

the other rather extensive Italian literature on the subject, is based on the survey given in NORIN's paper.

The volcanic activity in the Phlegrean Fields proper, seems to have started at the beginning of the first Würm Glacial (LGL₁) (KYRLE, 1947). It continued intermittently throughout the Würm and Postglacial time, the last eruption on record taking place in 1538 with the formation of the small Monte Nuovo conelet on the shore of the Gulf of Pozzuoli.

De LORENZO distinguished three periods of intense volcanic activity in the region, each period being separated from the following by a lengthy stage of volcanic quiescence. To the First Phlegrean Period he referred the very thick and widely distributed gray Campania tuff (*tufo grigio campano*), as well as an overlying younger series of lava beds and pyroclastics of similar petrographical character (*Ciclo eruttivo antico* of RITTMANN), which terminates with very large volcanic breccias and conglomerates, *breccia museo*, a formation found all over the Phlegrean Fields and also far outside the region. According to RITTMANN *et al.* (1951), the gray Campania tuffs represent the ejecta of enormous volcanic explosions of a pre-existing huge volcano, the Archiphlegraeous, which occupied the greater part of the present Phlegrean Fields. The following specimens of obsidians originate from the upper series of volcanics (*Ciclo eruttivo antico*):

- Spec. 11a, obsidian from a boulder of pipernoid tuff in the *breccia museo* at Soccavo;
- Spec. 11b, pipernoid lava from Hor. 7f or 7h in RITTMANN's section at Soccavo;
- Spec. 12, a bomb of obsidian from Hor. 3b in RITTMANN's section at Torre di Franco;
- Spec. 32, obsidian in pipernoid tuff from Hor. 5 in VIGHI's section No. 1 at Torre Gaveta.

The Second Phlegrean Period of De LORENZO is represented mainly by the Neapolitan yellow tuff (*tufo giallo napoletano*) which covers the products of the First Period almost everywhere and locally attains a thickness of some 200 m. An interval of extensive erosion during which humous soils were being formed, separates these tuffs from those of the First Period. This very thick formation of fine tuffs differs, petrographically, from most other tuffaceous formations in the Phlegrean Fields by the peculiar hydrochemical alteration to which the ashes have been subjected, an alteration which probably has taken place in close conjunction with the deposition of the ashes (NORIN 1955). As to their mode of formation, they are generally assumed to have erupted in the form of clouds of incandescent volcanic dust and gases, *nuées ardentes*. The tuff was ejected from a number of volcanoes, *int. al.* Mofete, Gerolomini, Chiaia, Capodimonte, Secche di Miseno and Gauro.

Sometimes, but rather rarely, lapilli or small bombs of quite fresh obsidian are to be found in the chaotic yellow tuff; these are supposed to represent the lava from which the tuff originates. Chemically these obsidians differ from those of the First Period in being highly potassic ($k = 0.62$ in the former, 0.42 in the latter in average). Three such bombs were collected at different localities, viz. the following:

- Spec. 10a, obsidian from the *tufo giallo* in Valle Verdolino, Camaldoli;
Spec. 21, obsidian from *tufo giallo* at Cuma;
Spec. 33, obsidian from the large pit in *tufo giallo* above Torre Gaveta.

The Third Phlegrean Period (*Ciclo eruttivo recente* of RITTMANN) extends into Historical times. Its products consist mainly of subaerial pyroclastic materials: ashes, scoriae, pumice, and breccias with only a few flows of lava and intrusive bodies. To the earlier part of this period belong, according to VENTRIGLIA (1951), the volcanoes of Agnano, Montagna Spaccata, and Pisano; to the later part belong the volcanoes of Solfatara, Cigliano, Averno, Astroni, Fossa Lupara, Senga, and Monte Nuovo. Chemical analyses of specimens from the following localities are available:

- Spec. 13, pumice from the western slope of Astroni;
Spec. 14, bomb of obsidian from the Senga tuff beds on the autostrada west of Senga;
Spec. 16, obsidian from Agnano tuff on the western side of Monte Spina.

1. Petrographical description of the material

1. Obsidians referable to the First Phlegrean Period

Specimen 11a from the *breccia museo*. The glossy velvety black obsidian of this rock forms thin outwedging cakes, seldom more than a few cm thick, embedded in light coloured pinkish brown, easily crumbling tuffaceous material (*piperno*), probably clods of lava ejected by lava fountains.

The tuff contains fragments of volcanics of various character, e.g. alkali-trachytes, trachytes, latites, vicoites etc., varying texturally from glassy to holocrystalline. There are also fragments of abyssal rocks such as alkali-syenites, plagioclase-bearing syenites, monzonites, sodalite foyaite, and hauyn foyaite; occasionally fragments of the green epomeo tuff, typically developed on Ischia, have been found in the breccia. At Camaldoli the *breccia museo* rests upon *piperno* and is overlain by white tuff (*tufi biancastri*).

