

DISTRIBUTION OF TRACE ELEMENTS IN ALTERED PYROCLASTITES FROM MONTE VULTURE VOLCANO (SOUTHERN ITALY)

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ABSTRACT

Three pyroclastic deposits from Monte Vulture volcanic area (Potenza, southern Italy) looking like paleosols in the field were investigated in a previous study for mineralogy and major elements to estimate the stage of the weathering. Here is dealt with the behaviour of some trace elements (Ce, La, Ba, Ni, Cr, V, Rb, Sr, Y, Zr and Nb) in the same deposits to give a comprehensive geochemical picture.

The distribution of the chemical elements within the whole rock and after its attack with Na-pyrosulfate (residue + solute) has been considered. Ba and Sr, as well as their distribution, appear to be controlled by the residual crystals in each of the deposits; La, Ce, Y and Nb are more concentrated in the solute that once was represented by vitric component, allophane, and Fe-Si-Al gels, biotite, carbonates and analcite; V, Cr, and Ni show similar trends in whole rock and in solute. In particular La, Ce, Y, V, Cr and Ni in the lowermost unit increase with the depth, as well as the contents of gels and allophane. Probably this behaviour was superimposed by the fluctuation of the water tables, as documented by the occurrence of a carbonate level upon the unit lies. It is concluded that the earliest stage of weathering did not affect the trace element distribution and that interpretations about chemical changes in deeply altered pyroclastic rocks should be always the outcome of careful accurate analyses.

Key words: *trace elements, pyroclastites, weathering.*

RESUMEN

En un trabajo previo se estudiaron tres depósitos piroclásticos, considerados como paleosuelos, del área volcánica del Monte Vulture (Potenza, Italia) para deducir su grado de meteorización. En el presente trabajo se estudia el comportamiento de algunos elementos traza (Ce, La, Ba, Ni, Cr, V, Rb, Sr, Y, Zr, Nb) en esos depósitos para intentar obtener una imagen geoquímica más completa.

Se ha estudiado la distribución de elementos traza en la roca total y después de un ataque con piro-sulfato-Na (residuo + solución). Ba y Sr parecen estar controlados por los cristales del residuo (piroxenos, feldespatos, anfíboles y accesorios); La, Ce, Y y Nb se concentran más en la solución, es decir en los componentes vítreos, alofana, geles Fe-Si-Al, biotita carbonatos y analcima; V, Cr y Ni no muestran ninguna tendencia a concentrarse en una fracción concreta. Hay que resaltar que La, Ce, Y, V, Cr y Ni aumentan con la profundidad en la unidad inferior, junto con el contenido en geles y en alofana. Este comportamiento puede ser debido a fluctuaciones del nivel freático, como se deduce por la presencia de un nivel calcáreo en la unidad superior.

Se concluye que los estados precoces de meteorización no afectan prácticamente a la distribución de los elementos traza, y que las interpretaciones sobre los cambios químico sufridos por las rocas piroclásticas deben hacerse sólo después de un detallado análisis.

Palabras clave: *elementos traza, meteorización, piroclastitas.*

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Introduction

Pyroclastic deposits consist of crystals, glass, lithic fragments having a highly variable density. The proportions of these components depend on the origin of magma, the mechanism of transport and emplacement, the topography of the area, etc. (e.g. Fischer and Schmincke, 1984). Such factors may cause granulometric, chemical and mineralogical vertical variations within a given pyroclastic deposit. So, geochemical and mineralogical variations shown by weathered and non-weathered pyroclastic rocks will reflect inherited characteristics and eventual modifications induced by alteration might be masked. These aspects were focused in a study by Fiore *et al.* (1992) on three buried pyroclastic flow units from Monte Vulture volcanic area (southern Italy). In this study was documented the existence of: (i) mineral alteration predating the eruptive events; (ii) persistence of grain-size distribution along the studied levels and low clay fraction content; (iii) alteration due to the circulating water and (iv) incipient weathering effects. The authors attributed to weathering the hydration and the loss of

