

Mineral chemistry of perpotassic lavas of the Vulsinian district, the Roman Province, Italy

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SYNOPSIS

THE Vulsinian district is the largest and northernmost of the Roman Provinces. There is very little modern mineralogical data on the Italian Pliocene to Recent perpotassic alkaline volcanic rocks and this account deals with the compositions of the phenocrysts in the Vulsinian lavas.

The lavas comprise two suites: a leucite-bearing undersaturated series of leucitites, leucite tephrites, leucite phonolites, and trachytes; and a subordinate hy-normative series of mainly trachytes and latites. All lavas are porphyritic with mostly 1-15 vol. % phenocrysts. No cumulates were found. Major elements, and Cr and Ni were determined in the phenocrysts by microprobe analysis and more than 20 trace elements were determined on mineral separates by PIXE.

The undersaturated suite. Ubiquitous clinopyroxene phenocrysts belong to the Di-Hed_{ss} series and range from Di₉₇ to Di₄₆. Important amounts of Fe³⁺ are always present. In the mafic rocks the diopside is chromian, but Ti is low. Al mainly substitutes in the Z positions in all lavas. Only minor Na enrichment occurs with increasing total Fe (0-7 mole % acmite) and thus Ca ferri-Tschermak's component is important. In many of the mafic lavas diopside mantles green cores of salite, which has a composition very like the salite of felsic lavas. Leucites contain 5-22 mole % orthoclase in solid solution, but show no systematic variation. Plagioclase, mostly An₉₃-An₇₂, occurs in the felsic lavas, and alkali feldspar only in some phonolites. They both have exceptionally high concentrations of Sr and Ba, with a maximum of 1.3 wt. % SrO and 5.6 wt. % BaO in hyalophanes. Olivine, Fo₉₂-Fo₆₆, occurs in some leucitic lavas

in mostly accessory amounts. Phlogopite, magnetite and nepheline are accessory phases of the felsic lavas. Apatite only occur as micro-phenocrysts of the felsic lavas. Häüyne in trace amounts is found in a few phonolites. Pargasitic amphibole micro-phenocrysts are found in one lava.

In most mafic members diopside ± leucite ± olivine were liquidus phases. This study does not confirm that these rocks are related by crystal fractionation. In more felsic lavas clinopyroxene (salite-ferrosalite) and leucite are joined by: plagioclase, magnetite ± phlogopite, and Ba-rich alkali feldspar ± häüyne. The felsic rocks are thought to be related by crystal fractionation.

Salitic green cores of phenocrystic pyroxene, mantled by diopside in rocks which also carry normally-zoned diopside, are relicts which provide evidence of either a relatively high P_{H₂O} prior to the crystallization of diopside or magma mixing in the earlier life of these lavas. Pyroxene chemistry points towards low-pressure crystallization (2 kbar), generally in a dry environment.

The hy-normative suite. All lavas have phenocrysts of augite, sanidine, plagioclase, magnetite, biotite, and olivine. The pyroxene is less calcic and has less alumina, but is otherwise rather similar to the salites of the undersaturated suite. Compared to the undersaturated suite, feldspars do not have high Sr and Ba, magnetite has higher TiO₂ and olivine crystallized from even the felsic lavas. The pyroxenes show the signs of low-pressure crystallization.

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MINERAL CHEMISTRY OF PERPOTASSIC LAVAS OF THE VULSINIAN DISTRICT.

THE ROMAN PROVINCE.

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The Vulsinian District (Fig. 1) lies at the northern extremity of the Italian Pliocene to Recent perpotassic alkaline volcanic province and is by far the largest district of this province, covering 2280 km² (Fischer, 1970). Although the Roman Comagmatic Region was made famous by Washington (1906), his classical petrographic work has not been brought up to date, and modern mineralogical data are sparse. Recent papers by Vollmer (1975, 1976, 1977), Turi and Taylor (1976) and Taylor and Turi (1976), considered the implications of the isotope geochemistry on a regional scale and pointed out the need for more detailed petrological work. Cundari and Mattias (1974) made a petrochemical study and Cundari (1975) a mineralogical study of the rather small Vice volcano, which borders the Vulsini district to the south. Recent studies of the Vulsinian district include those of Scheider (1965 - detailed mapping major element chemistry and petrology of lavas from Latera in the western part of the district), Mattias (1965 - similar studies of lavas + the south-eastern part) and Sparks (1975 - stratigraphy of the pyroclastics).

This paper presents part of an investigation of the lavas of the eastern and northern parts of the district and concentrates on the compositions of the minerals. Subsequent contributions will deal with petrochemistry and petrogenesis of the lavas (Holm, Lou and Nielsen, in prep.) and trace element contents of the minerals (Holm and Lou, in prep.). Phenocryst phases were analysed in a number of representative rock specimens, which were selected from a much larger collection.

Petrographic Summary

The lavas comprise two suites: 1) a predominant normatively undersaturated perpotassic, metaluminous, basic to intermediate suite and 2) a slightly oversaturated, hypersthene-normative, perpotassic, metaluminous, trachytic suite.

The undersaturated rocks are: tephritic leucites, leucite tephrites, phonilitic leucite tephrites, tephritic leucite phonolites, leucite phonolites and one very felsic tephritic leucite, using the nomenclature of Streckeisen (1967). Table 1 gives phenocryst modes of the main types of lavas. Diopside and leucite are the main phenocryst phases of the basic undersaturated lavas, while olivine may be an accessory phenocryst phase, and phlogopite is present in some rocks as microphenocrysts. In the less

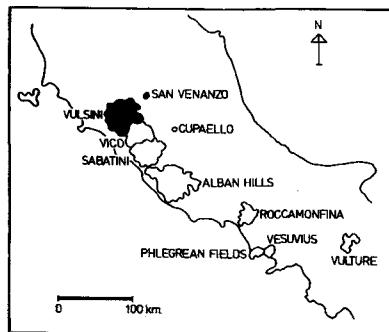


Fig. 1. Map of central and southern Italy showing important alkaline volcanic districts on the mainland. The Roman Province consists of the districts of Alban Hills, Sabatini, Vico and Vulsini, and the two small excentric centres of San Venanzo and Cupaello.

basic rocks plagioclase and Fe-Ti-oxide are present as additional phenocryst phases, and olivine is not seen. In the felsic rocks of this suite leucite, plagioclase and sanidine with accessory salite to ferrosalite, dark mica, nepheline, magnetite and rarely hauyne are the phenocryst phases. The basic rocks have a groundmass predominantly of diopside and leucite with accessory magnetite, plagioclase and dark mica. In the more felsic rocks plagioclase is the most important groundmass constituent with accessory amounts of clinopyroxene, dark mica, sanidine magnetite, and varying amounts of leucite.

Phenocrysts of sanidine, plagioclase, augite, olivine, biotite and magnetite are common to the rocks of the hy-normative suite while the groundmass consists mainly of sanidine. The lavas are mainly trachytes with a few tephrites.

The lava, 30670, has close mineralogical and geochemical affinity to the Radiofant lavas (Fischer, 1970) of the Tuscan Province. It is a latite with 12% olivine and accessory augite and biotite with xenoliths of sediments, gabbroic rocks and dunite as well as xenocrystal tridymite.

Table 1
Phenocryst modes of typical Vulsinian lavas (volume %, >1000 points)

D.T.*	TEPHRITIC LEUCITE	LEUCITE TEPHRITE	TEPHRITIC LEUCITE	LEUCITE PHONOLITE	SATURATED TRACHYTE
	(30601)	(30612)	(30632)	(30661)	(30664)
	31	52	73	82	80
diopside	5	+		+	
salite	+	2	3	4	
augite					+
olivine	5				+
mica		1	+	+	+§)
magnetite			2	+	5
leucite	+	1	7	13	
plagioclase		4	3	2	4
sanidine			+	14	22
others					parasite hauyne
(<1 vol %)					
major constituents	diopside leucite	salite leucite	plagioclase leucite	sanidine leucite	sanidine plagioclase
			plagioclase salite		

+) present - less than 1 vol %.

