

## TRACHYTE AMPHIBOLES IN THE EUGANEAN HILLS (NORTH-EASTERN ITALY)

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**ABSTRACT.** — This paper reports data on the chemistry of the amphiboles occurring as phenocrystals or megacrystals in the igneous rocks of the Euganean Hills. Microscopic observations and wet or microprobe chemical analyses strongly suggest that they must be considered as phenocrystals and not xenocrystals: their composition differs in Si, Al, Ti, Fe and Mn contents, which are variable with some continuity among the kaersutites (in the trachytic rocks) and edenites (in the alkali-rhyolitic rocks). The possible influence of the chemistry of the host rock on the composition of the amphibole is also discussed, in the light of data in the literature concerning both the amphibole of similar rocks and that of other kaersutite lithotypes. It is concluded that the occurrence, but not the composition, of kaersutitic amphibole is related to the chemistry of the host rock; in fact, it appears with more or less unvaried composition in many alkaline rocks, generally undersaturated and ne-normative, from basic to intermediate ( $\text{SiO}_2 < 63\%$ ), with an albitic index of less than 0.9. There are no significant suggestions for believing that the evolution of the composition of amphibole from kaersutitic to edenitic type (in spite of apparent correlations among  $\text{SiO}_2$ ,  $\text{TiO}_2$  and, perhaps,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , found between rock and amphibole in the Euganean Hills and in the saturated series of Mont Dore, France), may be ascribed to chemical variations of the host rock at least as may be inferred by observing titanium and alkali contents. Mineralogical features also seem to exclude sharp variations of  $f_{\text{O}_2}$  and  $H_{\text{H}_2\text{O}}$  as factors responsible for the modification of composition of the amphibole. In the light of the experimental results of HELZ (1973) and the thermodynamic considerations of VERHOOGEN (1962), it is suggested that this evolution may be ascribed to differences in crystallization temperature of the amphibole in the trachytic and alkali-rhyolitic magmas.

**RIASSUNTO.** — Vengono esposti i risultati delle ricerche sul chimismo degli anfiboli presenti come fenocristalli o megacristalli nelle vulcaniti dei Colli Euganei. L'osservazione microscopica e le analisi

chimiche, eseguite secondo i metodi tradizionali o alla microsonda, chiaramente suggeriscono che essi debbano essere considerati come fenocristalli e non xenocristalli; le composizioni degli anfiboli si differenziano per i tenori di Si, Al, Ti, Fe ed Mn, variabili con una certa continuità tra quelli di kaersutiti (nelle rocce trachitiche) e quelli di edeniti (in rocce alcaliriolitiche). Viene discussa una possibile influenza del chimismo della roccia ospite sulla composizione dell'anfibolo, anche alla luce dei dati reperibili in letteratura concernenti sia l'anfibolo di rocce analoghe che quello di altri litotipi a kaersutite. Si conclude che, alla presenza, ma non la composizione, dell'anfibolo kaersutitico sono condizionate dal chimismo della roccia ospite; esso infatti compare con composizione pressochè invariante in molte rocce alcaline, generalmente sottosature e ne-normative, da basiche ad intermedie ( $\text{SiO}_2 < 63\%$ ), con indice albitico inferiore a 0,9. Non ci sono indizi significativi per i quali l'evoluzione della composizione dell'anfibolo da kaersutitico ad edenitico, a dispetto delle apparenti correlazioni tra  $\text{SiO}_2$ ,  $\text{TiO}_2$  e, forse, tra  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$  riscontrate nelle rocce e nell'anfibolo Euganei e della serie satura del Mont Dore (Francia), possa essere ascritta a variazioni di chimismo della roccia ospite, almeno per quanto si può dedurre osservando i valori del titanio e degli alcali. I caratteri mineralogici sembrano escludere anche variazioni decise di  $f_{\text{O}_2}$  ed  $H_{\text{H}_2\text{O}}$  come fattori responsabili della modificazione di composizione dell'anfibolo. Sulla base dei risultati sperimentali ottenuti da HELZ (1972) e da considerazioni termodinamiche esposte da VERHOOGEN (1962) si suggerisce che questa evoluzione sia imputabile a differenze di temperatura di cristallizzazione dell'anfibolo nei magmi trachitici e alcaliriolitici.

### Introduction

This work is a further contribution to the study of the chemico-crystallographic features of the sialic and femic minerals of the acidic eruptive rocks of the Euganean Hills, undertaken some time ago by the writers

in collaboration with other Authors, with the aim of improving knowledge on the petrogenetic processes involving the Tertiary Volcanic Province of the SW Venetian area (North-Eastern Italy). This province is characterized by a subcrustal, substantially bimodal magmatism, prevalently basic and mildly alkaline, which took place in an anorogenic environment, of which the Euganean trachytes and rhyolites represent the only acidic lithotypes. The study is being carried out on the major and accessory minerals and on the groundmass of 26 rocks chosen among the most representative of the acidic lithologies which, chemically, may be aligned along a possible main evolutionary trend (DE PIERI et al., 1977).