The obsidian, apparently homogeneous to the naked eye, is seen under the microscope to possess a rather diversified texture: it is partly glassy, partly streaky by flowage, partly brecciated with fragments of various textural development. These fragments may consist of (1) partly altered brownish glass, (2) devitrified glass with spherulitic texture, and (3) fragments with

Table I a. Obsidians from the Phlegrean volcanic sequence

Period De LORENZO Anal.	Tufo giallo									
	I L&C.A.L.	I C.A.L.	I C.A.L.	I L&C.A.L.	II L.	II C.A.L.	II C.A.L.	III. 2 C.A.L.	III. 3 L.	III. 4 L.
	Torre Gaveta Sp. 32	Torre Franco Sp. 12	Soccavo Sp. 11b	Breccia Museo Sp. 11a	V. Ver- dolino Sp. 10a	Torre Gaveta Sp. 33	M. Cuma Sp. 21	Agnano Sp. 16	Astroni Sp. 13	Senga Sp. 14
SiO ₂	60.11	59.26	60.48	60.44	56.71	57.14		56.47	56.33	58.56
TiO ₂	0.71	0.50	0.42	0.71	0.59	0.53		0.66	0.17	1.00
Al ₂ O ₃	18.88	18.60	18.56	18.41	18.50	17.82		17.80	18.74	19.08
Fe ₂ O ₃	0.67	0.71	2.71	0.88	2.30	2.22		1.61	2.74	0.65
FeO	2.09	2.50	0.81	1.87	2.06	2.14		3.22	1.99	3.12
MnO	0.27	0.29	0.25	0.29	0.14	0.12		0.18	0.11	0.20
MgO	0.17	1.04	0.80	0.21	0.69	1.48		2.13	0.51	0.99
CaO	1.81	1.75	1.79	1.90	3.83	3.44		4.80	4.12	3.34
Na ₂ O	6.42	7.13	6.09	6.67	3.59	3.43	3.72	3.60	4.08	4.11
K ₂ O	7.14	7.11	7.21	7.20	8.96	8.45	8.12	7.85	7.98	8.70
H ₂ O ⁺	0.35	0.47	0.59	0.41	2.38	2.2		1.01	2.89	
H ₂ O ⁻	n.d.	n.d.	n.d.							
P ₂ O ₅	0.11	0.06	0.07	0.12	0.18	0.19		0.29	0.25	0.25
CO ₂	0.00	n.d.	n.d.							none
F		neg.	0.1							
		99.42	99.78	99.11	99.93	99.2		99.62	99.91	100.00

Table I b. Molecular norm

	Sp. 32	Sp. 12	Sp. 11b	Sp. 11a	Sp. 10a	Sp. 33	Sp. 16	Sp. 13	Sp. 14
Or	41.70	40.95	41.85	41.85	53.80	51.05	46.55	48.05	50.75
Ab	38.40	30.31	39.76	37.06	19.71	25.35	20.65	24.80	22.81
An	1.58		2.03		8.05	8.48	9.27	9.45	7.80
Ne	11.16	16.62	8.40	12.00	7.83	3.66	7.08	7.53	8.16
Sal	92.84	87.88	92.04	90.91	89.39	88.54	83.55	89.83	89.52
Ns		0.57							
Ac		1.96		1.48					
Di	5.26	6.46	5.08	6.02	6.92	6.16	10.26	6.46	5.52
Ol		2.35				1.78	3.01		2.39
Mt	0.69		0.99	0.34	2.45	2.37	1.70	2.93	0.68
Hm			1.20						
Il	0.98	0.68	0.58	0.98	0.84	0.76	0.92	0.24	1.37
Ap	0.24	0.11	0.13	0.27	0.40	0.40	0.53	0.53	0.53
Fem	7.17	12.12	7.98	9.09	10.62	11.45	16.45	10.16	10.49

Table I c. Niggli values

	Sp. 32	Sp. 12	Sp. 11b	Sp. 11a	Sp. 10a	Sp. 33	Sp. 16	Sp. 13	Sp. 14
si	226	207	220	226	197	199	180	194	201
qz	-36	-47	-33	-39	-31	-22	-28	-31	-30
al	41.86	38.19	39.82	40.60	37.86	36.64	33.45	37.96	38.64
fm	10.28	15.42	15.00	10.41	15.98	20.12	23.05	15.78	16.31
c	7.30	6.53	6.98	7.62	14.25	12.85	16.40	15.18	12.30
alk	40.55	39.86	38.20	41.37	31.91	30.39	27.09	31.08	32.76
k	0.42	0.40	0.44	0.42	0.62	0.62	0.59	0.56	0.58
mg	0.09	0.35	0.29	0.11	0.22	0.38	0.44	0.17	0.31

trachtyoidal pilotaxitic texture crowded with microlites of sanidine and minute stout crystals of pyroxene almost to the exclusion of glassy base. The fragments are embedded in a brownish glass with beautiful flowage structure containing scattered phenocrysts of sodic sanidine ($Or_{65}Ab_{35}$) up to about 5 mm in length along the a-axis, plagioclase ($Ab_{60}An_{40}$) (< 2 mm), augitic diopside (< 0.5 mm), and magnetite. The phenocrysts have acquired a preferred orientation with the long axis parallel to the plane of flowage.

Specimen 11b originates from RITTMANN's classical *piperno* locality at Soccavo, the horizon No. 7f or h in his section (1951, Fig. 13). Chemically this rock is almost identical with the pipernoid lava Spec. 11a in the *breccia museo*, the only essential difference being the state of oxidation of the iron (cfr. Table I). In handspecimen the rocks have a rather different appearance: Spec. 11a being a glassy black obsidian, Spec. 11b a flamy, gray phanocrystalline rock with rough surface. It contains scattered phenocrysts of sodic sanidine ($Or_{63}Ab_{37}$), more rarely andesine ($Ab_{63}An_{37}$), and pyroxene in a groundmass of devitrified glass with spherulitic texture. The rays of the spherulites probably consist of sanidine, elongated along the a-axis (negative elongation, $n < \text{Canada balsam}$, optic plane subparallel to a-axis, $2V < 40^\circ$).

The obsidian, Specimen 12, originates from Hor. 5 in RITTMANN's section Fig. 12 at Torre di Franco (1951, p. 152). The bed is 6 m thick. Its upper part (5b) consists of light gray, rather coarse vesicular pumice and cinders with scattered bombs and fragments of black obsidian (Spec. 12). In the lower part (5a) the bed becomes agglomeratic, the usually elongated bombs being enriched into lenticular masses in the pumice and forming a continuous layer at the base of the bed. It rests upon stratified, light gray pumiceous tuff (Hor. 4) which is capped by a layer of humous soil, indicating that a considerable interval of time elapsed after the deposition of the subjacent ashes.