§) most mica resorbed and present in table as magnetite.

*) Thornton-Tuttle differentiation index (Thornton & Tuttle, 1960)

Analytical Methods

The major elements together with Cr and Ni were determined by point analysis of polished thin sections by electron microprobe, partly using a Microscan 9 at Oxford University and partly a Hitachi XMA-5b at the University of Copenhagen. The Microscan 9 was operated at 20 kV and a sample current of 20 nA, the Hitachi at 15 kV and 20 kV or occasionally at 10 kV with a defocused electron beam (for nepheline and hauyne). Natural minerals were used as standards. The oxidation state of iron in some minerals was determined by the Wilson method (Maxwell, 1968).

Trace element analysis of very pure (at least more than 99 %) minerals, separated by standard methods and finally purified by handpicking, was carried out by Proton Induced X-ray Emission (P.I.X.E.) analysis at the Niels Bohr Institute, University of Copenhagen, using an accelerating voltage of 3 MeV. The method and results will be reported in more detail in a forthcoming paper Holm and Lou (in prep.). A few analyses of minerals using 10 μg samples were made on a Hilger Quartz Spectrograph. The method is described in Bollingberg and Bryhni (1972).

Clinopyroxene

In hand specimen clinopyroxene varies from green to black in colour, and in a thin section is colourless to pleochroic in shades of light green, yellow-green and grass-green. Oscillatory and sector zoning is ubiquitous. Some phenocrysts in the leucitic and tephritic lavas have two components: a green, sub- or euhedral inner part is surrounded by a clear or light green rim, very similar to pyroxenes from other alkaline rocks reported by Brooks and Prinzlau (1978). In some phonolites the reverse is found. Usually the green cores make up more than 90% by volume of the phenocrysts. This is thought to mean that the growth of the rim took place in a short time interval subsequent to the growth of the green cores. Absence of growth on fragmented phenocrysts with green cores indicates that the rim did not crystallize metastably (Thompson, 1974) after eruption. The rocks containing cored pyroxenes also always include some without green cores.

Representative analyses, structural formulae and calculated solid solution end-members (Kushiro, 1962) for the pyroxenes are presented in table 2. The formulae are calculated assuming stoichiometry on the basis of 6 oxygen ions. Often, a large correction for ferric iron is necessary to obtain 4 cations. It may be noted that a good correlation between total Fe and excess cations exists before correction, and that notable amounts of Fe³⁺ were confirmed by wet chemical analyses of mineral separates. Thus diopside in specimen 30601 contains 1.63 wt. % Fe₂O₃ and 1.95 wt. % FeO, and salite in 30672 has 4.9 wt. % Fe₂O₃ and 4.2 wt. % FeO. Pyroxene compositions are plotted in the molecular Mg-Ca-(Fe+Mn) diagram (Foldervaart and Heas, 1951) in figure 2.

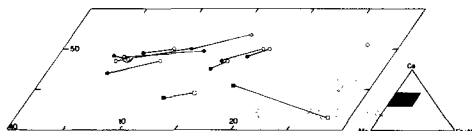


Fig. 2. Compositions of the pyroxenes of table 2 plotted in the pyroxene quadrilateral. Lines connect analyses of the same phenocryst. Open symbols are rim, closed symbols cores. Circles are phenocryst from undersaturated lavas, diamonds are green cores in these phenocrysts; squares are phenocryst from saturated trachytes.

All pyroxenes of the undersaturated suite are members of the diopside-hedenbergite solid solution series, ranging from diopside to salite and ferrosalite (di₉₇-di₁₆). The green cores of the two-component pyroxene

Table 2
Representative clinopyroxene analyses for major and trace elements.

rock type	TEPHRITIC LEUCITITES										TEPHRITIC PHONOILITES				TEPHR. LEUCITE	SATURATED TRACHYTES					
	core	rim	core	rim	core	inner	outer	core	rim	core	rim	core	rim	rim	core	rim	core	rim	microph		
sample no.	30601	30601	31337	31337	31337	31337	30682	30682	30682	30682	30632	30632	30634	30634	30633	30669	30669	30664	30664	30670	
SiO ₂	52.6	50.1	53.4	53.5	47.6	46.3	52.0	50.3	48.7	48.3	52.0	49.8	47.2	47.4	47.3	42.1	50.8	50.4	51.3	50.8	51.7
Al ₂ O ₃	2.13	4.08	1.71	2.12	6.11	7.2	1.79	4.18	5.97	6.02	3.01	4.08	6.3	5.88	6.2	8.2	2.99	3.13	1.53	1.22	.86
Fe ₂ O ₃ *	2.6	3.8	.72	1.5	6.5	5.9	2.5	3.9	4.8	5.3	2.3	3.4	5.3	6.2	4.7	10.9	1.9	2.4	2.0	1.6	.03
FeO	1.2	2.0	2.7	2.7	1.7	4.1	1.00	1.2	4.7	3.4	1.9	5.8	4.4	4.4	6.2	5.9	6.2	6.6	8.6	15.1	12.1
MgO	17.2	15.1	16.6	16.2	13.1	10.	16.9	15.2	11.1	12.9	15.9	13.0	12.2	11.5	10.4	7.2	14.8	14.0	13.1	10.4	10.0
CaO	24.0	23.9	24.6	24.7	24.3	24.3	24.8	24.7	23.3	23.6	24.5	23.1	23.2	23.3	23.0	22.9	21.6	21.8	22.8	20.0	24.5
Na ₂ O	.11	.13	.05	—	.33	.22	.15	.12	.40	.35	.13	.22	.22	.48	.63	.83	.17	.27	.22	.13	.04
MnO	.07	.13	.06	—	.14	.5	.06	.45	.34	.07	.25	.18	.37	.38	.19	.19	.22	.22	.15	.22	.12
TiO ₂	.25	.43	.23	.51	.94	.59	.23	.41	.83	.34	.29	.48	.74	.77	1.32	2.05	.68	.70	.68	.87	.04
Cr ₂ O ₃	.29	4	.10	5	5	4	.19	—	—	—	—	—	—	—	—	—	—	—	—	—	—
sum	100.3	99.7	100.2	100.2	100.6	99.9	99.6	100.0	99.8	100.6	100.1	100.1	99.8	100.3	100.3	100.4	99.2	99.4	100.2	100.4	99.6

* corrected assuming stoichiometry. † below LLD: Cr₂O₃ = .04, MnO = 0.6

Structural formulae on basis of 6 oxygen ions and assuming stoichiometry.