The chemical and roentgenographic data of the feldspar phenocrystals have already been illustrated (DE PIERI et al., 1974) together with the relations between their chemistry and the composition of the corresponding groundmasses and bulk rocks (PICCIRILLO et al., 1980). The chemistry of the phenocrystals of biotite, which represents the most abundant and common femic phase, and of pyroxenes have already been reported in previous works (DE PIERI et al., 1978; DE PIERI & MOLIN, 1980). In this note, the results of research on the chemistry of the amphiboles occurring as phenocrystals or megacrystals in the Euganean trachytes and alkali-rhyolites are presented.

### Petrographic and mineralogical features

The 26 acidic rocks supplying the minerals for this study show variable chemistry between that of latitic trachytes and perisilicic alkali-rhyolites (PICCIRILLO et al., 1980): their geographic location and geologic occurrence are reported in DE PIERI et al. (1977).

In the trachytes, always oversaturated (6-13 % normative quartz), silicic phenocrystals are represented mainly by anorthoclase or Na-sanidine and andesinic-oligoclase plagioclase; the femic phenocrystals by biotite, pyroxene, and amphibole. The biotite, occurring in all the samples in relatively abundant amounts, is a Mg-biotite which is quite different from that of the rhyolites, owing to its higher Al, Ti, Mg, Ca and Ba contents and lower Fe, Mn, H<sub>2</sub>O and Rb contents. The pyroxenes, barely

present only in six trachytes and in one quartz-trachyte, are of two kinds: the first, more frequent and pale green in colour, shows augitic composition very close to that of a salite, with low Al contents. The second, pale brown in colour, is sometimes found in a few trachytes and usually in the core of green pyroxene. Its composition is clearly augitic, with Al<sub>2</sub>O<sub>3</sub> contents reaching 9.8 % wt (Ca-poor pyroxene). The amphibole occurs only in 4 of the 10 trachytes studied, i.e. in samples 71 (Monte Merlo), 127 (northern side of Monte Gemola), 115 (southern side of Monte Lozzo) and 145 (southern side of Monte Cero). It always occurs only in very small quantities, except in sample 71, from which it was possible to separate it for wet chemical analysis. The phenocrystals are generally not more than 1.5 mm long, although they may sometimes be much larger (6 mm in sample 115). They show narrow re-absorption reaction with the development of an opacitic rim which generally encloses the brown amphibole.

It is interesting to note that the amphibole, in these trachytes associated with green pyroxene, was not found in those samples in which brown pyroxene also occurred, so that it appears to be an alternative.

In the Monte Lozzo trachyte (sample 115) idiomorphic megacrystals of amphibole were found, with prismatic habit and maximum sizes of 6 × 1.5 cm. In thin section, relations with the groundmass and optical characters were like those of the phenocrystals. Similar megacrystals were found in the trachytes of the Bonetti quarry, at Mandria di Montegrotto, and in a latitic dyke outcropping slightly west of this locality. These rocks, which were not included in the 26 chosen for mineral study, were chemically analysed (for analytical results, CIPW norms and a brief petrographic description of these samples, nos. 235 and 236, see appendix).

Apatite and zircon are frequent accessory minerals of these rocks, and study on them is almost complete. The groundmass is formed of Na-sanidine, one or two silica polymorphs (quartz and/or cristobalite  $\alpha$ ) and opaque minerals.

The alkali-rhyolites show Na-sanidine phenocrystals, sometimes associated with very rare anorthoclases, biotite and opaque

TABLE 1  
*Chemical analyses of the amphiboles  
 of the Euganean Hills*

	71F	115M	235M	236M
SiO <sub>2</sub>	41.06	40.58	41.00	40.65
TiO <sub>2</sub>	4.76	5.63	4.97	5.35
Al <sub>2</sub> O <sub>3</sub>	12.07	13.46	12.70	13.38
Fe <sub>2</sub> O <sub>3</sub>	2.86	2.51	3.16	4.16
FeO	10.15	10.02	9.74	7.92
MnO	0.19	0.15	0.19	0.14
MgO	12.75	12.31	12.51	12.89
CaO	10.87	10.99	10.83	11.70
Na <sub>2</sub> O	2.64	2.45	2.66	2.45
K <sub>2</sub> O	1.02	0.77	0.78	0.83
P <sub>2</sub> O <sub>5</sub>	0.41	0.10	0.05	0.08
H <sub>2</sub> O <sup>+</sup>	1.39	1.07	1.10	0.90
F	0.15	0.17	0.12	0.19
O=F	0.06	0.07	0.05	0.08
Total	100.26	100.14	99.76	100.56

