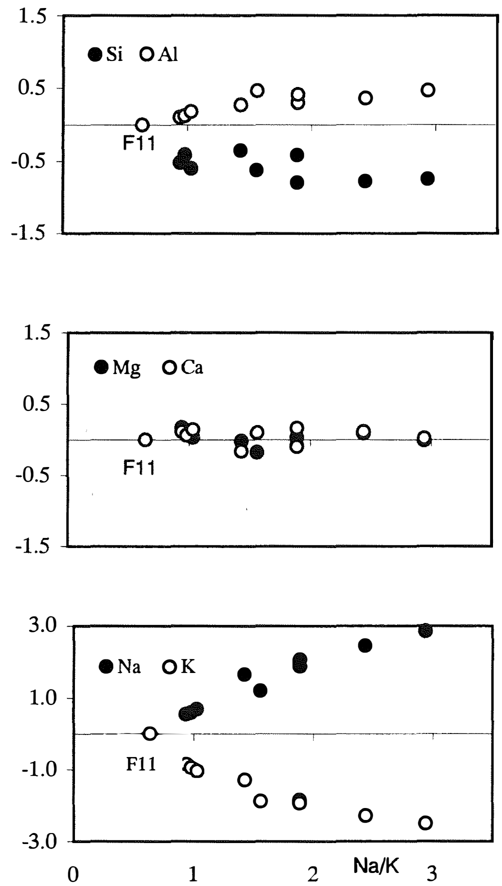

Fig. 8 – Chemical differences observed in the main elements involved during the analcimization process, with respect to the unaltered sample (F11) plotted against Na/K atomic ratio.

which in the more analcimized samples decrease (fig. 7). According to Blum *et al.*, (1994) and Matter *et al.*, (1991) during a fluid/rock interaction the fluid component is enriched in radiogenic strontium.

CONCLUSIONS

The latitic scoriaceous fragments collected from a single volcano show that the glassy matrix has experienced progressive stages of analcimization. Geochemical balances carried out on major elements suggest that the analcimization process takes place in an open system mainly involving a clear K and a low Si loss and Na and Al gain.

All the observed geochemical changes are mainly constrained by the chemistry of newly formed minerals (e.g. analcime); the K loss is likely due to the lack of favourable chemical conditions (e.g. Si/Al) in the system which do not allow a capture in order to form other secondary minerals.

On the basis of comparison with other analcimized rocks belonging to Roman province no general scheme can be proposed for the chemical and isotopic changes occurring in the widespread analcimization processes.

Most trace element concentrations, with the exception of Rb and Pb, are not modified by analcimization processes and therefore they can be used in petrogenetic modelling of Phlegraean Fields suites. On the contrary, isotopic ratios must be used with caution.

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