Si	1.911	1.850	1.947	1.918	1.761	1.742	1.908	1.848	1.792	1.782	1.900	1.857	1.772	1.777	1.779	1.624	1.910	1.949	1.928	1.949	1.980
Al ^{iv}	.088	.149	.052	.081	.238	.257	.077	.151	.220	.217	.099	.142	.227	.222	.220	.314	.089	.050	.068	.050	.019
Al ^{vi}	.003	.028	.020	.010	.028	.061	.000	.030	.040	.061	.030	.037	.051	.038	.057	.000	.020	.005	.000	.005	.019
Fe ³⁺	.070	.106	.039	.042	.181	.186	.056	.106	.133	.147	.082	.094	.150	.175	.134	.316	.058	.046	.052	.046	.019
Fe ²⁺	.035	.060	.081	.081	.053	.130	.040	.036	.056	.093	.059	.180	.139	.137	.196	.189	.220	.485	.271	.485	.588
Mg	.910	.834	.902	.885	.722	.614	.924	.832	.826	.703	.888	.725	.682	.643	.589	.418	.751	.595	.732	.595	.771
Ti	.007	.012	.006	.014	.026	.022	.006	.011	.016	.017	.008	.014	.021	.022	.037	.059	.012	.028	.021	.028	.001
Mn	.002	.004	.002	—	.004	—	.002	.003	.006	.002	.002	.008	.006	.012	.012	.006	.004	.006	.006	.004	.007
Cr	.008	.003	—	—	—	—	.005	.005	.005	—	—	—	—	—	—	—	—	—	—	—	—
Ca	.933	.947	.909	.966	.964	.982	.976	.966	.942	.976	.923	.931	.845	.929	.946	.904	.826	.917	.823	.907	.823
Na	.008	.010	.004	—	.024	.016	.011	.009	.010	.027	.009	.016	.016	.035	.046	.062	.018	.010	—	.010	.003

Solid solution end-members calculated after Kushiro (1962), Cr included in Fe³⁺

acmite	.9	1.0	.4	—	2.4	1.6	1.1	.9	1.1	2.8	1.0	1.7	1.7	3.6	4.7	6.3	1.1	1.3	.7	1.5	.4
CaAl ₂ Si ₂ O ₆	.7	1.2	.7	1.4	2.6	2.2	.7	1.2	1.6	1.8	.8	1.4	2.1	2.2	3.8	6.0	1.9	2.2	.0	.5	.1
Ca-Tschermak	.4	2.8	2.3	1.1	2.8	6.3	.0	3.0	5.2	6.2	3.1	3.7	5.1	3.8	5.7	.0	2.7	2.9	.3	.0	1.7
Ca-ferri-T	.0	.0	.0	.0	.0	1.3	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	4.9	3.4	.0
CaFeAlSi ₂ O ₆	7.0	9.7	1.9	4.2	15.7	15.1	3.8	9.8	12.3	12.0	5.2	7.8	13.4	14.0	8.8	25.2	4.0	5.2	29.4	51.4	.0
hedenbergite	3.8	6.5	8.4	8.2	5.3	13.6	4.2	3.9	6.0	10.0	6.2	18.9	14.6	14.9	20.9	19.6	19.9	21.6	36.5	26.4	39.6
diopside	81.5	74.5	82.9	81.8	69.9	61.2	88.3	79.2	71.5	64.3	80.6	60.7	57.9	58.6	53.8	41.8	57.8	54.4	8.0	16.6	37.1
willastonite	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	1.1
enstatite	5.8	4.3	3.7	3.4	1.1	.1	0.0	2.0	2.3	3.0	3.1	5.9	5.2	2.9	2.4	.0	12.4	12.7	5.6	4.6	.0
Mg/(Mg+Fe)	.90	.83	.90	.88	.76	.67	.91	.85	.77	.75	.88	.73	.70	.67	.64	.45	.77	.75	.69	.53	.59

*) normal zoned phenocryst

*) includes jadeite

**) phenocryst with green core (see text for explanation).

phenocrysts are salites of similar composition to the salites of the more felsic undersaturated lava-types, e.g. the green core of 31337 and the core of 30634 of table 2. The pyroxenes show the following features:

- Al, Ti, Mn, Na, Sr, Zr, Y, La and Ce increase with decreasing Mg.
- Acmite never exceeds 7 mole %, which is rather low compared with pyroxenes in many other alkaline provinces (Larsen, 1976).
- 3-18 atom % Al substitutes for Si in the Z positions, which leaves only small amounts of Al for the octahedral positions; thus the calculated amount of Ca-Tschermak's component is relatively low (<2-9 mole %). For pyroxene rim/groundmass pairs the Al-substitution in the tetrahedral sites appears to correlate with the alumina activity of the lavas or the differentiation index (i.e. D.I. of Thornton and Tuttle, 1960) rather than with the normative degree of undersaturation (LeBas, 1962). Thus the Al(IV) is compensated by ferric iron in the Y-position so that the CaFeAlSi₂O₆ molecule ranges from 0 to 25% of the pyroxenes thus becoming a major constituent.
- The Ti contents of the Vulsini pyroxenes are lower than those of pyroxenes in many alkaline igneous rocks. This probably reflects, as is the case for Na, the rather low concentration of this element in the host rocks: 0.8-0 wt % TiO₂ (and 0.7-3.4 wt % Na₂O). The Ti-trend of the rims of the pyroxenes is in contrast to the trend for the host liquids. It seems to be coupled with the Al(IV) content of the pyroxenes, which is controlled in turn by the availability of Al in the melt. Leucitic lavas often have diopside phenocrysts with 0 wt % Cr₂O₃, and in one instance a chrome diopside had 2.2 wt % Cr₂O₃. In table 2 both point analyses and analysis of separated chromian diopside from tephritic leucitite 30601 are shown. Pyroxenes of the hy-normative series are augites with low alumina and lower CaO and TiO₂ than the pyroxenes of the felsic undersaturated lavas. This probably reflects the higher silica-activity in the saturated lavas, and this is even more pronounced in the augite of the latite of Torre Aifina, 30670.

Olivine

In one tephritic leucitite (30601) 3% olivine is present and Washington (1966) describes a leucite basanite with 16% olivine from Fiordine. These examples appear to be rare exceptions to the general paucity of olivine in the undersaturated lavas of the district. Accessory or trace amounts of olivine phenocrysts are present in some of the basic rocks of the undersaturated suite, but olivine is absent in the felsic undersaturated rocks. Olivines occur as euhedral or embayed, fresh crystals up to a few mm in size and may form glomeraggregates. Chromite is a common inclusion. In some cases olivine is jacketed by pyroxene. Accessory amounts of olivine always occur as phenocrysts in the lavas of the trachytic suite. Representative analyses and structural formulae are presented in table 3 together with trace element contents in two mineral separates. Ca in the olivines presented here correlate with the Ca in the rocks. This corresponds with the results of Watson (1979), and indicates that

TEPHR. LEUCITITE	LEUCITE TEPHRITES		LEUCO-LEUCITITE
	DIOPSIDE 30601	SALITE 30672 31474	FERROSALITE 30633
V	250	270	442
Cr	40	—	—
Ni	276	—	—
Cu	30	26	40
Zn	56	37	129
Fe	26	23	31
As	1.7	4.1	10
Rb	5	15	10
Sr	201	684	407
Y	5	10	74
Zr	33	734	530
Nb	12	—	15
Sn	16	15	21
Ca	128	61	77
Na	40	27	97
Ce	169	107	254
FeO	2.92	8.50	8.18
total	—	—	15.40

Clinopyroxene separates

Below detection limit:

Se, Mo, Cd, Sb and as shown in table.

the olivines equilibrated with their host liquids. The effect of Ca-content of the liquid will probably obscure the effects of pressure and silica-activity on the Ca-content of the olivines. The olivine of the most basic undersaturated lavas and the lava of Torre Aifina (30670) have Fe³⁺₈₉₋₉₂ and high Ni contents which indicate that these may be nearly primary magmas. The olivine of the trachytic suite are fayalite rich reflecting the high Fe/(Mg+Fe) of these magmas. The forsteritic olivine of the Torre Aifina lava is very unlike other olivines of the saturated lavas indicating that this lava differs from the other lavas of the district.

Mica

Phlogopite and biotite are found as rare phenocrysts in the phonitic lavas, the felsic leucite tephrites and the hy-normative lavas. Usually they show resorption caused by the decreasing % H₂O during degassing of the magmas. Pseudomorphs are mainly aggregates of magpseudite. Phlogopite is red-brown in thin section and is mostly a microphenocryst phase. Biotite is brown with stronger pleochroism and anomalous interference colours. Dark mica occur in small amounts in the groundmass of most lavas.