Numbers of atoms on the basis of 24(O,OH,F)

Si	6.080	6.021	6.111	6.001
P	0.052	0.012	0.007	0.011
Al <sup>IV</sup>	1.868	1.967	1.882	1.988
Al <sup>VI</sup>	0.238	0.385	0.349	0.340
Ti	0.530	0.628	0.557	0.594
Fe <sup>3+</sup>	0.318	0.280	0.354	0.463
Fe <sup>2+</sup>	1.257	1.243	1.214	0.978
Mn	0.024	0.019	0.024	0.018
Mg	2.812	2.720	2.778	2.835
Ca	1.724	1.746	1.728	1.850
Na	0.758	0.704	0.768	0.700
K	0.192	0.146	0.149	0.156
OH	1.373	1.059	1.094	0.887
F	0.070	0.080	0.056	0.089

minerals, the latter two almost absent in the persilicic alkali-rhyolites, in some of which typical idiomorphic phenocrystals of quartz appear. Apatite and zircon are accessory minerals. Quartz and Na-sanidine are essential components of the groundmass. In alkali-rhyolite 52 (Monte Moscalbò, north of Villa Brunella) and 114 (Monte Cinto, near the summit), phenocrystals of greenish-brown amphibole were also found, maximum size being respectively 0.3 and 1 mm, partly re-absorbed and replaced by minute aggregates of opaques.

### Analytical methods

As already said, the amphiboles studied come from samples 71, 127, 115, 52, 235 and 236, in which they are present as phenocrystals. The megacrystals were extracted from samples 115, 235 and 236. Only from sample 71 was it possible to obtain a concentrate of phenocrystals sufficiently plentiful for wet analysis. The rock was finely ground and, from the fraction with grain sizes between 100 and 140 mesh, silic minerals, pyroxenes, heavy accessories and groundmass were removed using a Frantz isodynamic separator and heavy liquids (bromoform, methylene iodide), so as to obtain amphibole and biotite concentrates: most of the phyllosilicates were then eliminated by putting the concentrates on a sheet of paper and tilting and vibrating it slightly. After removing incrustations on the granules by using ultrasonics, further separation with methylene iodide and removal of the last impurities by hand pinking under a binocular microscope gave a practically pure sample for analysis.

As regards the megacrystals, one for each of samples 115, 235 and 236 were isolated, sufficiently large to supply material for wet chemical analysis. The concentrates were treated like the phenocrystals of sample 71, allowing practically pure materials to be obtained here too.

Magnesium, calcium, manganese, sodium, potassium, phosphorus and total iron were assayed by means of atomic absorption (using a Perkin Elmer AA 5000, when necessary equipped with a graphite oven). Ferrous iron was obtained by trititation with K MnO<sub>4</sub>; « water » was measured by loss on ignition and the value obtained corrected for iron oxidation. Fluorine was determined potentiometrically using an ion-selective electrode (INGRAM, 1970).

Silicon, aluminium and titanium were valued by means of X-ray fluorescent spectrometry according to the technique described by DE VECCHI et al. (1968); the same methodology was also used to check calcium, potassium and total iron (which had already been determined by the above methods). The analytical results and number of atoms on the basis of 24 (O, OH, F) are shown in table 1.

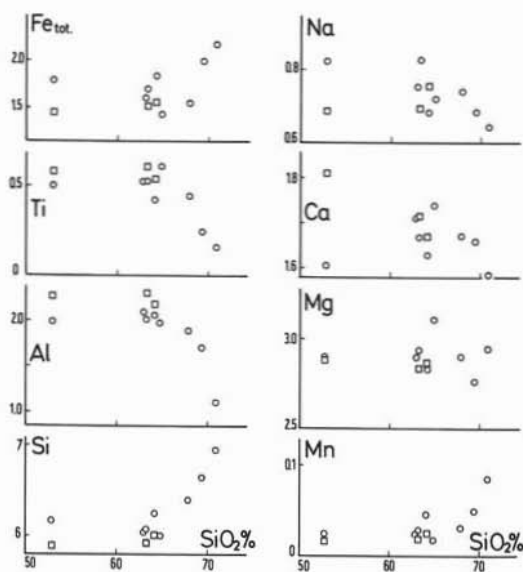


Fig. 1. — Relations between elements (numbers of atoms on the basis of 23(O) of Euganean amphiboles and  $\text{SiO}_2$  concentrations of corresponding host rocks. Squares = megacrystals; circles = phenocrystals.