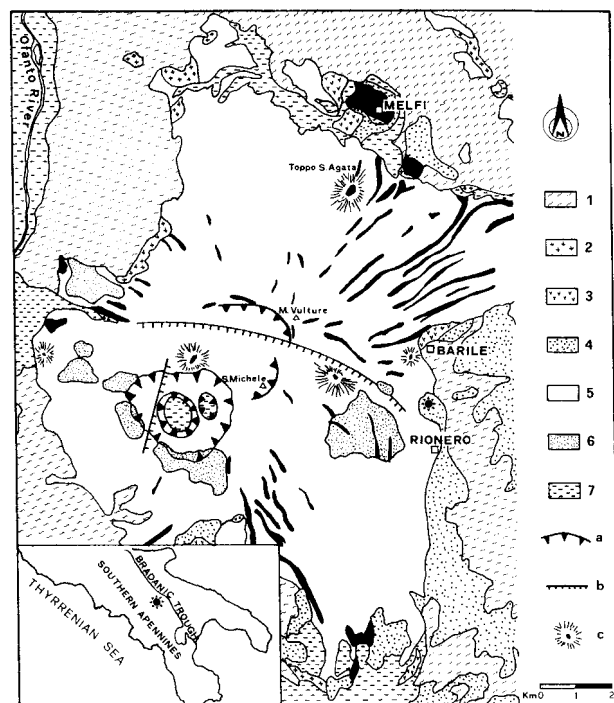


Fig. 1.—Schematic map of Monte Vulture volcanic complex (after Baldassarre *et al.*, 1989, simplified) and locality of the sampling. 1. Pre-pleistocenic terrains. 2. Ignimbrites A and B and phonolitic lava domes. 3. Masseria Boccaglio Tephra. 4. Rionero Barile Tephra. 5. Mt. Vulture-San Michele Tephra. 6. Case López-Masseria Granata Tephra. 7. Fluvio-lacustrine, travertine and present day deposits. a. Crater and caldera rims. b. Faults. c. Cinder cones. Star: sampling site.

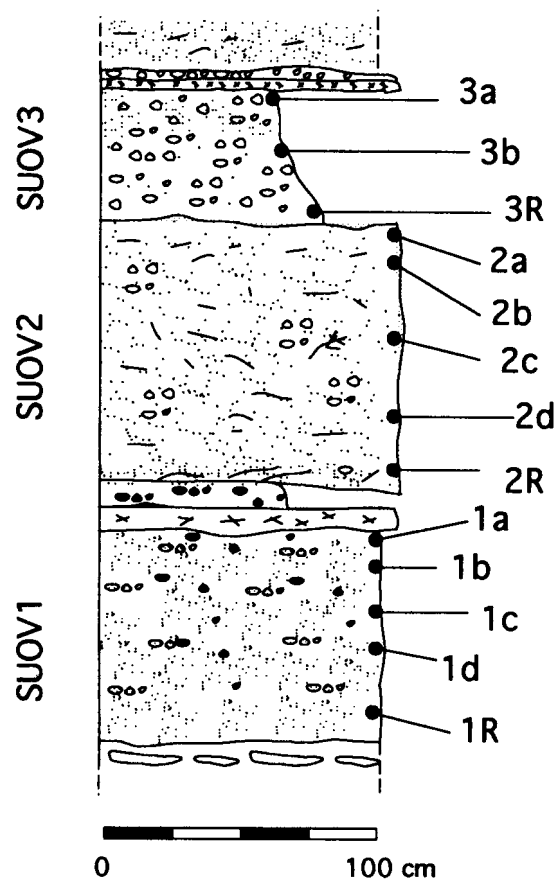


Fig. 2.—Schematic stratigraphic section of the sequence collected at San Antonio quarry (after La Volpe and Principe, 1989, modified) and position of the samples in study.

alkalis from the vitric components and the increase of allophane and Si-Al gel contents in the higher part of the levels. Therefore, the eventual chemical modification in the content of major elements during weathering was masked. In the deposits studied by Fiore *et al.* (1992), although mineralogical transformation and mineral dissolution by weathering were lacking, components characterised by high chemical reactivity (glass, allophane, Si-Al gels, phlogopite, analcite) were abundant.

This circumstance induced us to complete the investigation considering also the behaviour of some trace element during the early stage of weathering in the same samples analysed for major elements and mineral contents.

Geology and methods

Geology and field sampling

The Monte Vulture volcanic area (fig. 1) is located on the eastern margin of the Apennine chain, in