Partial analyses of mica are presented in table 4 with structural formulae calculated on a volatile-free basis. About a third of the Z-position is occupied by Al, but very little Al is present in the Y-position. Al in Z is balanced by ferric iron in Y. The incompleteness of the microprobe analyses prevents an estimation of the ferric iron contents. Iron was determined in a phlogopite separated from trachyte 31474 as 10.2 wt. % Fe₂O₃ and 3.2 wt. % FeO. In the X-sites, Na and Ba substitute for K, the former in small amounts, the latter often in significant amounts. Ti shows a wide range of concentrations, which in general does not reflect the rather low TiO₂ contents of the lavas. Trace element analyses show that V, Rb and Cs are also present at relatively high levels.

Table 3

Representative olivine analyses for major and trace elements.

rock type	TEPHRITIC LEUCITITE		LEUCITE TEPHRITES				SATURATED TRACHYTES			
			core		rim		core		rim	
	30601	30601	31475	31475	30682	30682	30684	30684	30670	30670
SiO ₂	41.3	40.8	40.8	40.6	39.2	37.8	32.9	33.1	41.3	40.8
FeO*	8.2	10.0	9.2	11.7	19.0	27.7	52.1	51.1	8.2	10.0
MgO	49.8	47.5	49.9	46.0	41.6	35.0	13.9	14.6	50.2	47.8
CaO	.55	.66	-	.49	.50	.43	.26	.26	-	-
MnO	-	-	-	.24	-	-	-	-	-	-
Cr ₂ O ₃	.5	.08	-	-	-	-	-	-	-	-
sum	99.9	99.0	99.9	99.1	100.3	100.9	99.2	99.1	99.7	99.1

Structural formulae calculated on the basis of 4 oxygen ions.

Si	1.005	1.011	.998	1.014	.999	.999	1.010	1.011	1.005	1.009
Fe ²⁺	.188	.207	.189	.245	.406	.611	1.336	1.306	.168	.217
Mg	1.807	1.752	1.816	1.712	1.582	1.582	.635	.663	1.822	1.785
Ca	.014	.018	-	.013	.014	.012	.009	.009	-	-
Mn	-	-	-	.005	-	-	-	-	-	-
Cr	.002	-	-	-	-	-	-	-	-	-
sum	2.994	2.989	3.002	2.990	3.001	3.001	2.990	2.989	2.995	2.991
Mg/Mg+Fe	92	89	91	89	70	66	32	34	91	89

*) total Fe as Fe²⁺.

§) below LLD: Cr=.04

Table 3 continued

Olivine separates by P.I.X.E. (ppm)

	30601	30670
Cr	850	1630
Co	110	-
Ni	1320	2510
Zn	-	150
Se	-	3.4
Rb	21	-
Sr	33	-
Zr	38	-
Nb	3	-
Cs	8	-
Ba	68	-

*) Emission Spectrometry of Cr, Co and Ni.

Se and V both below LLD = ppm.

*) Analysis by P.I.X.E. - below LLD: V, Ga, As, Se, Y, Mo, Cd, Sn, Sb, La, Ce.

Table 4

Representative mica and amphibole analyses for major and trace elements.

rock type	TEPHRITIC LEUCITITE		LEUCITE TEPHRITE		PHONOLITIC L. TEPHRITE		SATURATED TRACHYTES				TEPHRITIC L. PHONOL. 30632
	sample no.	31337	31474 core	31474 rim	31457	30669 core	30669 rim	30664	30670		
SiO ₂	36.8	36.2	35.6	36.3	36.3	36.4	36.2	34.6	40.1		
Al ₂ O ₃	14.5	16.2	15.0	15.7	13.9	14.0	13.9	15.5	10.4		
FeO	7.5	11.3	12.8	13.7	14.6	14.1	19.4	17.3	16.0		
MgO	18.1	17.6	15.8	17.6	15.1	14.9	9.8	10.6	10.7		
CaO	.04	-	-	-	-	-	-	-	11.5		
Na ₂ O	.51	.41	.59	.27	.31	.36	.29	.25	2.11		
K ₂ O	7.53	9.48	9.26	9.55	9.65	9.62	8.94	9.34	2.17		
MnO	.12	-	-	-	.15	.15	-	-	1.77		
TiO ₂	1.51	3.46	6.50	2.94	5.51	5.43	6.21	6.31	.04		
BaO	6.9	1.68	.65	1.08	-	-	-	.64	94.8		
sum	93.6	96.3	96.3	95.2	94.8	94.9	94.7	94.5	84.8		
formula based on 22 oxygen ions											
Si	5.566	5.320	5.267	5.392	5.458	5.474	5.566	5.325	6.243		
Al(IV)	2.434	2.680	2.617	2.608	2.462	2.483	2.434	2.675	1.757		
Al(VI)	.056	.124	-	.144	-	-	.090	.137	.155		
Fe	.954	1.395	1.577	1.458	1.758	1.776	2.487	2.224	2.079		
Mg	4.085	3.860	3.469	3.907	3.393	3.329	2.242	2.420	2.487		
Mn	.014	-	-	-	.019	.019	-	-	2.487		
Ti	.172	.383	.733	.329	.624	.614	.718	.730	.207		
Ca	.002	-	-	-	-	-	-	-	1.912		
Na	.150	.117	.169	.078	.090	.105	.086	.075	.636		
K	1.453	1.779	1.746	1.812	1.854	1.846	1.753	1.834	.431		
Ba	.779	.185	.072	.121	-	-	-	.074	.005		
sum	15.769	15.843	15.649	15.848	15.659	15.646	15.374	15.493	15.912		
Z	8.000	8.000	7.884	8.000	7.920	7.957	8.000	8.000	8.000		
Y	5.381	5.762	5.779	5.838	5.794	5.738	5.537	5.511	4.949		
X	2.388	2.081	1.985	2.011	1.945	1.951	1.839	1.983	2.984		
Annis	19	27	31	27	34	35	53	49	ferromargarite		

*) below limit of detection: CaO = .02.

§) SrO below limit of detection. LLD. SrO = .05.

23 oxygen ions

	Leucite
Mn	424
V	966
Zn	84
Ca	8
Rb	967
Sr	342
Zr	95
Cs	223
Ba	6960

Below detection:

Cr, Ni, Cu, As, Se, Y,

Nb, Mo, Cd, Sn, Sb,

La, and Ce

The Rb content is similar to those in other Roman phlogopites (Fornaseri, 1972). Although Sr is rather high, its partition coefficient with the lava is only 0.2. Ba was not determined by Cundari (1975) in the micas of Vico volcano, but a deficiency in X-sites, as he pointed out, may be ascribed to this element. The concentration of 6.86 wt. % BaO in late crystallizing micro-phlogopite from a leucite, 31337, is among the highest recorded for magmatic phlogopites. Other Ba-rich micas are reported by Thompson (1977) in the groundmass of a leucite from Alban Hills (7.32 wt. % BaO) and by Vendlandt (1978) in a monticellite peridotite from the Highwood Mts. (8.62 wt. % BaO). In the leucites of Vulturno, Ba is concentrated in the residual liquid by the crystallization of phenocrysts of leucite, diopside and, in some rocks, olivine. Mica crystallization in small amounts from this liquid thus attained very high Ba concentrations. Micas of the felsic undersaturated lavas could not be analysed because of total resorption. It is therefore not possible to compare the micas of the two suites of lavas. However, Ba is low in the micas of the saturated trachytes.

Spinels

Two spinel-group minerals occur: a chromite, which is found only as inclusions in olivine, and magnetite, which is present both as phenocrysts in felsic tephrites, phonolitic rocks and trachytes, and as a ubiquitous groundmass constituent. One or two magnetite grains frequently adhere to silicic pyroxenes. Green cores in pyroxenes sometimes have magnetite inclusions. Representative analyses, formulae and endmember compositions for chromites (after Irvine, 1965) and for magnetites on the basis of ulvöspinel (after Carmichael, 1967a) are given in table 5. Magnetite is titaniferous and alumina-rich and is often seen in reflected light to be partly martinitized or to have exsolution lamellae of ilmenite. The trace elements show high V, Zn, Sr and Zr.