Of the rare amphibole phenocrystals in samples 127, 115, 52 and 114, analysis had to be carried out by ETEC Autoscan-Autospec microprobe at the Institute of Mineralogy of the University of Padua, with counting times of 30 seconds, and accelerating voltages of 15 KV for Na, Mg, Al, Si, and 20 KV for Ca, Ti, Mn, Fe, K. The programme of MASON *et al.* (1969) was used to convert the counts to weight per cent oxides. As standards were used « Kakanui augite, New Zealand » and the same amphibole of sample 71, which turned out to be homogeneous within the limits required for its use as a standard. This technique was in fact used to search for possible zonation phenomena, both on the phenocrystals and on the powder specimens of megacrystals. The analysis showed that all the amphiboles were nearly homogeneous: in table 2, for example, next to analyses 71 N and 52 N showing the chemistry of the amphibole of samples 71 and 52 deduced from the average of many analyses, are analyses 71 P and 52 P, representing the largest deviation from average chemistry. For the analyses carried out using this technique in table 2, the number of atoms on the basis of 23 (O) is given.

## Results and discussion

The chemical data shown in tables 1 and 2 indicate clearly that there is some difference in chemistry between the amphiboles of the trachytes and alkali-rhyolites. In particular, the former show lower Si, Fe and Mn contents and higher Al and Ti contents with respect to the latter. As regards the remaining elements, no definite variation trend can be inferred, although a certain reduction of Na and Ca with increasing acidity of the host rock may be noted. As regards nomenclature, referring to the site occupancies according to LEAKE's (1978) classification, all the amphiboles analysed must be considered members of the calcic amphibole group, since they all have  $(\text{Ca} + \text{Na})_B > 1.34$  and  $\text{Na}_B < 0.67$  in the cubic site. Moreover, on the basis of the same classification, amphiboles 71, 71N, 71P, 115M, 115F, 236M, 236F, 235M and 127 may be defined as kaersutites, since they show  $\text{Ti} > 0.50$ ,  $6.50 < \text{Si} < 5.70$  and  $\text{Mg}/\text{Mg} + \text{Fe}^{2+} > 0.50$ . The rest of the amphiboles, showing  $(\text{Na} + \text{K})_A > 0.50$ ,  $\text{Ti} < 0.50$ ,  $\text{Mg}/\text{Mg} + \text{Fe}^{2+} > 0.50$ , according to Si values may be classified as follows:

- Samples 145 and 235F: « ferroan pargasitic or magnesian hastingsitic hornblends », since the ratio between  $\text{Fe}^{3+}$  and  $\text{Al}^{\text{VI}}$  is not available;
- Samples 52N and 52P: edenitic hornblends;
- Samples 114: edenite.

Microscopic observations indicate that the amphibole of all these rocks must be considered present as a phenocrystal and not as a xenocrystal. Moreover, its chemical composition turns out to be different in the trachytes and alkali-rhyolites — a feature which it would be difficult to justify if this were a xenocrystal. A similar genesis also seems very probable for the megacrystals, since they show chemistry very like that of the smaller amphiboles associated with them in the various trachytes. With respect to these, in effect, the megacrystals show slightly lower Si, Fe, Mn and Na contents and higher Al, Ti and Ca contents, thus following (although in a less pronounced manner) the variation trend of these elements observed between the amphibole phenocrystals of the trachytes and alkali-rhyolites. As regards the



TABLE 2

*Microprobe analyses of the amphiboles of the Euganean Hills*

	71N	71P	127	115F	145	52N	52P	114	236F	235F
SiO <sub>2</sub>	40.5	39.7	41.3	40.6	43.8	44.4	45.1	45.8	41.5	42.3
TiO <sub>2</sub>	4.81	5.54	5.53	4.68	4.06	2.24	2.37	1.41	4.53	3.82
Al <sub>2</sub> O <sub>3</sub>	12.2	12.9	11.6	11.5	11.0	9.79	9.76	6.19	11.4	11.8
Fe <sup>M</sup>	13.2	12.9	11.5	13.4	12.5	15.9	15.8	17.1	14.2	14.7
MnO	0.21	0.14	0.15	0.23	0.25	0.39	0.38	0.66	0.20	0.36
MgO	13.4	13.4	14.8	12.9	12.9	11.4	11.6	12.7	12.6	12.1
CaO	10.5	10.6	11.2	10.5	10.7	10.4	10.4	9.74	10.1	10.3
Na <sub>2</sub> O	2.42	3.18	2.56	2.86	2.63	2.37	2.54	2.19	2.87	2.38
K <sub>2</sub> O	1.02	1.00	1.03	1.05	0.86	1.19	1.18	0.69	0.77	0.73
Total	98.26	99.36	99.67	97.72	98.70	98.08	99.13	96.48	98.17	98.49