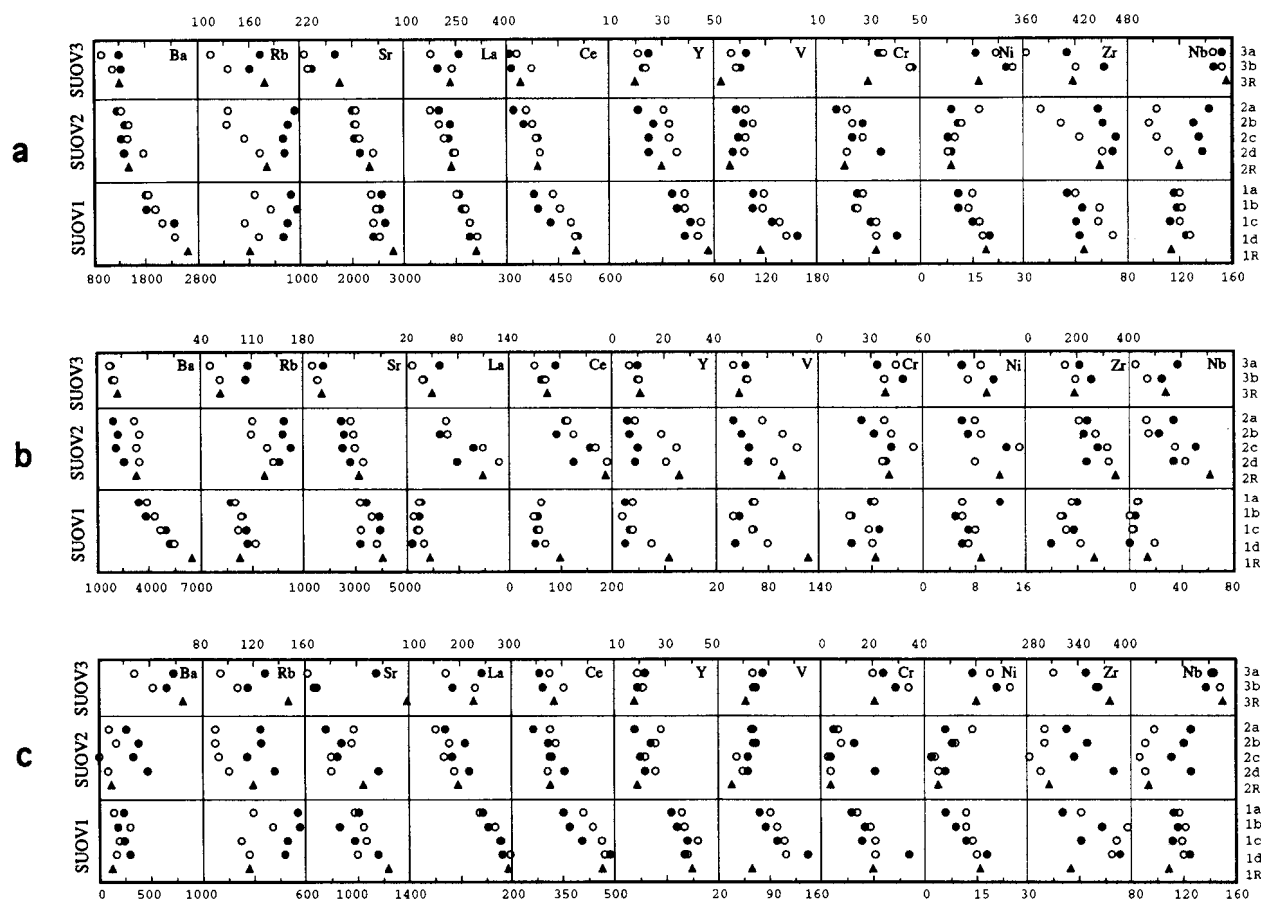


Fig. 3.—Distribution of the trace element contents (in ppm) of untreated samples (a) «residuum», (b) and «soluble», (c) (see text) along the sequence. (Triangles = basal level; filled circles = > 2,000 μm fraction; open circles = < 2,000 μm fraction).

southern Italy. It is a composite volcano, 1,327 m above sea level, lying on a sedimentary substratum mostly formed by flyschoid sediments. According to La Volpe and Principe (1994), the volcanic complex was built up in the middle Pleistocene and its climax occurred between 740 ka and 590 ka. The volcanic sequence started with phonotrachytic ignimbrites (Fara d'Olivo Unit) and followed with: Masseria Boccaglie Unit, made up of phonolitic tephritic and tephritic tephra; Rionero-Barile Unit, consisting of thin stratified pyroclastites; Monte Vulture-San Michele Tephra and Case Lopes-Masseria Granata Unit, made up of tephritic and phoiditic pyroclastites and lavas; Laghi di Monticchio Unit consisting of pyroclastic deposits having carbonatitic-melilititic composition. The pyroclastic levels described in this paper are from the Masseria Boccaglie unit.

The three paleoweathered pyroclastic units outcrop along a wall of the S. Antonio quarry (Rionero in Vulture, Potenza, Italy). The uppermost part of each level consists of brown and fine grained centri-

metric material. The higher level (SUOV3) and the intermediate (SUOV2) level lay one upon another whereas the intermediate level is separated, by some pyroclastic flows, from the lower one (fig. 2). The stratigraphic interval considered is 3.2 m thick.