The obsidian Spec. 12 has a streaky appearance caused by lenticular layers of dark grayish devitrified (?) glass alternating with black pitch-like glass. The latter is also layered by streaks of vesicles elongated in the direction

of flowage. The glass contains fluidally arranged microlites of sanidine and pyroxene but only a few and rather small phenocrysts of sanidine.

The obsidian, specimen 32, was collected from the horizon 5 in VIGHI's section at Torre Gaveta on the west coast of the peninsula of Procida (1951, *sezione 1*, p. 186). This bed, about 0.5 m thick, consists of rather incoherent pipernoid tuff with stripes and clods of much variable size of black glassy obsidian parallel arranged in a dark gray cineritic tuff. The clods of obsidian have probably been ejected by lava fountains.

Besides the entirely hyaline large clods of black obsidian with phenocrysts of sanidine ($\text{Or}_{67}\text{Ab}_{33}$), plagioclase ($\text{Ab}_{61}\text{An}_{39}$), and augitic diopside, the tuff also contains fragments of devitrified hyaline lava with sanidine and pyroxene, and glass of different colours.

Chemically, all these obsidians are very similar. (Table 1.) They are all of *nordmarkitic-leucosyenitic* magma type, characterized by k -values about 0.42, high content of normative nepheline (8.40–16.62 mol. %), and no or very low content of normative anorthite.

2. Obsidians referable to the Second Phlegrean Period

Specimen 10a is a large piece of black obsidian embedded in the yellow tuff at Valle Verdolino. The glass exhibits flow structure and is partly vesicular. Rare phenocrysts of sanidine ($\text{Or}_{76}\text{Ab}_{24}$), labrador ($\text{Ab}_{42}\text{An}_{58}$), augitic diopside, and idiomorphic biotite (lepidomelan) occur.

Specimen 21 from *tuffo giallo* at Cuma is an obsidian of similar appearance as Spec. 10a, but phenocrysts occur more abundantly, viz. sanidine ($\text{Or}_{80}\text{Ab}_{20}$), labrador ($\text{Ab}_{42}\text{An}_{58}$), augitic diopside, and lepidomelan.

Specimen 33, a rounded piece of obsidian from the quarry in the yellow tuff above Torre Gaveta. It consists of a brownish glass with flow structure and phenocrysts of sanidine ($\text{Or}_{75}\text{Ab}_{25}$) up to 4 mm in length, labrador ($\text{Ab}_{43}\text{An}_{57}$) which usually are smaller, augitic diopside, and small (< 0.6 mm) crystals of lepidomelan.

Chemically these obsidians differ markedly from those of the First Period by a strong predominance of potassium over sodium with k -values about 0.6, by higher content of normative An and lower normative Ne; the magma type has become more pronouncedly *leucosyenitic*. This change in the composition of the magma, which persists also in the obsidians of the Third Period, supports the opinion of De LORENZO that a considerable space of time intervened between the eruptions of the lavas of the First Period and those of the Second, the *breccia museo* representing the concluding stage of the former.

3. Obsidians referable to the Third Phlegrean Period

Specimen 13 from the western slope of Astroni is rather pumiceous with numerous phenocrysts of sanidine (about $\text{Or}_{70}\text{Ab}_{30}$), labrador ($\text{Ab}_{42}\text{An}_{58}$), augitic diopside, and lepidomelan ranging in size between 2 and 1 mm.

Specimen 14 is an oblong ($35 \times 15 \times 15$ cm) bomb of obsidian with beautiful breadcrust structure collected in the pumiceous tuff of the Senga volcano. The obsidian is partly rather vesicular and contains numerous phenocrysts of sanidine (about $Or_{80}Ab_{20}$) which occasionally attain a size of 4 mm, labrador ($Ab_{40}An_{60}$), augitic diopside, and lepidomelan.

Specimen 16, a large fragment of obsidian, brownish and with numerous cracks when studied under the microscope. Phenocrysts occur fairly abundantly, viz. sanidine (about $Or_{80}An_{20}$), labrador ($Ab_{43}An_{57}$), augitic diopside, and lepidomelan.

Chemically these lavas are very similar to those of the Second Period; they are all of leucosyenitic type with potassium greatly predominant over sodium.

II. Mineral descriptions

For the determination of the relation K/Na in the feldspars three methods have been used. 1. Chemical analysis, 2. the variation of $d_{(\bar{2}01)}$ by the DEBYE-SCHERRER powder method, and 3. determination of the optical angle $2V_{\alpha}$ on the universal stage.

Chemical analysis

In the specimens 11a, 14, and 32 feldspar phenocrysts of such size occur that material sufficient for quantitative chemical determination of K_2O , Na_2O , and CaO could be picked out under the preparation microscope, a proceeding which is facilitated by the tabular habit of the crystals. The analyses were made by the Central Analytical Laboratory of the University of Uppsala under the supervision of Professor F. NYDAHL.

X-Ray analysis

In an important paper on the high temperature system albite-sanidine, N. L. BOWEN and O. F. TUTTLE (1950) found that the magnitude of the spacing $d_{(\bar{2}01)}$, as measured on the powder photogram, is a linear function of the content of Ab in the Or-Ab mixed crystal. The accuracy amounted to about 2% of the total variation of 2θ . Quartz and olivine were used as reference standards. The radiation was registered with G.M. tube.

Further investigations of the albite-sanidine system at temperatures up to $900^{\circ}C$ have been carried out by W. S. MACKENZIE and J. V. SMITH (1956) including, besides powder and single crystal analyses, also measurements of the optical axial angle of the feldspars. Unfortunately no data concerning the dispersion of $2V_{\alpha}$ are given.