Numbers of atoms on the basis of 23(O)

Si	6.002	5.836	5.999	6.069	6.393	6.620	6.655	6.957	6.164	6.251
Al <sup>IV</sup>	1.998	2.164	1.986	1.931	1.607	1.380	1.345	1.043	1.836	1.749
Al <sup>VI</sup>	0.133	0.071	--	0.095	0.285	0.339	0.351	0.064	0.159	0.307
Ti	0.536	0.612	0.604	0.526	0.445	0.251	0.263	0.161	0.506	0.424
Fe <sup>2+</sup>	1.635	1.586	1.397	1.674	1.525	1.982	1.949	2.171	1.764	1.816
Mn	0.025	0.018	0.018	0.029	0.031	0.049	0.048	0.085	0.025	0.045
Mg	2.958	2.934	3.203	2.872	2.804	2.532	2.550	2.874	2.788	2.664
Ca	1.666	1.669	1.742	1.681	1.673	1.661	1.644	1.585	1.606	1.630
Na	0.694	0.906	0.721	0.828	0.743	0.684	0.727	0.644	0.826	0.682
K	0.192	0.187	0.190	0.201	0.160	0.226	0.222	0.133	0.146	0.138

problem of the appearance of megacrystals in these trachytic and latitic rocks, we believe that this may only be discussed when systematic field research, now under way, has clarified whether their occurrence is limited only to the already identified masses or whether it is more generalized in the other Euganean bodies too, in particular those of latitic or basaltic type.

The chemical data reported here show that the chemistry of the amphibole varies according to the lithotype in which it appears: the deduction is that its composition was influenced by the chemistry of the host rock. This is apparent from the diagrams of fig. 1, in which the number of atoms of some elements, all uniformly calculated for the sake of comparison on the basis of 23 (O), are related to the SiO<sub>2</sub> contents of the host rock: variation trends may be seen for Si, Al, Ti, Mn, total Fe and, perhaps, for Ca and Na. Similar correlations are also apparent with the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents of the host rock. The diagrams of fig. 2 again suggest correlations between the corresponding

contents of Si, Ti, and, less evidently, Al, Ca and Na in the amphibole and in the host rock.

On the basis of these observations, we believed it would be interesting to see whether these trends were confirmed by data inferred from the literature on both trachytic rocks and other kaersutite lithotypes. A careful bibliographical investigation showed that reports on trachytes with kaersutite phenocrystals are not common. Our work was also made more difficult by the frequent lack of chemical data concerning host rocks, so that it was often necessary to refer to « trachytes » only on the basis of their definition as proposed by workers who described them. There are about 30 reports of trachytes without amphibole or in which the nature of the amphibole is not defined or is rather vague (deduced, for example, from the colour in thin section). Instead, about 20 reports deal with trachytes containing alkali amphiboles of riebeckitic, arfvedsonitic and katophoritic type, or of barkevikitic and hastingitic type, although

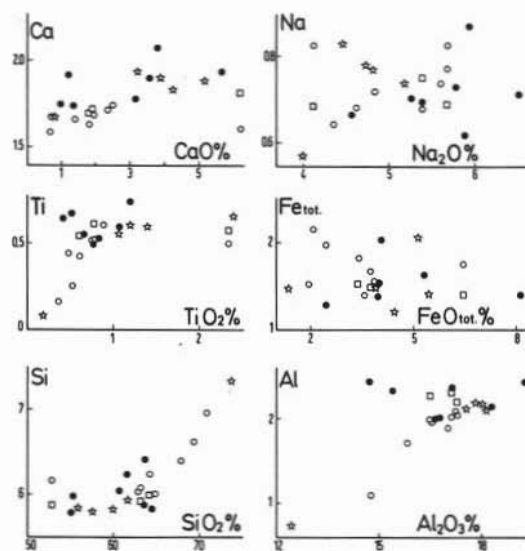


Fig. 2. — Relations between elements (numbers of atoms on the basis of 23(O) of amphiboles and corresponding oxides of host rocks. Squares = mega-crystals and open circles = phenocrysts of the Euganean amphiboles; solid circles = trachyte kaersutites from the literature; stars = amphiboles from the K-benmoreites and rhyolites of Mt. Dore (MAURY, 1976).

these too are often only identified on the basis of their optical features in thin section. Kaersutite trachytes are mentioned far less frequently: they have been found on Iki Island (AOKI, 1963), at Dunedin (New Zealand) (BENSON, 1939); in the French Massif Central (BENTON, 1954; CARMICHAEL, 1967; BERGER et al., 1978); on North Island (Lake Rudolf) (BROWN et al., 1971), on the Atlantic island of Nuku-Hiva (MAURY, 1976; MAURY et al., 1978), at Hockeifel (Germany) (GUTBERLETT et al., 1965) and, on the basis of optical data only, on Tahiti (MCBIRNEY, 1968) and on Panape (Caroline) (YAGI, 1960). Of these kaersutitic trachytes, three are ne-normative (BENSON, 1939; GUTBERLETT et al., 1965; MAURY, 1976); the others are saturated or over-saturated; and they are all alkaline according to KUNO (1968), and miaskitic.