Experimental methods

The samples were subdivided into two grain-size fractions (< 2,000 μm and > 2,000 μm), according to soil granulometric classification, which were subjected to a selective chemical dissolution with Na-pyrosulfate (Kiely and Jackson, 1965) to separate vitreous, amorphous or easily soluble minerals from those more resistant ones. X-ray powder diffraction analyses revealed that this chemical compound dissolved glass, phlogopite, analcite, calcite, allophane, Al-Si gels, Fe-Mn hydroxides and did not attack pyroxenes, feldspars, quartz, garnets, amphiboles, magnetite (hereafter called «residuum»), present in the studied materials. Quartz is sedimentary in origin and torn up from the flyschoid basement during the explosive activity (the products of Monte Vulture are undersaturated in SiO₂). The chemical composition of such dissolved material (hereafter called «soluble») was calculated subtracting the composition of the «residuum» from that of the untreated samples, taking into account the mass balance. Trace element contents were obtai-

Table 1a.—Trace element contents (in ppm) of the < 2,000 μm fraction (s), > 2,000 μm fraction (g) and basal level (R) of the untreated samples (see text)

Sample	Ba	Rb	Sr	La	Ce	Y	V	Cr	Ni	Zr	Nb
3a g	1284	173	1694	260	310	25	98	34	16	411	153
3a s	944	115	1095	180	331	21	81	36	22	364	146
3b g	1336	160	1243	200	315	23	92	47	25	454	147
3b s	1163	135	1154	241	376	24	86	46	27	421	153
3R	1309	179	1777	237	343	20	69	30	17	418	157
2a g	1254	214	2024	204	321	21	86	18	9	447	143
2a s	1325	135	2080	177	360	31	97	22	17	381	103
2b g	1400	206	2061	235	352	27	95	28	11	452	131
2b s	1476	133	2084	204	378	33	106	24	12	404	97
2c g	1328	200	2055	231	393	25	89	24	8	467	135
2c s	1453	154	2153	217	388	33	97	28	10	425	103
2d g	1389	202	2167	244	400	25	82	35	9	463	138
2d s	1751	172	2416	249	400	36	96	22	8	451	112
2R	1482	181	2352	240	393	30	79	21	9	449	120
1a g	1798	209	2575	260	381	34	106	26	11	411	116
1a s	1849	166	2371	252	437	39	119	28	15	420	120
1b g	1802	216	2539	268	394	36	105	25	11	428	118
1b s	1984	185	2469	278	457	39	117	26	14	448	122
1c g	2334	205	2640	292	429	41	128	31	15	421	113
1c s	2116	154	2417	290	488	45	137	33	17	447	120
1d g	2344	200	2416	291	508	39	158	41	20	425	125
1d s	2348	171	2535	313	501	44	145	33	18	463	128
1R	2601	160	2796	311	504	48	115	33	19	431	114

Table 1b.—Trace element contents (in ppm) of the < 2,000 μm fraction (s), > 2,000 μm fraction (g) and basal level (R) of the residuum (see text)

Sample	Ba	Rb	Sr	La	Ce	Y	V	Cr	Ni	Zr	Nb
3a g	1854	104	1786	59	90	10	55	34	6	208	37
3a s	1745	53	1375	27	49	7	41	45	9	153	5
3b g	1903	101	1550	41	62	10	56	49	11	253	25
3b s	2024	66	1525	39	70	10	56	38	7	193	14
3R	2224	67	1739	50	74	11	48	39	10	191	28
2a g	1948	154	2489	67	108	6	41	25	6	238	34
2a s	3174	110	2843	66	113	9	75	38	8	207	13
2b g	2247	152	2601	59	92	7	50	32	7	225	23
2b s	3450	109	2950	68	124	19	99	42	9	270	15
2c g	2098	163	2536	98	156	10	59	42	13	279	51
2c s	3300	131	3006	109	167	25	115	55	15	315	35
2d g	2589	148	2826	79	125	9	58	39	8	235	34
2d s	3453	139	3340	128	190	21	88	37	8	321	43
2R	3305	127	3160	109	187	26	98	41	12	346	62
1a g	3438	80	3436	37	62	5	63	30	12	198	7
1a s	3920	86	3188	34	61	8	65	32	6	177	6
1b g	3824	97	3946	34	54	4	47	19	5	143	4
1b s	4335	95	3650	28	46	4	40	18	6	135	0
1c g	4985	101	3957	32	52	7	64	35	7	185	3
1c s	4637	90	3233	31	57	8	62	29	8	155	2
1d g	5231	103	3210	26	49	5	42	19	6	97	0
1d s	5463	114	3830	40	69	15	80	31	7	212	19
1R	6497	93	4082	47	98	22	128	33	9	264	14