For the present investigation the author has used a Philips 114 mm powder camera and CuK_{α} radiation. The powder was enclosed in 0.2 mm Mark capillaries. As reference standard lead nitrate, $Pb(NO_3)_2$, calibrated against quartz, has been used: the value 4.537 \AA of the (111) spacing has been adopted.

Optical analysis

This analysis was made with a Zeiss-Winkel Standard WL Pol microscope provided with a four-axis universal stage adapted for conoscopic measurement of axial angles, a great advantage when studying the variation of $2V_\alpha$ in zonary built sanidines.

MACKENZIE and SMITH tacked on to an earlier optical investigation by O. F. TUTTLE (1952), who had established the existence of a low-temperature and a high-temperature form of sanidine, which was further confirmed by single crystal X-ray analysis. Optically the difference between the two forms is expressed in the position of the axial plane, which is parallel to (010) in the high-temperature form but perpendicular to (010) in the low-temperature form (see TUTTLE, 1952). KOZU *et al.* (1916, 1921, and 1923) has studied the dispersion of the optical axis in a sanidine from Eifel. He found, after heating the specimen, $V_{\alpha \text{ blue}} > V_{\alpha \text{ red}}$ and the reverse for the unheated specimen. The position of the axial plane was parallel to (010) in the former case, perpendicular to (010) in the latter. This property has been used for distinction between the two forms. In both, the axial angle $2V_\alpha$ seems to vary regularly with the Or/Ab relation of the crystal. A zoned sanidine crystal with two different axial plane positions has been reported by A. HIMMELBAUER (1912, p. 328), and by J. F. OSTEN (1951).

Optical measurements are hampered by difficulties of two kinds. One is the unmixing into two phases of the solid solution. To avoid this, MACKENZIE and SMITH homogenized the crystals by heating at 900°C for 24 hours. When the sanidines are too small to be isolated, as was usually the case with the Phlegrean sanidines, the method is not applicable. The second difficulty arises from the temperature-dependency of the optical axial angle in the low-temperature sanidine. This relation is still unsettled.

The degree of accuracy of the optical measurements is hard to evaluate. The actual measurements can be made with high degree of accuracy, but the inhomogeneity of the material studied makes the accuracy illusory. The axial angle of the low-temperature form of the sanidine is not constant for a given chemical composition. Sanidines with low content of Ab exhibit begin transition into the high-temperature phase on heating, as emphasized by MACKENZIE and SMITH. Optically, the transition begins with a decrease of $2V_\alpha$ to zero, the axial plane rotates 90°, and then $2V_\alpha$ again increases. Discrepancies between the optically and the analytically determined composition of the feldspars are small in the obsidians of the First and Second Phlegrean Periods, but become considerable in those of the Third Period.

The amplitude of the variation of $2V_\alpha$ due to factors, the nature of which is uncertain, appears on the graphs of MACKENZIE and SMITH (*op. cit.*, Fig. 4), featuring the variation of $2V_\alpha$ with varying (Ab + An)/Or ratios, partly on natural material, partly on feldspar heated at 900°C for 24 hours. The varia-

tion may be visualized by boundary lines through the extreme points on both sides of the ideal graph and parallel to the latter. The amplitude is of the magnitude ± 20 wt %. Therefore the optical analytical method is not well suited for petrographical work when a homogenizing of the feldspar is not possible.

A. The sanidines in the obsidian of the First Phlegrean Period

Spec. 11a. The optical axial angle $2V_\alpha$ of the sanidines in this obsidian fluctuates slightly about 30° , corresponding to a mixed crystal of the composition Or_7Ab_3 , according to the graph of TUTTLE (1952). Only in two crystals, both with nicely zoned structure, larger axial angle was found, viz. 38° – 40° . The dispersion is $\rho > v$ in all crystals studied, indicating that the axial plane is \perp (010). Twinning according to the Carlsbad, Manebach, and Baveno laws is observed, the first mentioned being the most common.

A partial chemical analysis of the isolated crystals gave: K_2O – 10.7 %, Na_2O – 4.02 %, CaO – 0.7 %, corresponding to $Or_{62}Ab_{35}An_3$.

The X-ray analysis gave $d_{(\bar{2}01)} = 4.167$ Å. According to the graph of BOWEN and TUTTLE (1950, p. 493) this spacing corresponds to 31.5 % of weight of Ab or a molecular ratio $Or_{67}Ab_{33}$ in good agreement with the chemical analysis.

The optical analysis as well as the diffraction analysis postulates, however, a homogeneous feldspar, into which both components enter in solid solution. This probably holds because no trace of unmixing can be distinguished even by high magnification under the microscope.

The pipernoid lava, *Spec. 11b*, represents, according to RITTMANN, a lava ejected during the same stage as the one to which the agglomeratic obsidian, *Spec. 11a*, is due or an eruption closely preceding it, from the same magma chamber. The chemical composition of both rocks is very similar. The *piperno* sanidine differs from the sanidine of *Spec. 11a* by a notably larger $2V_\alpha$ which varies between 38° and 44° with a mean value of 41° in 14 crystals measured, corresponding to the composition Or_5Ab_5 , which, however, seems too high.

The diffraction value 4.157 Å of the $d_{(\bar{2}01)}$ spacing (average of 3 samples), which corresponds to $Or_{63}Ab_{37}$ is probably more plausible. In all crystals studied, the dispersion exhibited $\rho > v$. No zonal structure was observed.