The magnetite phenocrysts of the two suites of lavas contrast in TiO₂. The specimens 31457 and 30674 are comparable to 30669 and 30664 with respect to D.I. (table 9), but the magnetites of the hy-normative lavas are c.5% higher in TiO₂ than those of the undersaturated suite. Plagioclase thermometry indicates a lower crystallization temperature for the hy-normative lavas. These features may be interpreted in two ways. Either

the difference in ulvöspinel (14-15% between pairs) was caused by a lower f₀ in the hy-normative lavas on the basis of T Buddington & Lindsley (1964), or the difference was caused by a slightly higher TiO₂ content (c.0.2wt%) in the hy-normative lavas.

Amphibole

According to Washington (1966) amphibole is extremely rare in the Roman and Campanian Provinces. It has not previously been reported from the Vulturno District, but was observed in one tephritic leucite phonolite, 30632, where it is present in accessory amounts as a microphenocryst. In this section it is pleochroic in brown and olive green colours, and shows an extinction angle, γ₁ of 25°. It has the same chemical composition throughout the thin section. Following Leake (1978), and assuming that Fe³⁺ is less than Al (VI), it is a potassium ferromargarite. The analysis and calculated volatile-free formula are given in table 6. This amphibole is similar to the average composition of groundmass amphiboles from the Sabatinian District (Cundari, 1979).

Leucite

Clear or milky leucite is a major constituent of all of the undersaturated lavas, and is a phenocryst phase in most. It does not occur in the hy-normative rocks. The wide range of size of leucite crystals, commonly up to 1 cm, gives the rocks a seriate texture. Plagioclase microphenocrysts in the felsic rocks are often nucleation centers for large leucite phenocrysts, which commonly include 1-5 mm long salites. In the tephritic lavas, leucite occurs in aggregates, 0.5-2 cm in diameter, together with small crystals of salite, magnetite and minor phlogopite. Myriads of concentrically or euhedrally arranged, micron-sized inclusions of gas bubbles or spherules of glass are not uncommon in the larger crystals. Most leucites are rather fresh, but a few analcimized crystals occur in hydrothermally altered lavas. No pseudoleucite was observed.

Major and trace element analyses and structural formulae are given in table 6. No clear systematic variation in chemistry was detected, although the amount of the orthoclase molecule in solid solutions shows some tendency to increase towards the rims of the phenocrysts. The range of this solid solution, 5-22 mole %, is comparable to that in leucites from the Vico volcano (Cundari, 1975). The maximum uptake of orthoclase in leucite

Table 5. Representative spinel analyses for major elements, and one trace element analysis.

rock type	TEPHRITIC LEUCITES		LEUCITE		PHON.		TEPHR.		TRACHYTES	
	sample no.	30601	30682	31812	31878	31877	30634	30669	30664	30664
SiO ₂	.06	-	-	-	-	-	-	.08	.08	-
Al ₂ O ₃	9.6	10.5	7.0	5.20	3.97	3.25	3.42	2.45	-	-
Fe ₂ O ₃	4.1	12.9	51.1	50.4	54.5	48.9	48.5	39.7	-	-
FeO	17.0	22.8	12.2	36.7	14.3	36.9	36.7	43.2	-	-
MgO	10.4	5.95	2.71	-	1.90	1.28	1.96	.27	-	-
CaO	-	-	-	-	-	.21	.01	-	-	-
MnO	.30	.52	.47	.74	-	1.42	.61	.79	-	-
TiO ₂	.47	.42	5.39	6.13	4.05	9.07	9.10	13.7	-	-
Cr ₂ O ₃	55.4	42.3	5	.10	-	-	-	-	-	-
sum	97.2	95.2	98.9	99.2	98.5	100.7	100.4	100.2	-	-

*) Fe³⁺/Fe²⁺ obtained from formula-calculations. †) below LLD: .05

Structural formulae on basis of 32 oxygen ions and 24 cations:

	magnetite on ulvspinel-basis* (Charmichael, 1965) and chroitite after Irvine (1967)									
Si	.016	-	-	-	.024	.024	-	-	-	-
Al	3.066	3.517	2.393	1.838	1.404	1.129	1.186	.862	-	-
Fe ₂	.830	2.772	11.239	11.372	12.770	10.844	10.739	8.918	-	-
Fe ₃	3.858	5.429	7.888	9.194	8.065	9.027	9.022	10.790	-	-
Mg	4.186	2.531	1.179	-	.849	.567	.859	.120	-	-
Ca	-	.433	-	-	.067	.003	-	-	-	-
Mn	.069	.125	.117	.188	-	.352	.152	.200	-	-
Ti	.096	.090	1.184	1.383	.913	2.011	2.011	3.086	-	-
Cr	11.880	9.533	-	.238	-	-	-	-	-	-
sum	24.001	23.997	24.000	24.000	24.000	24.000	24.000	24.000	-	-

Submembers:

ulvspinel	2.8	2.2	17.4	19.6	12.5	27.1	27.3	40.9
chroitite	45.6	58.9	-	-	-	-	-	-
Mg-ferrite	27.6	-	-	-	-	-	-	-
spinel	18.9	21.7	-	-	-	-	-	-
Mg-ferrite	5.1	5.6	-	-	-	-	-	-
magnetite	7.6	82.6	80.4	87.5	72.9	72.7	59.1	-

*) give better totals than calculations based on ilmenite

Magnetite separates by P.I.X.E. (ppm)

TEPHRITIC LEUCO-LEUCITITE, 30633	
V	1540
Zr	237
Cu	47
Nb	36
Zn	698
Cd	1.6
Ca	33
Sn	13
Rb	1
Ba	110
Sr	299
La	106
Ce	160
Pb	47

Analysis by P.I.X.E. in ppm.

Below LLD: Cr, As, Br, Mo, Cd, Sb, Cs

Table 6. Representative leucite phenocryst analyses for major and trace elements.

rock type	TEPHRITIC LEUCITES		LEUCITE		PHONOLITIC LEUC. TEPHRITE		TEPHRITIC LEUC. PHONOL.			
	sample no.	31418	30682	31425	31474 /phxx	31474	31457 core	31457 rim	30634 core	30634 rim
SiO ₂	56.4	56.8	56.5	57.0	55.6	57.0	56.8	55.3	56.2	56.2
Al ₂ O ₃	22.3	22.7	22.2	22.4	22.8	22.3	22.5	22.4	22.4	22.4
Fe ₂ O ₃	.44	.30	.50	.27	.24	.33	.36	.40	.30	.30
FeO	.50	.07	.63	.28	.35	.16	.79	.26	.04	.04
MgO	20.5	21.0	20.8	20.1	20.6	20.9	19.5	20.7	20.9	20.9
sum	100.2	100.9	100.6	100.1	99.7	100.6	100.0	99.1	99.8	99.8

t) total iron as Fe₂O₃

Structural formulae on basis of 6 oxygen ions. Or = 4 x (Si-Al-Fe-Na-K).

	30672	31474	30633	30633	30633	30633	30633	30633	30633
Si	2.033	2.034	2.033	2.048	2.018	2.045	2.040	2.021	2.035
Al	.950	.958	.943	.949	.977	.941	.953	.967	.955
Fe	.027	.008	.014	.007	.007	.009	.010	.011	.008
Na	.035	.005	.044	.017	.025	.011	.055	.018	.003
K	.845	.961	.853	.822	.925	.956	.896	.965	.868
sum	3.976	3.966	3.987	3.944	3.980	3.963	3.954	3.982	3.969
Index	12.0	13.6	10.5	20.4	7.2	17.1	16.8	8.0	13.5

Leucite separates by P.I.X.E. (ppm)

	LEUCITE TEPHRITES		TEPHR. LEUCITITE	
	30672	31474	30633	30633
Ce	4120	5110	209	4400
Ti	285	309	-	278
Mn	14	-	-	40
V	37	55	-	20
Cu	17	24	18	20
Ca	16	11	22	19
As	8.2	8.0	8.3	12.1
Hf	-	4.8	-	13.5
Rb	1280	1690	1210	1200
Sr	14	32	18	40
Zr	10	-	-	-
Nb	-	-	-	24
Cd	3.4	-	-	-
Mo	-	1.0	-	-
Sn	-	3.3	-	-
Ce	73	147	86	84
Ba	964	118	132	132
La	12	30	14	43

Below LLD and not shown in table: Cr, Ni, Zn, Br.
* Phenocryst size.