Table 1c.—Trace element contents (in ppm) of the < 2,000 μm fraction (s), > 2,000 μm fraction (g) and basal level (R) of the soluble (see text)

Sample	Ba	Rb	Sr	La	Ce	Y	V	Cr	Ni	Zr	Ng
3a g	721	141	1152	242	283	22	81	24	14	348	142
3a s	342	97	620	171	314	19	67	20	19	311	144
3b g	655	124	688	185	293	19	72	29	21	363	138
3b s	521	114	670	229	354	21	68	34	25	360	149
3R	816	164	1391	226	327	18	58	21	15	376	151
2a g	264	136	759	170	266	18	65	5	6	326	126
2a s	95	92	978	151	316	28	68	7	14	301	98
2b g	382	137	882	208	310	24	72	13	8	350	121
2b s	164	92	962	178	331	26	68	8	9	301	91
2c g	332	123	851	184	319	20	61	4	2	335	111
2c s	0	95	799	168	313	22	45	3	3	283	87
2d g	471	150	1165	216	356	22	61	21	6	380	126
2d s	83	105	803	187	308	26	53	4	4	296	91
2R	118	129	1048	195	316	19	39	4	4	306	94
1a g	237	173	1015	243	353	32	77	12	6	321	113
1a s	142	129	983	237	410	36	91	14	12	343	117
1b g	181	175	866	254	371	34	85	17	9	367	116
1b s	300	148	1051	267	439	37	101	19	12	396	122
1c g	242	163	979	279	407	38	101	16	12	343	112
1c s	190	117	1074	277	464	42	111	21	14	383	119
1d g	298	160	1161	281	489	37	142	34	18	387	125
1d s	163	125	1003	297	473	38	113	21	15	378	120
1R	129	125	1243	293	467	40	66	20	16	331	109

ned by X-ray fluorescence spectrometry (XRF, Philips® PW1410 apparatus) on pressed powder pellets and elemental abundance was computed by the matrix correction effect method, following the procedures suggested by Franzini *et al.* (1972; 1975) and Leoni and Saitta (1976). The analytical precision, checked on international rock standards, was better than 5 % for Ni, Cr, V, Rb, Sr, Y, Zr, Nb and than 10 % for Ce, La and Ba.

Results

The results of the chemical analyses carried out on the untreated samples for both grain-size fractions are given in table 1 and graphically represented in figure 3a. A variability is evident along a given pyroclastic level and among the levels. The data-points relative to SUOV1 and SUOV2 show clear trends; on the contrary SUOV3, formed only by few sublevels, doesn't exhibit tendency.

Ba, Sr, La, Ce, Y abundance increases towards the bottom of SUOV1 and SUOV2 levels and this tendency is decidedly more evident in SUOV1. The abundance of V, Cr, and Ni arranges in a similar way only in the SUOV1 level.

As for the two grain-size fractions, some splitting of the values is noticed: Rb contents are distinctly lower in the < 2,000 μm fraction of all the deposits; Zr and Nb are depleted in the < 2,000 μm fraction of SUOV2 whereas they are, or tend to be, enriched

in the same fraction of SUOV1; Ce and Y contents tend to be higher in the finer fraction. Interestingly, in the finer fraction Rb, Zr and Nb increase downward in SUOV2.

Again in figure 3a, we observe that some elements, such as Ba, Y, Ce, La, Sr, progressively decrease in their abundance upward from the bottom (SUOV1R) of the lower level to the upper part (SUOV3a) of the higher level.

Figure 3b and figure 3c illustrate, respectively, the distributions of the elements determined in the «residuum» and those calculated for the «soluble» after the attack with Na-pyrosulfate. Numerical values are given in tables 1b-c. Ba and Sr in the «residuum», composed by px, Kf, pl, qtz and accessory phases, mimic the behaviour of the untreated samples both in a single level and in the entire sequence. Cr and Ni were enriched in the «residuum» of SUOV2 and did not vary in the SUOV1 and SUOV3. The other elements here considered are concentrated mostly in the «soluble» of the three pyroclastic levels.