The kaersutites of these rocks, inserted into the diagrams of fig. 2, seem to restrict correlations between elements corresponding to Si and Ti alone.

Further careful bibliographical research (which unfortunately excludes the Russian Authors, since their works are not available)

shows that 130 Authors have reported the occurrence of kaersutite, sometimes in lithotypes chemically similar to trachytes, more commonly in rocks which are more or less markedly different (\*). This amphibole is generally found as a megacrystal or xenocrystal in undersaturated alkaline rocks, generally ne-normative, ranging from basic to intermediate in type; it may also be found as a primary phase in basic and ultrabasic enclaves of alkaline rocks. Sporadic reports also exist of its occurrence in metamorphic rocks as eclogites, metagabbros, amphibolites, pyroxene granulites and vaguely defined « green rocks ». In igneous, plutonic and volcanic rocks, kaersutites are reported in the following lithotypes (listed according to the name assigned by the Authors who studied them): a) trachyandesite, andesite, K-mugearite, K-benmoreite, ordanchyte, analcymite, hawaiiite, andesitic basalt, trachybasalt, trachydolerite, diabase, basanite, basanitoid, camptonite, picrite, syenite, diorite, monzodiorite, monzonite, gabbro, peridotite, pegmatitic vein, pulaskite, plagifoyaite, essexite, teschenite, yamarskite; b) in enclaves of the type: trachytic, syenitic, gabbroic, hornblenditic, pyroxenitic, werhilitic, peridotitic, eclogitic, and in poorly defined ultramafic nodules or cumulates; c) as megacrystals in: benmoreites, hawaiiites, analcymites, alkali olivine basalts, camptonites, basanites, tuffs or scoriae cones. About 100 analyses of kaersutite, reported by about 30 Authors, are accompanied by analyses on the host rock: using these data, we compared the contents of all the elements measured in the amphibole and the  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ , total  $\text{FeO}$  and  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$  of the corresponding rocks. The correlations suggested by the Euganean amphiboles have not been confirmed, since well-defined and pronounced trends were not observed in the various diagrams. The only confused correlation appears to be that, with increasing  $\text{SiO}_2$  and decreasing  $\text{MgO}$ , there is an increase in  $\text{FeO}$  and a reduction in  $\text{Al}_2\text{O}_3$  in the amphibole.

Instead, the silicon, titanium and alkali contents of the kaersutite are not sensitive

(\*) This bibliography is available from the authors, upon request.

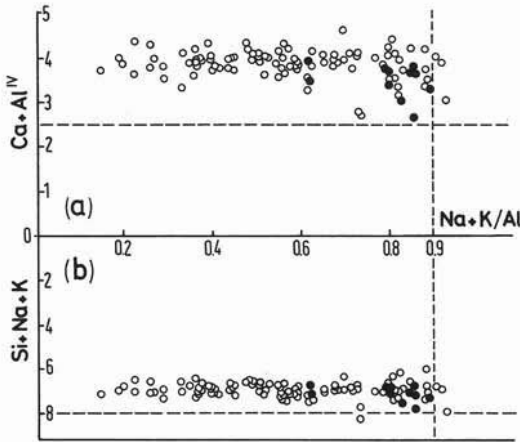


Fig. 3. — Relationship between  $\text{Ca} + \text{Al}^{\text{IV}}$  (a) and  $\text{Si} + \text{Na} + \text{K}$  (b) in the amphiboles and apgaitic coefficient in their host rock. *Solid circles* = Euganean amphiboles; *open circles* = literature kaersutites.

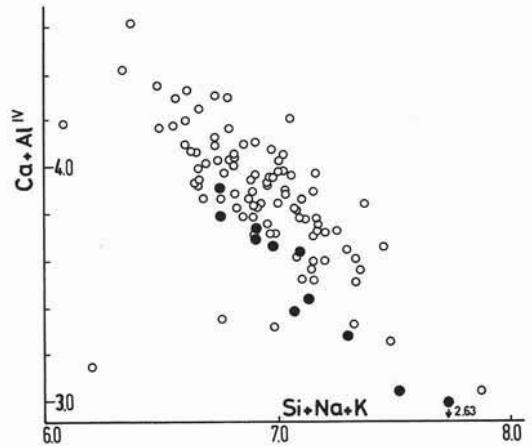


Fig. 4. — Relationship between  $\text{Ca} + \text{Al}^{\text{IV}}$  and  $\text{Si} + \text{Na} + \text{K}$  in the Euganean amphiboles (*solid circles*) and in the literature kaersutites (*open circles*).