Table 7. Representative alkali feldspar analyses for major & trace elements

rock type	TEPHRITIC LEUCITE PHONOLITES				SATURATED TRACHYTES			
	sample no.	30632	30634	30633	30669	30669	30664	30664
SiO ₂	65.0	60.9	61.2	59.7	63.8	64.3	66.0	64.3
Al ₂ O ₃	18.9	20.0	20.6	19.8	19.1	18.9	18.5	18.6
Fe ₂ O ₃ t)	.24	.36	.33	.43	.26	.24	.19	.19
FeO	.86	.79	.79	.56	.66	.73	.57	.37
MgO	3.44	3.28	3.94	2.17	1.97	2.70	2.53	2.20
K ₂ O	10.96	8.71	7.77	9.84	12.7	12.6	12.2	13.1
Na ₂ O	-	1.34	1.21	1.15	.28	.28	-	-
BrO	.07	4.53	3.75	5.61	.68	.59	.20	.37
sum	99.5	99.9	99.6	99.7	99.3	100.8	100.2	99.1

*) sanidine mantle on plagioclase phenocryst, t) total iron as Fe₂O₃

†) below LLD: SrO = .05wt%

Structural formulae on basis of 32 oxygen ions.

	30632	30634	30633	30669	30669	30664	30664
Si	11.881	11.388	11.372	11.391	11.811	11.760	12.001
Al	4.084	4.414	4.523	4.427	4.175	4.124	3.972
Fe	.034	.051	.046	.118	.036	.033	.026
Ca	.168	.158	.157	.113	.091	.091	.111
Na	1.219	1.190	1.421	.796	.707	.958	.892
K	2.555	2.079	1.844	2.376	3.004	2.943	2.832
Ti	-	.010	-	-	-	-	-
Sr	-	.098	.088	.085	.020	.020	-
Ba	.010	.636	.533	.793	.094	.081	.027
sum	19.949	20.014	19.975	20.012	19.939	20.095	19.862

Alkali feldspar separates

	TEPHR. LEUCIT. 30633	TRACHYTE 30664	Rb 516	Sr 1250	Zr 221	Ce 4160
Rb	300	467	516	1250	221	4160
Li	68	31	31	28	28	28
Cu	31	28	28	28	28	28
Ga	28	28	28	28	28	28
Ba	9.4	9.4	9.4	9.4	9.4	9.4

Below LLD in P.I.X.E.: Cr, Ni, Zn, Br.

Nb, Mo, Cd, Sn, Sb, La and Ce.

ite at 1 kbar was determined to about 30 wt. % by MacKenzie et al. (1974), who also found that the solubility was temperature dependent. The excess silica might also reflect the increasing SiO₂-activity in the melt as large amounts of leucite precipitate from the magma. Other occurrences of leucites with excess silica are cited by Comdar (1975). Sodium covers about half the known range of solid solution in natural leucites (Fundall, 1963). Ca is a minor element and substitutes for Na in 6-coordination (5-positions). In contrast to the leucites from the Leucite Hills (Car-

michael, 1967b) only small amounts of iron are present. This is probably caused by the contrasting activity of alumina in the two provinces. Only a few trace elements are present in high concentrations in the leucites. These are Rb, Cs, Br and, in some instances, Ba, substituting in 12-coordination for K, and As, substituting for Si. Previously, Thompson (1977) reported the possible existence of two types of leucites in a lava from Colli Albani, the difference being evident from the Ba content. Large amounts of Ba are also present in the leucites analyzed by Hender-

Alkali Feldspar

In the undersaturated series, alkali feldspar only appears as a phenocryst phase among the most felsic phonolites, where it occurs in low concentrations (less than 2 vol %) of euhedral prisms a few millimeters in length. In a few lava flows phenocrysts of alkali feldspar make up around 10 vol %. In the hy-normative rocks alkali feldspar is ubiquitous. Sanidine occurs as tabular crystals up to centimeter size, and comprises between 5 and 23 vol % of the rock.

Representative analyses, structural formulae and calculated end-members are given in table 7. It is evident that both BaO and SrO are major oxides in many of the alkali feldspars of the undersaturated rocks, in contrast to the alkali feldspars in the hy-normative rocks, which are Ba- and Sr-poor. According to the nomenclature of Deer et al. (1963), the most Ba-rich alkali feldspars are hyalophanes and the rest are sanidines. The highest concentration of Sr in natural magmatic sanidines outside the Roman Province was recorded by Kutolin and Pralova (1970), and their value of 1.51 wt. % SrO is not much higher than the values in the Vulsini sanidines. Larsen et al. (1941) report higher Ba-contents in magmatic alkali feldspars of the Highwood Mts. than those found in Vulsini. The sanidines of the Vico volcano (Cundari, 1975) do not contain Sr or Ba in more than trace amounts. The unusually high levels of the two elements in alkali feldspar have also recently been reported by Cundari (1979) from the Sabatini District, south of Vulsini. As suggested for Ba-phlogopite, it is believed that sanidine crystallized late from a liquid enriched in Sr and Ba. The Rb contents of the hyalophanes and sanidines are much lower than Sr and Ba. The alkali feldspars of the hy-normative suite are much lower in Sr, Ba and Ab-component. This is thought to be a consequence of lower Sr and Ba concentration in the hy-normative lavas, while the higher Ab-component of the undersaturated phonolitic lavas may be due to depletion of K in the melt by leucite crystallization.

Plagioclase

In the undersaturated lavas, plagioclase is present as phenocrysts in rocks of tephritic and phonolitic composition, but it is not abundant. It forms euhedral to rounded, short, albite-twinned prisms, generally less than 0.5 mm in length. Plagioclase is present in the groundmass of all lavas of the district. In the hy-normative lavas it is abundant as a phenocryst phase, where it usually forms sub- to euhedral, 1-20 mm long laths or prisms, which are mostly albite-twinned, but occasionally Carlsbad and Bavens twins are seen. All plagioclase is strongly oscillatory zoned with 50-100 zones of amplitude of a few mole % An, combined with a progressive zonation of up to An between cores and rims.

Analyses and formulae are presented in table 8. The plagioclases are calcic, even in phonolites and trachytes: An 93-An 72. Only some extreme rim compositions are of labradorite. Normal zonation is the rule. The Sr content is very high, and in the Vulsini plagioclases exceeds the upper

Table 8.