The petrography of the *piperno*, *Spec. 11b*, has been ably described by RITTMANN (*op. cit.* p. 163). He records the presence of fluorite, scapolite and sodalite, interspersed in the devitrified glassy groundmass. The devitrification and non-magmatic mineral paragenesis is ascribed to intense autopneumatolysation due to soaking of the rock with very hot magmatic gases which contained besides water vapour, also HF, HCl, and H_2S .

The abnormally large optical angle of the sanidine may be due to subsequent heating of the crystals at high temperature (MACKENZIE and SMITH,

op. cit. p. 419), but it is doubtful whether such high temperatures are to be expected in pneumatolytical processes. The amount of plagioclase in the norm is considerably larger in the *piperno* than in the obsidian, Spec. 11a. Therefore a higher content of (Ab + An) is to be expected in the sanidine of the former, but hardly as high as Ab_{50} .

The chemical composition of the obsidian, Spec. 32 from Torre Gaveta is very similar to that of the *piperno*, Spec. 11b, and the obsidian, Spec. 11a; it also appears in similar stratigraphical position. The chemical analysis gave $K_2O - 10.4\%$, $Na_2O - 3.90\%$, and $CaO - 0.8\%$ corresponding to the composition $Or_{61}Ab_{35}An_4$.

The optical angle of the sanidine in this rock fluctuates between 27° and 30° with an average value of 29° in seven crystals, corresponding to the composition Or_7Ab_3 . The crystals exhibit faint traces of unmixing under high power magnification.

The optically derived composition agrees very well with the result of the X-ray analysis, according to which the proportion of the alkali components is $Or_{68}Ab_{32}$ ($d_{(\bar{2}01)} = 4.166 \text{ \AA}$). It should be noted, however, that the graph of BOWEN and TUTTLE, on which this value is based, refers to pure Or-Ab mixed crystals; the effect of the entrance of anorthite into the system is not known.

B. The sanidines in the obsidians of the Second Phlegrean Period

The obsidians of this period occur in the form of lapilli or small bombs embedded in the Neapolitan yellow tuff.

Spec. 33. Torre Gaveta. According to the diffraction method, the sanidine phenocrysts in this obsidian have the composition $Or_{79}Ab_{21}$ ($d_{(\bar{2}01)} = 4.187 \text{ \AA}$). The axial angle $2V_\alpha$ varies between 16° and 24° corresponding to about Or_7Ab_3 .

The crystals often exhibit, however, a zoned structure, the content of Ab increasing towards the margin; within each zone a gradual decrease of $2V_\alpha$ outwards is to be seen. The dispersion exhibits $\rho < v$; the axial plane should therefore be parallel to (010). Only within a thin zone in one crystal a dispersion $\rho > v$ was observed.

The composition of the associated plagioclase phenocrysts is $Ab_{43}An_{57}$ (average of 8 crystals measured).

Spec. 21. Cuma. The composition of the sanidine in this obsidian is $Or_{83}Ab_{17}$ ($d_{(\bar{2}01)} = 4.199 \text{ \AA}$). The axial angle $2V_\alpha$ varies between 23° and 26° with dispersion $\rho < v$, corresponding to the composition Or_7Ab_3 .

The composition of the associated plagioclase phenocrysts is $Ab_{42}An_{58}$ (average of 6 crystals measured).

Spec. 10a. Valle Verdolino. In this obsidian only a few small phenocrysts of sanidine were found, too small to be isolated for X-ray analysis. The axial angle $2V_\alpha$ varies between 25° and 33° with $\rho < v$. According to the graph of

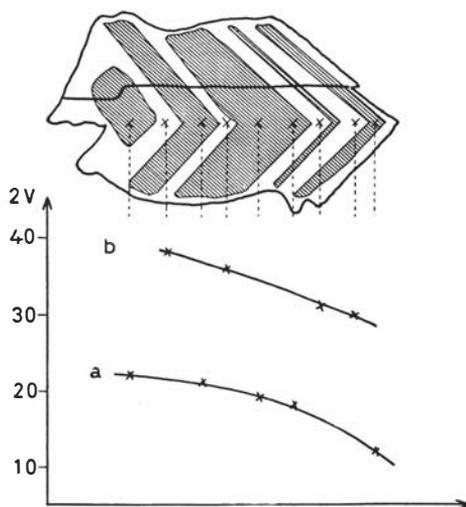


Fig. 1. Phenocryst of sanidine in Spec. 14 exhibiting repeated zoning. Magn. c. $20\times$.

TUTTLE these values correspond to a content of Ab about 20–30%. The composition of the associated phenocrysts of plagioclase is $Ab_{42}An_{58}$ (average of 3 crystals measured).

Common to all sanidines investigated in the obsidian from the Neapolitan yellow tuff, as compared to those in the obsidians of the First Period, is the much lower content of Ab. Another difference is the position of the optical axial plane parallel to (010), with dispersion $\rho < v$. The crystals usually exhibit a zoned structure with a core surrounded by a shell with slightly higher extinction angle. Usually more or less distinct traces of unmixing are in evidence.

C. The sanidines in the obsidians of the Third Phlegrean Period

The sanidines contained in the obsidians of this period have been studied in Spec. 14 (Senga), Spec. 16 (Agnano), and Spec. 13 (Astroni).