Data analysis and conclusions

As discussed in Fiore *et al.* (1992), the vertical variations along the examined pyroclastic levels

Table 2.—Mineralogical composition of the < 2,000 μm fraction (s), > 2,000 μm fraction (g) and of basal level (R). Data from Fiore *et al.* (1992)

Sample	Px	Kf	Pl	Qz	Phl	Anl	Cal	Σ
1a s.....	6	24	4	10	3	6	1	54
1b s.....	4	26	4	5	2	12	1	54
1c s.....	6	24	4	8	3	5	tr.	50
1d s.....	6	27	3	4	2	6	0	48
2a s.....	7	22	2	8	2	4	4	49
2b s.....	8	22	1	6	1	4	5	47
2c s.....	11	28	3	4	2	4	3	55
2d s.....	10	35	tr.	3	2	4	1	55
3a s.....	4	10	3	18	2	3	1	41
3b s.....	4	11	4	13	3	4	tr.	39
1a g.....	6	29	5	5	2	12	1	60
1b g.....	4	30	5	3	2	15	0	59
1c g.....	6	28	4	4	4	10	2	58
1d g.....	4	27	5	4	3	7	0	50
1R.....	9	23	3	3	3	7	8	56
2a g.....	5	36	6	5	1	4	1	58
2b g.....	6	33	3	4	2	5	1	54
2c g.....	6	31	7	3	3	4	2	56
2d g.....	5	28	1	1	3	6	4	48
2R.....	10	29	0	3	2	4	5	53
3a g.....	3	16	3	8	2	4	37	37
3b g.....	4	17	3	12	6	5	tr.	47
3R.....	2	10	2	7	3	5	6	35

Px = pyroxene; Kf = feldspar; Pl = plagioclase; Qz = quartz; Phl = phlogopite; Anl = analcite; Cal: calcite; tr. = trace; Σ = summation.

depend on: (i) syndepositional mineralogical variations along a level and among the diverse levels; (ii) effect of weathering in a given level before the next volcanic products was deposited; (iii) influence of magmatic fluids or of the water table after the deposition of the sequence.

In the study case, the increase of some elements from the upper sublevel to the lower one gives the idea that the alteration effects are induced by water freely moving downward through the sequence. Indeed, the cause of such a variation cannot be ascribed to water alteration.

To test the influence of minerals on abundance and distribution of trace elements in the pyroclastic flow deposits under study, R-mode factor analysis with VARIMAX rotation was performed between trace elements and mineral contents of the «residuum» (table 2; data from Fiore *et al.*, 1992). Obviously, the factors will join to the minerals considered in the statistical analysis also the elements entering the crystal lattice of coexisting accessories.

Factor analysis shows that three factors account for 88 % of the total variance (table 3) and that: (i) the first factor (F1) is controlled by Y, V, Zr, Cr, Ce, Ni and pyroxene contents; (ii) the second factor (F2) corresponds essentially to K-feldspar together with Rb, La, Nb and Ce; (iii) the third factor (F3) likely links K-feldspar to Sr and Ba. K-feldspar and quartz are negatively correlated in both the cases, because of the sedimentary origin of quartz and the magmatic origin of K-feldspar.

The presence of K-feldspar in F2 and F3 may be related to the different chemical composition of this mineral. Microscopic observations and chemical analyses (carried out by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer) pointed out the presence of two types of K-feldspar. One of them has a very high content in barium, both in the same level and in distinct levels. On the other hand, the presence of crystals of sanidine having different Or-percentage was already documented (De Fino *et al.*, 1986) in the lowermost magmatic products cropping out in the Monte Vulture volcanic area. The sanidine richer in Ba prevails in the lower level (SUOV1) of the examined sequence.

Plots of F1-F3 and F2-F3 are shown in figure 4a and figure 4b respectively. It emerges that the three levels examined are clearly discriminated by F3. Furthermore, it is relevant that the deepest level (SUOV1) is characterised by the highest positive value for F3 that, in turn, gradually decreases going upwards in the sequence. In addition, the ability of

Table 3.—R-mode factor analysis between minerals of the «residuum» and trace elements

	F1	F2	F3
Y.....	0.940	0.144	0.077
Px.....	0.916	0.117	0.326
V.....	0.907	0.017	0.359
Zr.....	0.806	0.502	-0.184
Cr.....	0.726	-0.064	-0.573
Ce.....	0.698	0.657	-0.147
Pl.....	-0.673	-0.237	-0.106
Ni.....	0.669	0.090	-0.312
Rb.....	0.120	0.941	0.032
Kf.....	-0.046	0.800	0.564
Qz.....	-0.100	-0.726	-0.647
La.....	0.637	0.698	-0.206
Nb.....	0.478	0.685	-0.429
Sr.....	0.074	0.177	0.953
Ba.....	0.109	-0.208	0.935
V(%).....	38.56	25.81	23.20

Bold number indicate the higher statistical charges. V(%) = explained variance. Symbols as in table 2.