either to the contents of the corresponding elements or to the variations of other elements of the rock; titanium in particular is not only independent of  $\text{TiO}_2$  in the rock, but also appears not to vary with changing rock acidity or alkalinity. Moreover, the kaersutites seem to be independent of the apgaiticity index (fig. 3), in agreement with the observations of GIRET et al. (1980) on the amphiboles coming from undersaturated rocks with an A.I. up to 0.9, for which the predominant pattern of replacement  $\text{CaAl}^{\text{IV}} \rightleftharpoons \text{NaSi}$  is confirmed (fig. 4).

The conclusions which may be drawn from these comparisons and descriptions of rocks lacking in chemical analysis in which kaersutite is reported, agree with indications partly inferred from other Authors. In short, the composition of this amphibole does not appear to be affected by variations in chemistry of the host rocks, on the contrary of its occurrence. The latter is indeed related to well-defined petrochemical conditions: kaersutite appears only in alkaline rocks of basic to intermediate type, that is with  $\text{SiO}_2$  less than approx. 63 %, generally undersaturated and ne-normative; all kaersutitic alkaline rocks, under- or over-saturated, show an A.I. of less than 0.9; in the peralkaline rocks alkaline amphiboles are an alternative to kaersutite.

The interpretation of the correlations between  $\text{SiO}_2$ ,  $\text{TiO}_2$  and, perhaps, between  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$  found in the Euganean rocks and amphiboles, appears problematic at the present time. Indeed, only MAURY (1976) analysed the evolution of the amphiboles in a « differentiation » suite similar to the Euganean suite (Mont Dore; stars in fig. 2), in which some lithotypes (« K-benmoreites ») of composition similar to that of our trachytes showed kaersutite. MAURY's data agree perfectly with ours, showing the same evolutionary trends, at least for  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ . In particular, the amphibole of his rhyolite is not titaniferous.

The alkali contents of the host rocks are certainly not responsible for these chemical variations and for other, being practically constant in the Euganean trachytes and alkali-rhyolites.

In oversaturated rocks, the composition of the amphibole of the slightly alkaline rocks and that of the sub-alkaline types therefore seem to approach each other.

The reduction in Ti contents of the host rocks (from about 0.8 % to nearly 0.4 % on average) is not in itself sufficient to explain the facts. Apart from the general observation that in orogenic sub-alkaline rocks with equal  $\text{SiO}_2$  and  $\text{TiO}_2$  contents, kaersutite is not reported (JAKES & WHITE,

1972), it should be noted that during the crystallization of an only slightly titaniferous amphibole in the Euganean alkali-rhyolites, a much more abundant biotitic phase crystallized more or less contemporaneously, with  $TiO_2$  contents slightly less than that of kaersutite and only slightly lower of that of biotites in trachytes (on average 4.8 % vs. 5.6 %). As well as this silicate, other titaniferous phase subcontemporaneously crystallized as phenocrystals, represented by iron and titanium oxides, equal in composition to that of the corresponding trachyte phases (GM. MOLIN, pers. comm.). The latter mineralogical characters indicate that oxygen fugacity conditions and water concentration remained substantially the same during crystallization of the Euganean trachytes and alkali-rhyolites, therefore suggesting that it is unlikely that the modification of the composition of the amphibole (from kaersutitic to edenitic) are linked to sharp variations of these factors, as the experimental data of FORD (1976) may indicate. According to FORD, as a matter of fact the upper stability limit of the kaersutite of a certain composition falls with decreasing  $f_{O_2}$ , with a similar water content in the vapour phase ( $H_{H_2O}^v$ ), of 20° C at 1 kb and of 40° C at 5 kb; instead, with equal  $f_{O_2}$ , it rises with the diminishing water content of the vapour phase. The temperature range through which that type of kaersutite can disappear, due to variations in  $f_{O_2}$  and  $H_{H_2O}^v$ , is 1040° C to 1075° C at 1 kb and 1015° C to 1110° C at 5 kb.