The chemical compositions of the sanidine agree rather closely with those of the Second Period, the average molar composition being $Or_{81}Ab_{19}$ (cfr. Table II). They exhibit, however, several features observed only seldom in the sanidines of the earlier periods. Thus, the sanidines of the Third Period, which have been studied, usually exhibit a pronouncedly polyzoned structure, the dispersion of the axial angle in each zone being reversed to that of the adjoining zones. The phenomenon is particularly nicely developed in a sanidine phenocryst in Spec. 14 from Senga: a fragment of a large phenocryst twinned to the Carlsbad law, in which 5 zones (a) alternating with 6 zones (b) with different optics can be distinguished (Fig. 1). In the zones *a*, $\rho < v$; in *b*, $\rho > v$. In series *a*, the optical axial angle $2V_x$ decreases from 23° in the kernel to 12° in the outermost zone; in series *b* it also decreases from 38° in zone *b*₂ to 27° in the marginal zone *b*₅. The change in optics takes place

Table

Period	Spec.	Chemical analysis						Mol comp.
		Obsidian			Sanidine			
		Na ₂ O	K ₂ O	CaO	Na ₂ O	K ₂ O	CaO	
		Weight %						
I	11a	6.67	7.20	1.90	4.02	10.7	0.7	Or ₆₂ Ab ₃₅ An ₃
	11b	6.09	7.21	1.79				
	12	7.13	7.11	1.75				
II	32	6.42	7.14	1.81	3.90	10.4	0.8	Or ₆₁ Ab ₃₅ An ₄
	10a	3.59	8.96	3.83				
	21	3.72	8.12	3.44				
III	33	3.43	8.45					Or ₈₀ Ab ₁₈ An ₂
	13	4.08	7.98	4.12				
	14	4.11	8.70	3.34	1.93	13.1	0.3	
	16	3.60	7.85	4.80				

abruptly at the boundary between two zones. An attempt to trace the variation of chemical composition of these various zones from the magnitude of the optical axial angle according to the graph of TUTTLE leads to unreasonable results. The bulk composition of a number of phenocrysts which were isolated and chemically analysed gave K₂O – 13.1 %, Na₂O – 1.93 %, CaO – 0.3 %, or the molar proportions Or₈₀Ab₁₈An₂. In tolerable agreement with these values is also the diffraction analysis which gave Or₈₃Ab₁₇.

Although the optical axial angle values thus cannot be used for determination of the actual content of Ab in the mixed crystal accurately, the values probably reflect differences in composition in the various zones. According to the graph of TUTTLE there would be a gradual increase in Ab from the kernel outwards in the zones of series *a*, but a gradual decrease in the zones of series *b*. In the rare cases when zoning of the sanidines have been observed in the earlier obsidians, the optical orientation has been found to be the same throughout the crystal.

The associated phenocrysts of plagioclase exhibit a distinctly zoned structure, the composition of the kernel being An₆₆ (average of 8 measurements), bordering with sharp contact on a marginal zone of the composition An₅₄ (in average).

Spec. 13. The axial angle $2V_{\alpha}$ of the sanidine phenocrysts in this rock fluctuates between 19 and 28° with dispersion $\rho < v$, corresponding to a content of about 30 mol. % Ab according to the graph of TUTTLE. The An content of the associated phenocrysts of plagioclase averages An₅₈.

II

X-ray analysis		Optical analysis				
$d_{(\bar{2}01)}$ Å	Mol comp.	$2V_\alpha$	Disp.	Pos. of opt. plane	Mol comp. of sanidine	Zoning
4.167	Or ₆₇ Ab ₃₃	30°	$\rho > \nu$	$\perp (010)$	Or ₇ Ab ₃	None
4.157	Or ₆₃ Ab ₃₇	38°-44°	$\rho > \nu$	$\perp (010)$	Or ₅ Ab ₅	"
4.166	Or ₆₈ Ab ₃₂	27°-30°	$\rho > \nu$	$\perp (010)$	Or ₇ Ab ₃	"
		25°-33°	$\rho < \nu$	// (010)	Or _{8.7} Ab _{2.3}	Distinct
4.199	Or ₈₃ Ab ₁₇	23°-26°	$\nu > \rho$	// (010)	Or ₇ Ab ₃	"
4.187	Or ₇₉ Ab ₂₁	16°-24°	$\nu > \rho$	// (010)	Or ₇ Ab ₃	"
		19°-28°	$\nu > \rho$	// (010)	Or _{9.7} Ab _{1.3}	Very distinct with several alternating shells
4.199	Or ₈₃ Ab ₁₇	12°-23°	$\nu > \rho$	// (010)		
		38°-27°	$\rho > \nu$	$\perp (010)$		
4.195	Or ₈₂ Ab ₁₈	17°-27°	$\nu > \rho$	// (010)	Or _{10.7} Ab _{0.3}	
		27°-23°	$\rho > \nu$	$\perp (010)$		

Spec. 16. The axial angle $2V_\alpha$ of the sanidine phenocrysts fluctuates between 17° and 27° with dispersion $\rho < \nu$; $2V_\alpha = 27^\circ$ corresponds to about 20 mol. % Ab. According to TUTTLE pure potassic-sanidine with dispersion $\rho < \nu$ should have an axial angle of 18-19°. The value of $2V_\alpha = 17$, seems rather low. MACKENZIE and SMITH (*op. cit.*) as well as SCHWARZMANN (1957) point out the close temperature dependency of the axial angle during crystallisation. The low gradient of the curve makes the readings very uncertain. In two cases sanidine phenocryst with dispersion $\rho > \nu$ were found, with $2V_\alpha$ varying between 23° and 27°, corresponding to about 30 mol. % Ab.

Diffraction analysis of an average sample gave $d_{(\bar{2}01)} = 4.195$ Å, corresponding to 18 mol. % Ab.

D. The Plagioclases

The composition of the plagioclases has been determined on the universal stage, in some cases using the zone method of RITTMANN, when the crystals were too small for complete measurements of the position of the indicatrix. Twinning according to the Albite, Carlsbad-Albite, Pericline-Albite and Manebach laws have been observed.