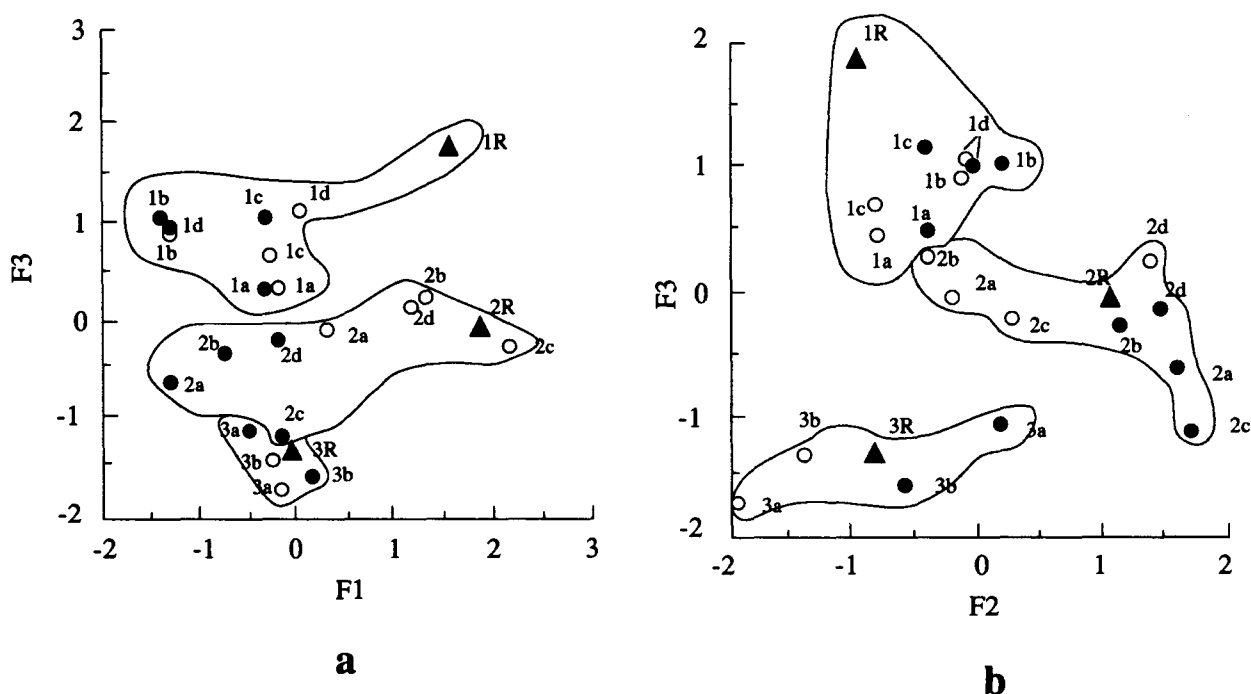


Fig. 4.—Plots of F1 and F2 versus F3 showing the discrimination induced by the F3-factor. Field-line is arbitrary. Symbols as in figure 3.

F1 to discriminate the grain-size fractions suggests the coexistence of two pyroxenes, different in chemical composition, within the deposits. This interpretation is supported by literature data (e.g. De Fino *et al.*, 1986; Caggianelli *et al.*, 1990) indicating the presence of chemically different phenocrysts of pyroxenes in the lowermost Monte Vulture volcanics, just under the deposits here studied.

The mineralogical variations are not confined to a given sublevel. A chemical variation related to the stratigraphic position of the sublevels within the pyroclastic sequence is evident. Simple linear correlation between depth and abundance of Ce, La, Ba, Sr and Y indicate, with a level of significance $\alpha < 0.001$, that the elemental decrease within the three levels is not casual. This variation, because of its regularity, seems to suggest some primary features of the deposit.