Representative plagioclase analyses for major and trace elements.

rock type	LEUCITE TEPHRITE		PHONOLITIC LEU. TEPHRITE		TEPHRITIC LEUCITE PHONOLITES				SATURATED TRACHYTES				
	sample no.	31412 core	31412 rim	31457 core	31457 rim	30632 core	30632 rim	30634 core	30634 rim	30669 core	30669 rim	30664 core	30664 rim
SiO ₂	45.1	47.3	52.2	45.3	48.1	45.7	48.1	47.9	50.6	46.1	50.3	48.1	51.3
Al ₂ O ₃	33.8	32.4	29.4	33.8	32.1	33.3	31.7	32.2	30.4	33.8	30.3	32.1	31.1
Fe ₂ O ₃ t)	.90	.92	.76	.80	.86	.80	.87	.87	.69	.67	.79	.57	.49
CaO	18.6	16.4	12.3	16.7	15.3	17.7	15.5	15.5	13.4	18.4	14.1	16.0	14.2
Na ₂ O	.63	1.20	3.89	1.23	1.87	1.02	2.06	2.01	2.93	1.06	2.70	1.94	2.86
K ₂ O	-.	.21	.56	.28	.47	.33	.39	.15	.53	.25	.73	.33	.47
SrO	.39	.61	-	1.11	1.22	.44	.60	1.13	1.05	-	-	.20	.13
BaO	-.	.05	-	-	-	8	.07	.12	.13	-	-	5	5
sum	99.7	99.7	99.0	99.2	100.0	99.3	99.3	99.8	99.7	100.2	98.9	99.2	100.5

t) total iron as Fe₂O₃. s) below LLD: BaO<.05wt%

Structural formulae on basis of 32 oxygen ions.

Si	8.393	8.774	9.570	8.474	8.896	8.528	8.926	8.864	9.310	8.500	9.283	8.899	9.300
Al	7.413	7.093	6.354	7.458	6.999	7.323	6.941	7.021	6.608	7.338	6.598	7.005	6.643
Fe	.126	.129	.105	.113	.120	.112	.122	.121	.096	.093	.110	.079	.067
Ca	3.715	3.253	2.434	3.358	3.034	3.530	3.083	3.066	2.646	3.636	2.802	3.169	2.768
Na	.299	.684	1.384	.447	.706	.369	.742	.722	1.046	.379	.967	.697	1.056
K	.050	.050	.131	.067	.111	.079	.092	.055	.125	.059	.172	.078	.109
Sr	.028	.044	-.	.081	.088	.032	.044	.082	.076	-	-	.015	.009
Ba	-.	.007	-.	-.	-.	-.	.006	.018	.010	-.	-.	-.	-.
sum	19.987	20.033	19.958	19.998	19.954	19.978	19.959	19.938	19.924	20.004	19.932	19.946	19.902
X	4.04	4.04	3.93	3.95	3.94	4.02	3.97	3.92	3.91	4.07	3.94	3.96	3.89
Y	15.95	16.00	16.03	16.05	16.02	15.96	15.99	16.02	16.01	15.93	15.99	15.96	16.01
Ab	91.9	80.6	61.5	84.9	77.1	87.9	77.6	78.2	67.7	89.3	71.1	80.0	71.2
An	7.4	16.9	35.2	11.3	17.9	9.1	18.7	18.4	26.7	9.3	24.5	17.6	25.8
Or	0	1.2	3.3	1.7	2.8	2.0	2.1	1.9	3.2	1.4	4.4	2.0	2.8
Sr-plg.	.7	1.1	0	2.1	2.2	.8	1.1	2.1	1.9	0	0	.4	.6
Ba-plg.	0	.2	0	0	0	.2	.3	.4	.5	0	0	0	0

limit of SrO in plagioclases reported by Smith (1974) and is only surpassed by poikilitic Sr-Ba-feldspars described by Cundari (1979). The plagioclases of the hy-normative suite are much less enriched in Sr and Ba than those of the undersaturated series.

The crystallization temperatures of the plagioclases were estimated using the plagioclase thermometer of Mathes (1973) and although the lavas differ in composition from those considered by Mathes, the temperatures calculated for the rim compositions are consistent in the sense that a steadily falling temperature is obtained, (table 9) which correlates with increasing D.T. Groundmass compositions were used in the calculations. The results are in contrast to those for the Vico lavas (Cundari, 1975), where a rising temperature was found with increasing D.T.

Nepheline

Nepheline is common as a vesicle-filling and a late-crystallizing phase in the groundmass, but it has only been observed in a few specimens as phenocrysts. In table 10 the analysis of a nepheline microphenocryst in a leucite tephrite is presented. The temperature of crystallization is calculated by the method of Hamilton (1961) to be 1070°C.

Häbyne

Häbyne is present in notable amounts in one tephritic phonolitic leucite, 30633. It occurs as euhedral clear micro-phenocrysts (2.5 vol. %). An analysis is given in table 10. In several other phonolitic rocks, häbyne occurs in trace amounts as tiny inclusions in sanidine (or hyalophane). In the latter case häbyne has the characteristic blue colour and black rim.

Table 9.

Temperatures of assumed equilibrium between rims of plagioclases and their host liquids (i.e. calculated groundmasses). Calculations are based on Mathes (1973).

rock-type	sample no.	D.T.	T
Leucite tephrite	31412	54	1230°C
Phonolitic leu.tephrite	31457	65	1225°C
Tephritic leu.phonolite	30632	73	1200°C
Tephritic leu.phonolite	30634	80	1200°C
Trachyte	30669	64	1125°C
Trachyte	30664	80	1120°C

Tridymite

Numerous rounded, partly fragmented tridymite crystals, about 1 mm in size occur in the latite trachyte, 30670. The silica is surrounded by a rim of glass and a corona of small pyroxene laths showing that it is not in equilibrium with its host liquid. Trace element analysis (PIXE) reveals only few elements above the limits of detection: 44 ppm Fe, 0.5 ppm Pb, 0.5 ppm V, 1.3 ppm Zr and 11 ppm Cu.

Discussion

The undersaturated suite.

The texture of those basic lavas (leucitites and tephritic leucitites), which do not carry two-component clinopyroxenes, indicate that diopside + olivine was the liquidus assemblage. Chromian diopside and olivine, Fe₈₉₋₉₂ with high Ni indicate that these lavas may be nearly mantle-derived liquids. Among the basic undersaturated lavas, it is significant that olivine is present only in some of the most mafic flows. This is contrary to the implications from the phase boundaries

Table 8 continued.

Plagioclase separate by P.I.X.E.(ppm)

TRACHYTE 30664			
Rb	75	Rb	27
Na	84	Sr	2740
Ca	37	Y	19
Zn	27	Zr	134
Ba	59	Ba	162
As	19	La	26
		Ce	43

Below LLD: Cr, Ni, Br, Mo, Cd, Sn, Sb.

explored by Gupta (1972) for a liquid evolving by crystal fractionation. Either a reaction relationship between olivine and melt is present (e.g. O'Hara, 1968), or alternatively the basic lavas have not evolved by crystal fractionation.

Towards more evolved felsic lavas (clinopyroxene and leucite are the sole phenocryst phases). Subsequently they are characterized by the following additional phases: a) plagioclase, magnetite, ± minor dark mica, b) sanidine (or hyalophane), c) häbyne. In terms of the felsic minerals only, this is similar to what would be expected for a liquid in the phonolite pentahedron of Carmichael et al. (1974) starting at a point near the surface boundary of leucite and plagioclase. These lavas are thought to be related by crystal fractionation along a line of evolution analogous to a liquid in the phonolite pentahedron (Carmichael et al., 1974).

Table 10. Nepheline and baryne analyses.

rock type	TEPHRITIC	
	TEPHRITE	LEUCO-LEPTEPHRITE
sample no.	31362 uph.xx	30633 uph.xx
SiO ₂	45.25	31.64
Al ₂ O ₃	34.76	26.84
Fe ₂ O ₃ (t)	.38	.68
MgO	.05	.03
CaO	1.04	8.05
Na ₂ O	15.43	11.73
K ₂ O	3.48	6.67
TiO ₂	.08	-
SO ₃ +)	-	13.95
Cl	-	.16
sum	100.47	99.75
less O=Cl	-	-.04
sum	-	99.71

Structural formulae on basis of: 4 oxygens; 21 oxygens in Al-Si-framework

	LEUCITE	TEPHRITE
Si	1.059	5.958
Al	.959	5.959
Fe	.007	.096
Mg	.002	.008
Ca	.026	1.625
Na	.700	4.284
K	1.104	1.602
Ti	.001	-
S	-	4.453
Cl	-	.119
sum	2.859	24.107

+) total iron as Fe₂O₃, +) total S as SO₃

The saturated suite.