According to Table III, the plagioclases of the First Period are notably richer in albite than those of the Second and Third Periods averaging about 39 mol. % An. No zoning occurs. In those of the Second Period some zoning can be traced and the composition of the core usually differs only slightly

Table III

Period	Spec.	Number of crystals measured	Zonation	Mol. % An		
				Shell	Core	MV
I	11a	6	none			40
	11b	1	"			37
	32	7	"			39
II	10a	3	some			58
	21	6	"	58	53	
	33	8	"	57	50	
III	13	3	"			58
	14	8	"	54	66	
	16	6	"			57

from that of the shell; in the few cases when measurements were possible, the shell was more calcic than the core. The plagioclases of the Second Period average about An_{58} .

The content of An in the plagioclases of the Third Period is similar to that of the Second Period or perhaps slightly higher as an average. The zoning of the crystals is "normal" with a more calcic core, as a rule. Glassy inclusions occur occasionally, orientated preferably along (010) and (001).

It should be noted that the appearance of zoned plagioclases in the obsidians of the 2nd and 3rd Periods coincides with the appearance of zoning in the associated sanidine phenocrysts. Therefore, the zoning may be due to the same environmental factor in both cases (see below p. 85).

E. Biotite

No phenocrysts of biotite were found in the obsidians of the First Period but solitary crystals occur in those of the Second and Third Periods. In the specimens investigated the axial angle $2V\alpha$ varies between $25^{\circ}.5$ and $33^{\circ}.5$ with $v > \rho$, $\gamma - \alpha$ about 0.06 and $\alpha =$ brown, $\beta = \gamma =$ dark brown. It is a lepidomelan, probably with rather high content of iron.

F. Pyroxene

Judging from the optics, the composition of the pyroxenes differs only slightly in the various obsidians, no systematic differences being in evidence.

Zonal structure was noticed in some cases. In one crystal, exhibiting a hour-glass structure (Fig. 2), the angle $c \wedge \gamma$ was 41° in the core and 47° in the shell indicating a more alkalic shell (TRÖGER). A few crystals exhibit twinning parallel (010). The pyroxen ought to be classed as a sodic augitic diopside.



Fig. 2. Phenocryst of pyroxene with hour-glass structure.

Table IV

Period	$2V_{\gamma}$			c/γ			Disp.	Pleochroism
	Ampl.	M.V.	Number of meas.	Ampl.	M.V.	Measurements		
I	59°-67°	64°	9	44°-50°	47°	8	$\rho > v$	α = very pale yellowish green,
II and III	55°-66°	61°	16	41°-47°	45°	15	$\rho > v$	γ = very pale green

III. Discussion

According to P. NIGGLI (1941), in an ideal ternary system Or-Ab-An at constant temperature and pressure, the series of lines of coexistence (*Koexistenzgeraden*) connecting the alkali feldspar with the corresponding plagioclase in stable equilibrium (each line representative of the respective magma composition) group themselves in a characteristic pattern, the lines being parallel, converging or diverging depending on the physical conditions and the chemical composition of the magma. Provided K, Na, and Ca enter only in the feldspars and eventual foids, then the point denoting the composition of the rock, expressed by the relation Or : Ab : An, should fall on the line of feldspar coexistence of the rock, on condition that perfect equilibrium is obtained.

In the present case, it is doubtful whether the latter condition is realized. If, none the less, the chemical data of the feldspars and the rocks are plotted in the Ne-Kp-Cal diagram according to NIGGLI (Fig. 3), the inclination of the lines of feldspar coexistence assumes a trend similar to that in rocks of the calc-alkalic suite as exemplified by Fig. 5 in NIGGLI's paper, converging towards the region of medium sodic sanidines. The composition points of the rocks fall, however, outside the corresponding lines of feldspar coexistence in the Phlegrean obsidians.

According to T. W. BARTH (1951, 1956), the composition of the coexisting feldspars in a volcanic rock is largely a function of the temperature of crystallization. The feldspar molecules Or, Ab, and An usually will form two phases, corresponding to the two series of solid solutions: Ab in An and Ab in Or, resp., the relation (mol. of Ab in Or)/(mol. of Ab in An) being constant (k') at fixed T and P according to the law of distribution of NERNST, provided equilibrium has been established and the substance dissolved is in

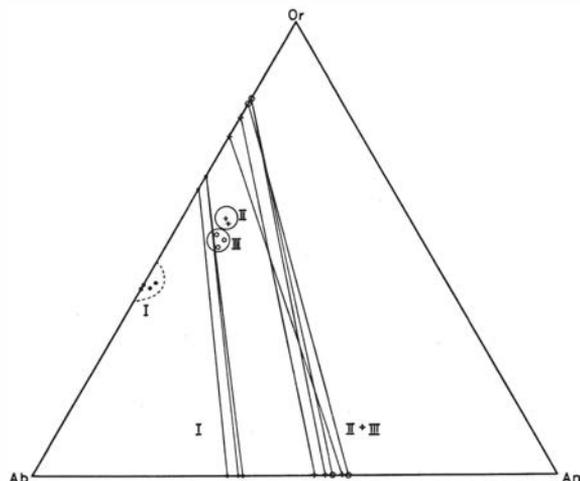


Fig. 3. Feldspar coexistence graph of the Phlegrean feldspars.

the same molecular state in both phases. BARTH, contrary to NIGGLI, is of the opinion that the chemical environment has little effect on the sodium distribution ratio.