On the other hand, the stability field of kaersutite seems to be very wide (cfr. for instance, FRISH et al., 1971; GREEN et al., 1974): according to the experimental data of YAGI et al. (1975), kaersutite and Ti-poor clinopyroxenes are stable between 950° C at 1050° C at  $P < 10$  kb, and at lower temperatures (770° C), associated with perovskite, at higher pressures (20 kb): slightly beyond these limits (23 kb at 650° C) kaersutite disappears. At lower temperatures than those quoted for the various pressures, kaersutite is stable alone. Interesting indications on the control exercised by the volatile contents ( $H_2O$ ,  $F_2$ ) rather than by differences in condensed bulk composition

on the appearance of kaersutite are shown by the experimental results (obtained on basaltic rocks) by HELZ (1973). The amphiboles obtained at  $P_{H_2O} = 5$  kb with a *QFM* buffer in a tholeiitic rock range in composition from common hornblendes at relatively low temperatures (750° C) to kaersutites at around 1000° C, as a consequence of steady increases in the numbers of atoms of  $Al^{IV}$  and Ti (from 1.0 to 2.0 and from 0.16 to 0.45 respectively). For titanium in particular, the maximum increase is noted in the 970°-1000° C range. Its absolute content seems to be a function of the oxygen fugacity, since hornblendes formed on the *HM* buffer show much less Ti than that of hornblendes crystallized on the *QFM* buffer, at constant temperature and bulk composition.

These results also agree with the suggestions of VERHOOGEN (1962) on the basis of thermodynamic considerations: according to this Author, while silicates (olivine, pyroxenes) and iron and titanium oxides coexist, the low silica activity and high temperature favour the entry of titanium into the silicates, other things being equal.

In the light of the data obtained on basalts, HELZ (1973) suggests that the restricted occurrence of kaersutite in nature (where it is associated only with mafic to intermediate alkali rocks) is controlled by contents of volatiles ( $H_2O$ ,  $F_2$ ). It should be noted that the compositions of the amphiboles obtained, in the above-mentioned experimental conditions, at 750° C and 1000° C, are surprisingly similar to those found in the Euganean amphiboles of the alkali-rhyolites (e.g. sample 114) and the trachytes.

Assuming, on the basis of our data and those referred by the above Authors, that the chemistry of these inosilicates is essentially unaffected by the composition of the rocks (apart perhaps from  $SiO_2$  contents), it seems reasonable to assume that the factor responsible for the differences in chemistry observed in the Euganean amphiboles is essentially the difference in crystallization temperature. Referring to the crystal-liquid relations on feldspars and other research carried out on the Venetian Tertiary Province, PICCIRILLO et al. (1980) concluded that « trachytic » melts, probably water-poor and aphyric, coming from rather deep lithospheric



zones moved to superficial crustal levels, perhaps less shallow than 10 km, forming differentiation basins. The products corresponding to the present outcropping rocks formed by means of direct outpourings from these basins, or through a further and even more superficial differentiation of trachy-rhyolitic and rhyolitic residua slightly more undersaturated in water.

This picture satisfactorily reconciles the

different degree of Ti and Al<sup>IV</sup> enrichment of the Euganean amphiboles with the experimental results of HELZ (1973) and the theoretical ones of VERHOOGEN (1962), since the essential condition is present in both cases, i.e. reduction in temperature.

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## APPENDIX

### Petrography and chemistry of the trachyte and latite of Mandria di Montegrotto

#### SAMPLE 235: *Trachyte from Bonetti quarry, Mandria di Montegrotto*

Under the microscope this rock shows sialic phenocrystals of anorthoclase, plagioclase (sometimes including brown amphibole) and rare amoeboid fine-grained quartz; biotite, opaques and scarce amphibole, sometimes bordered with biotite, represent the femic phenocrystals. The groundmass is composed of alkali feldspar, silica and opaques.

#### SAMPLE 236: *Latite, dyke west of Bonetti quarry, Mandria di Montegrotto*

Macroscopically, the rock is vesicular, with a marked abundance of amphibole megacrystals, and some geodes coated with fine crystals of secondary calcite. Analysis was carried out on fragments carefully selected from those lacking in megacrystals. Under the microscope phenocrystals of brown pyroxene, brown amphibole, opaques and, in subordinate quantities, plagioclase, alkali feldspar and biotite relics could be recognized. The groundmass was composed mainly of plagioclase felt with alkali feldspar, silica and opaques in the interstices.

### Chemical analyses

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sup>+</sup>	Σ
S. 235	64.13	0.61	17.25	3.28	0.44	0.08	0.47	1.81	5.38	4.60	0.33	1.95	100.33
S. 236	52.78	2.34	16.48	7.04	0.11	0.09	2.17	6.20	4.11	3.17	0.61	4.87	99.97

### Norms C.I.P.W.

	Q	C	Or	Ab	An	En/Hy	Hm	Il	Ru	Ap	Wo/Di	En/Di	Tn
S. 235	11.58	0.91	27.18	45.52	6.82	1.17	3.27	1.10	0.03	0.78	—	—	—
S. 236	4.01	—	18.73	34.77	17.15	4.59	7.03	0.42	—	1.44	0.93	0.81	5.19

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