Although the saturated lavas are all trachytes they differ considerably in content of mafic minerals. It is not possible however, to conclude whether they evolved by fractionation, because they generally have the same phenocryst assemblages.

Evidence of low-pressure crystallization.

The relation of the undersaturated lavas to the system di-le-fo which was investigated at 1 atm by Gupta (1972) will be discussed first. Thompson (1977) argued that for many leucitites the system di-le was at least as representative as the system hy-di-ol-ne/Q is for basalts. The normative compositions of the most basic Vulsinian lavas are not far from the modal composition, if only the minerals diopside, leucite and olivine are considered. For example the tephritic leucitite, 30601, has normative di₆₁lc₃₁ol₇ (representing 60 % of the norm) and modal (wt. %): diopside₅₉ leucite₃₆ olivine₉ (representing 85 vol % of the mode). The system di-le-fo is therefore considered a good approximation to these lavas.

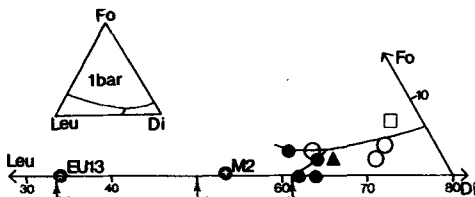


Figure 3. The system di-le-fo with the cotectics and piercing point at 1 atm from Gupta (1972), the eutectic on the join di-le at 1 atm (Bowen and Schairer, 1929) and those at 4 and 12 kbars from Dolfi et al. (1978). The positions of EU 13 and M2 taken from Thompson (1977) are shown together with the positions of representative Vulsinian mafic lavas. The symbols designate the probable liquidus phases: Circles - diopside, square - forsterite plus diopside, filled circles - diopside plus leucite, and triangle diopside, forsterite plus leucite.

Superimposed on the experimental results in fig. 3 are the compositions of some Vulsinian lavas and the compositions of the leucitites, EU13 and M2, taken from Thompson (1977). In spite of the good fit of the mode and

the norm it is not expected in the simple experimental system that the lavas plot in strict accordance with the physical conditions during their crystallization. It is nevertheless seen that even though the modal phenocryst mineralogy does not correlate very well with the experimentally determined phase boundaries, it is reasonable to state that the basic Vulsinian lavas crystallized at low pressure. Both EU 13 and M2 seem to have crystallized at higher pressures. According to Triguila's (1969) experimental results, the M2 lava may have crystallized at 1 atm. Whether this is so or not, the present lavas almost certainly did not crystallize at higher pressure than M2.

The variation within pyroxene phenocrysts of sample lavas is generally large compared with the inter-lava variation. The diagram also stresses that the green cores do not form a special chemical group although they are similar to the salites of the phonolitic rocks (Table 2). The general trend of variation within single phenocrysts, as well as between lava-types from leucitites to leucitite phonolites, parallels the line Fe³⁺Al, in accordance with the major variation in the CaFeAl SiO₆-component of these pyroxenes.

The areas covered by the natural phenocrysts of Thompson's (1974) EU13, leucitite, coincide with the Vulsinian pyroxenes. In clinopyroxenes formed at high dry pressure, Fe³⁺ and Ti decrease and Al and Na increase with rise of pressure (Thompson, op.cit.). This trend is in contrast to that of the Vulsinian clinopyroxenes. Representative clinopyroxene analyses from the V₁ leucite tephrite of Dolfi and Triguila (1978) also fall within the range of the Vulsinian pyroxenes. On the other hand these experiments (Dolfi and Triguila, 1978 and Dolfi, 1978, show that, as the role of P_{H₂O} is increased relative to P_{total} at 2kbar the CaFe AlSiO₆ molecule becomes successively more important. The Vulsinian pyroxenes crystallized from a wide range of magma-types and a direct comparison cannot be made with the experimental data. Several of the lavas, however, are similar to the ones used for the experimental runs. Therefore, some implications seem justified. The large variation in single phenocrysts compared with the inter-lava variation parallel to this trend suggests that the role of water or f_{O₂} imposes an influence on the solubility of the CaFeAlSiO₆-molecule which is large compared with the effects of chemical variation in the lavas. The diagram also confirms the conclusion that the P_{total} was less than 10kbar and possibly less than 2kbar.

As olivine and leucite coexist in the mafic lavas, leucite and clinopyroxene in all the lavas, and because phlogopite is only an accessory or trace phase, P_{H₂O} must have been low during the crystallization of the lavas of the undersaturated series (Luth, 1967, Ruddeck and Hamilton, 1978).

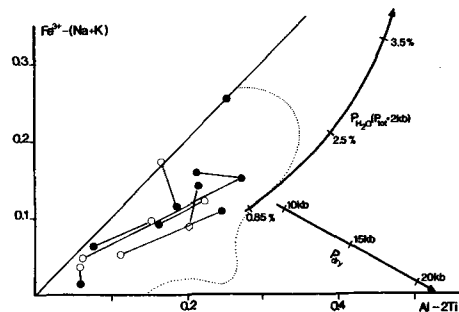


Fig. 4. Molecular Fe³⁺-(Na+K) versus Al-2Ti in the clinopyroxenes of the leucite-bearing suite (representing Ca-ferri-Tschermak's molecule corrected for calcite versus Ca-Tschermak's molecule corrected for CaAl₂O₆). Key: microprobe analyses of phenocrysts: ● cores, ○ rims, ● green cores. The stippled line indicates the area covered by 110 phenocryst analyses (Hela, 1978), which also include the analyses of Thompson (1977). Bold lines indicate dry high pressure experiments by Thompson (1977) on clinopyroxene from a Roman leucitite, and the experiments of Dolfi and Triguila (1978) at P_{total} = 2kbar and wt.% water content as indicated.

The green cored pyroxenes

The occurrence of two-component pyroxene phenocrysts in many of the Vulsinian undersaturated lavas is believed to be an important feature. Although some of the lavas may be incorporated xenocrysts of salite from wall-rock, their frequent occurrence (in 30 of 85 leucitites and leucite tephrites) and large relative number compared to the total number of phenocrysts (they often make up half the amount of phenocrysts in the lavas) indicate that they are relicts. The green cores may either be a phase once crystallizing from the lava in a different environment, or be phenocrysts in a phenolitic magma batch which were sized with a more basic one. The only other phenocryst phase ubiquitous in the basic lavas is leucite which unfortunately does not exhibit any systematic variation in its chemistry, which might otherwise be used to solve the problem of the origin of the phenocrysts of the basic lavas.

Summary

The undersaturated rock series of the Volsinian District includes rock-types ranging from mafic leucites to leucite phonolites. In the most basic members diopside \pm leucite \pm olivine are on the liquidus. This study does not confirm that these rocks are related by crystal fractionation. Salitic green cores of phenocryst pyroxenes mantled by diopside in rocks which also carry normal zoned diopsides are relicts which witness either a relatively high P_{H_2O} prior to the crystallization of diopside or magma mixing in the earliest life of these lavas. The chemistry of the pyroxenes of the whole suite reveal crystallization under low pressure, possibly less than $P_{\text{at}} \pm 2$ kbar in a relatively dry environment. The latter is confirmed by the rarity of phlogopite. The more felsic lavas carry phenocrysts of clinopyroxene (salite-ferroalbite), and leucite joined subsequently by plagioclase, magnetite \pm dark mica, and Ba-rich alkali feldspar \pm halimite. The felsic rocks are thought to be related by crystal fractionation. The trachytic suite of hy-normative lavas is much less voluminous and they all carry phenocrysts of sanidine, plagioclase, augite, olivine, biotite and magnetite in variable amounts. The pyroxenes of these rocks show equivalent signs of low-pressure crystallization.

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