To point out any relation between the behaviour of trace elements and the products of alteration, another factor analysis was performed. This analysis was necessarily restricted to the $< 2,000 \mu\text{m}$ fraction in which the weathering products are concentrated. A first analysis (results not given) showed that both calcite and phlogopite don't give any contribution to the variance; therefore, to constrain the system, these two variables were excluded and the statistical analysis recalculated. The results

(table 4) show that the four factors account for 89 % of the total variance and that there are no relationships between chemical elements and gels and allophane. Among the four factors, F1 calls for attention because of the negative weight of Rb and glass. This feature might be explained in two ways; (i) Rb contents reflects original feature and this element may be concentrated in the dissolved minerals and/or in glass or (ii) Rb is the only trace element mobilised from glass during the earliest stage of weathering. The first hypothesis is suggested by the similarity of the Rb contents in the products here studied and those of the trachytic-phonolitic volcanics of the Monte Vulture (De Fino *et al.*, 1986 and references therein). The second hypothesis is also possible, as suggested by the linear correlation between H₂O and Rb in the whole rock ($r = 0.775$; $\alpha < 0.001$). The geochemical affinity of Rb for K, which was mobilised from glass (Fiore *et al.*, 1992), supports this interpretation. The available data, however, do not remove the ambiguity.

The second factor (F2) refers to the elements that were associated with the pyroxene in the previous statistical analysis; F3 clusters Nb, Cr, Ba, Ni, Zr and H₂O⁺; F4 is determined by Sr and, with a lower statistical weight, by Kf. The available data do not permit to establish the causes that determined the grouping of the F3. Nevertheless, the con-

Table 4.—R-mode factor analysis between phases of the «soluble», structural water and trace elements of the < 2,000 µm fraction

	F1	F2	F3	F2
All.....	0.963	-0.038	-0.026	-0.103
Glass.....	-0.923	-0.072	0.181	0.127
Gels.....	0.920	-0.114	-0.259	-0.066
Rb.....	-0.855	0.346	-0.124	-0.065
H ₂ O.....	0.659	0.028	0.564	-0.273
Y.....	0.043	0.965	-0.145	0.037
Ce.....	0.018	0.937	0.076	0.217
La.....	-0.329	0.850	0.219	0.183
V.....	-0.050	0.829	0.326	-0.050
Anl.....	-0.487	0.588	-0.259	-0.465
Nb.....	-0.272	-0.084	0.916	-0.031
Cr.....	-0.113	0.375	0.873	0.037
Ni.....	0.256	0.259	0.859	-0.032
Ba.....	-0.372	-0.350	0.787	0.176
Zr.....	-0.431	0.503	0.586	0.149
Sr.....	-0.307	0.364	-0.018	0.789
V(%).....	29.75	27.67	24.91	6.81

Bold number indicate the higher statistical charges. All = allophane; Anl = analcite; V(%) = explained variance.

tribution of the primary chemical signature in the pyroclastics here studied seems to be of importance. Indeed, in the SUOV1 Rb, as well as La, Ce, Y, and Nb are more concentrated in the amorphous fraction that consists of vitric components and its derivative (allophane, Si-Al gels). Instead, in the SUOV2, Rb is concentrated in the minerals of the «residuum» that are more abundant than in SUOV1 and in SUOV3. On the other hand the overall values of Rb contents are quite similar to those of chemically comparable products of Monte Vulture (De Fino *et al.*, 1982).

The data obtained clearly imply that the minerals of the «residuum», and sometimes the glass, play a dominant role in controlling the distribution of the trace elements both in distinct levels and in the two grain-size fractions of the same level. Therefore, it appears that, notwithstanding the important loss of sodium from glass (Fiore *et al.*, 1992), the distribution of the trace elements in the pyroclastic sediments, affected by an early stage of weathering, essentially reflects inherited characteristics. This conclusion is apparently in disagreement with the results of Price *et al.* (1991) who point out and enrichment in Ba-content for basalts affected by an «early stage of weathering». The rocks here studied are decidedly less altered than those studied by Price *et al.* (1991), who reported mineralogical transformation (e.g. olivine → «iddingsite»), indicating a more advanced stage of alteration. The problem then becomes of what to mean as «early

stage». In this respect, it is suggested that the first stage of weathering should be considered as the one characterised by partial dissolution of glass (if present), local dissolution of primary minerals and without their transformation, precipitation of alumina and silica gels, possible neoformation of protominerals (e.g., allophane, imogolite).

The data presented in this paper show that the earliest stage of alteration of the pyroclastic deposits examined did not substantially influence the distribution of Ba, Ce, La, Ni, Cr, V, Rb, Sr, Y, Zr, Nb. This absence of variation of trace element abundance coexists with the presence of neoformed phases (allophane, gels) originated by weathering. This implies that neoformation occurred with very small modifications in trace element contents, undetectable by this approach. The gradual variations of the abundance of the trace elements here determined reflects original characteristics of the pyroclastic rocks. A direct consequence of the geochemical variability evidenced in a few meters thick sequence is that interpretation of behaviour of elements during intense weathering of pyroclastic flow deposits should be done with a particular attention, because original chemical variation and modification induced by weathering might overlaps.

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