In a graph (1956, Fig. 9) BARTH has arranged the k' -values of a number of analyses of coexistent alkali-feldspars and plagioclases in various effusive and intrusive rocks according to decreasing temperature of crystallization as indicated by their geological relations. As emphasized by BARTH, the k' -value is a function not only of the temperature but also of the degree of lattice disorder in the feldspar and, to some extent, the *chemical composition*. Within the low temperature region, the graph is constructed to follow the microcline/plagioclase line, at moderate temperature the orthoclase/plagioclase line, and at high temperatures the sanidine/high plagioclase line; the average curve,

Table V

Period De Lorenzo	Spec.	Mol. % Ab in plag.	Mol. % Ab in sanidine	k'	Barth temp. C°	Niggli k' -value of lava
I	32	61	34	0.55	820°	0.42
	11b	63	37	0.58	850°	0.44
	11a	60	34	0.57	830°	0.42
II	10a	42	25	(0.51)	(760°)	0.62
	33	43-50	21	(0.47)	(730°)	0.62
III	21	42-47	17	(0.38)	(640°)	
	16	43	17	(0.40)	(670°)	0.59
	14	46-34	18	(0.45)	(710°)	0.58

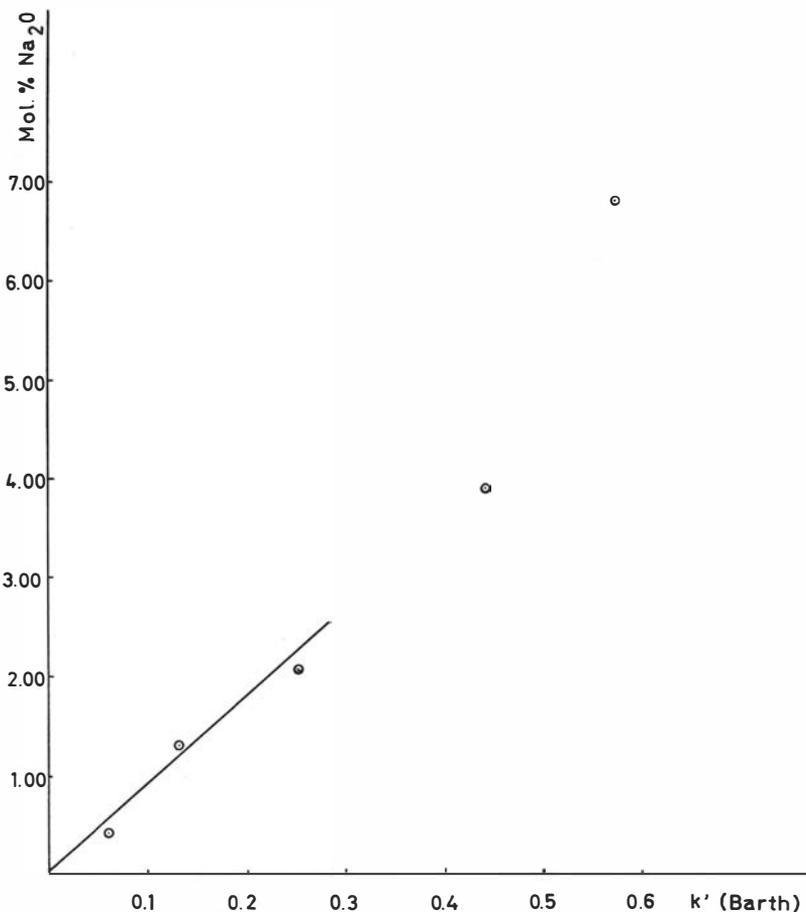


Fig. 4. Position of the Phlegrean feldspars in the sodium quotient graph of H. WINKLER & H. v. PLATEN 1958.

thus obtained, is provisional and is referred to by BARTH as the “1956 values for the feldspar crystallization temperatures”.

According to this graph, the albite distribution ratio of the Phlegrean lavas would correspond to the temperatures given in Table V.

Professor BARTH, who has kindly commented upon these results on my request, emphasizes the importance of the zonal structure in the feldspars in the lavas of the 2nd and 3rd periods where zoning is markedly in evidence not only in the plagioclase but, as much so, also in the sanidine. “Thus, the sanidine composition used for the calculation of the temperatures is an average composition which does not represent an equilibrium relationship to an average plagioclase composition. I don’t believe it is possible to state anything about the temperatures (or the k' -values) of the feldspars of the 2nd and 3rd periods” (letter of 8/1 1959, translated by the present author).

Another peculiar fact, also stressed by professor BARTH, is that in spite of the position of the rock analyses well inside the leucite field in the foid-feldspar diagram of SCHAIRER (1950), sanidine crystallizes, and the sanidine of the I Period appears *lower* on the crystallization curve than the sanidines of the Second and Third periods, indicating different environmental conditions in the two groups of lavas.

Recently, the distribution of the Ab component on the feldspars has been studied experimentally by H. WINKLER and H. von PLATEN (1958) in hydrothermal systems at 2000 atm. and temperatures between 620° and 720°C. They found that a linear relation exists between the quotient k' and the amount of Na₂O used for the formation of feldspars in the melt and, thus, the composition of the associated feldspars is, on the first hand, a function of the chemical composition of the rock.

Turning again to the data of Table V it is evident that the values obtained group themselves into two series: one characterized by k' -values about 0.57, all members of which belong to the First Phlegrean period; the other series is characterized by more variable k' -values which fluctuate between 0.38 and 0.51, comprising obsidians of the Second and Third periods. The tendency to lower k' -values in the feldspar of the latter periods as compared with those of the First period, although the former must be very approximate, is obvious. This disconformity in the series of k' -values coincides with the rather marked difference in the content of sodium in the obsidians of the first group as compared with those of the second group, which is reflected in the Niggli k -values of the obsidians. Plotting the average Na₂O mol. % and the average k' -values of the obsidians and associated feldspars of each of the two groups in the graph of WINKLER and v. PLATEN, the points fall rather near the linear extension of the graph (Fig. 4). Therefore we cannot disregard the possibility that the lowering of the feldspar distribution ratio in the Phlegrean obsidians of the Second and Third periods may be due largely to the chemical factor.

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