

## Mineralogy and petrology of an unusual osumilite + vanadium-rich pseudobrookite assemblage in an ejectum from the Vico Volcanic Complex (Latium, Italy)

GIAN CARLO PARODI

Museum National d'Histoire Naturelle, Laboratoire de minéralogie, URA 286 CNRS, 61, rue Buffon, 75005 Paris, France

GIANCARLO DELLA VENTURA

Dipartimento di Scienze della Terra, Sezione mineralogico-cristallografica, Università di Roma "La Sapienza,"  
P. Aldo Moro 5, 00185 Roma, Italy

JEAN-PIERRE LORAND

Museum National d'Histoire Naturelle, Laboratoire de minéralogie, URA 286 CNRS, 61, rue Buffon, 75005 Paris, France

### ABSTRACT

Osumilite occurs as rare, transparent, flattened, hexagonal light-blue prisms in vugs of a volcanic ejectum from Fosso Ricomero (Viterbo province, Latium, Italy) inside the basal trachytic flow of the Vico Volcanic Complex. The mineral is intimately associated with a V-rich mineral of the pseudobrookite group and hematite. The measured cell parameters are (in Å)  $a = 10.095(5)$  and  $c = 14.352(1)$ . The formula derived by WD-EMPA is  $(\text{Ca,Na,K})_{0.91}(\text{Mg,Fe,Mn})_{2.04}(\text{Al,Mg})_3(\text{Si,Al})_{12}\text{O}_{30}$ . The pseudobrookite-group mineral was indexed assuming a space group of *Bbmm*. The cell parameters are  $a = 9.751(2)$ ,  $b = 9.956(1)$ , and  $c = 3.720(1)$ . The proposed general formula is  $(\text{Fe,Mg})_{1\pm x}(\text{Fe,Al})_{2\pm x}(\text{Ti,V,Hf})_3\text{O}_{10}$ .

Secondary pseudobrookite was also found in the groundmass together with sanidine, Ti-rich phlogopite, Fe-Ti oxides (titanomagnetite and titanohematite), and hercynite-rich spinel.

High oxygen fugacity (above that of hematite-magnetite), rapid crystallization, low  $P$  (less than 0.8 kbar), and high  $T$  (720–850 °C) may be inferred as the conditions of formation of the osumilite + pseudobrookite assemblage. The crystallization of these unusual minerals is ascribed to accumulation of the fluid phase in the vesicles after the crystallization of the ejectum.

### INTRODUCTION

Osumilite, a hexagonal mineral structurally related to milarite, was first reported and described by Miyashiro (1956). Since then, less than ten occurrences have been reported in different rock types, mainly in granulites and acid lavas (e.g., Deer et al., 1986).

Although secondary pseudobrookite solid solutions are extremely common in subaerially extruded basaltic suites, occurrences of primary pseudobrookite-group minerals are relatively rare. These occurrences are confined to igneous rocks and include tholeiitic lava flows, open cavities in rhyolites, lamproitic dikes, and kimberlitic vents (e.g., Haggerty, 1976). Because pseudobrookite-group minerals are unstable below 600 °C, all primary pseudobrookite-bearing rocks have a common history of relatively rapid chilling, except for one occurrence of ultramafic cumulates (Lorand and Cottin, 1987).

Osumilite and pseudobrookite have been found to coexist in vugs of a xenolith collected at Fosso Ricomero near Vetralla (Latium, Italy) inside the "basal trachytic

flow" (Locardi, 1967) of the Vico Volcanic Complex, one of the five complexes constituting the Roman Comagmatic Province. The type of xenolith where osumilite and pseudobrookite were found commonly occurs in the pyroclastic deposits of the Pliocene-Pleistocene volcanic apparatus from Latium. The origin of these xenoliths, composed of 90% sanidine with minor phlogopite and oxides, is not clear. They are interpreted either as (1) ejecta from a thermometamorphosed and/or metasomatized pelitic envelope of a shallow magma chamber (Di Sabatino and Della Ventura, 1982; van Bergen, 1983) or (2) fragments of a syenitic body intruded at shallow depth (Durazzo et al., 1982) or even the cumulates of the K-rich lavas. They were ejected and brought into the present setting by the explosive activity following their crystallization, possibly related to late phreatomagmatic eruptions (ignimbrites). In any case, they are unrelated to the host rock and represent equilibria attained deeper in the crust.

The crystallization conditions ( $T$ ,  $P$ ,  $f_{\text{O}_2}$ ) deduced from the mineralogical study of the vugs and the groundmass minerals of the xenoliths provide constraints to the petrological history of the enclosing rocks.

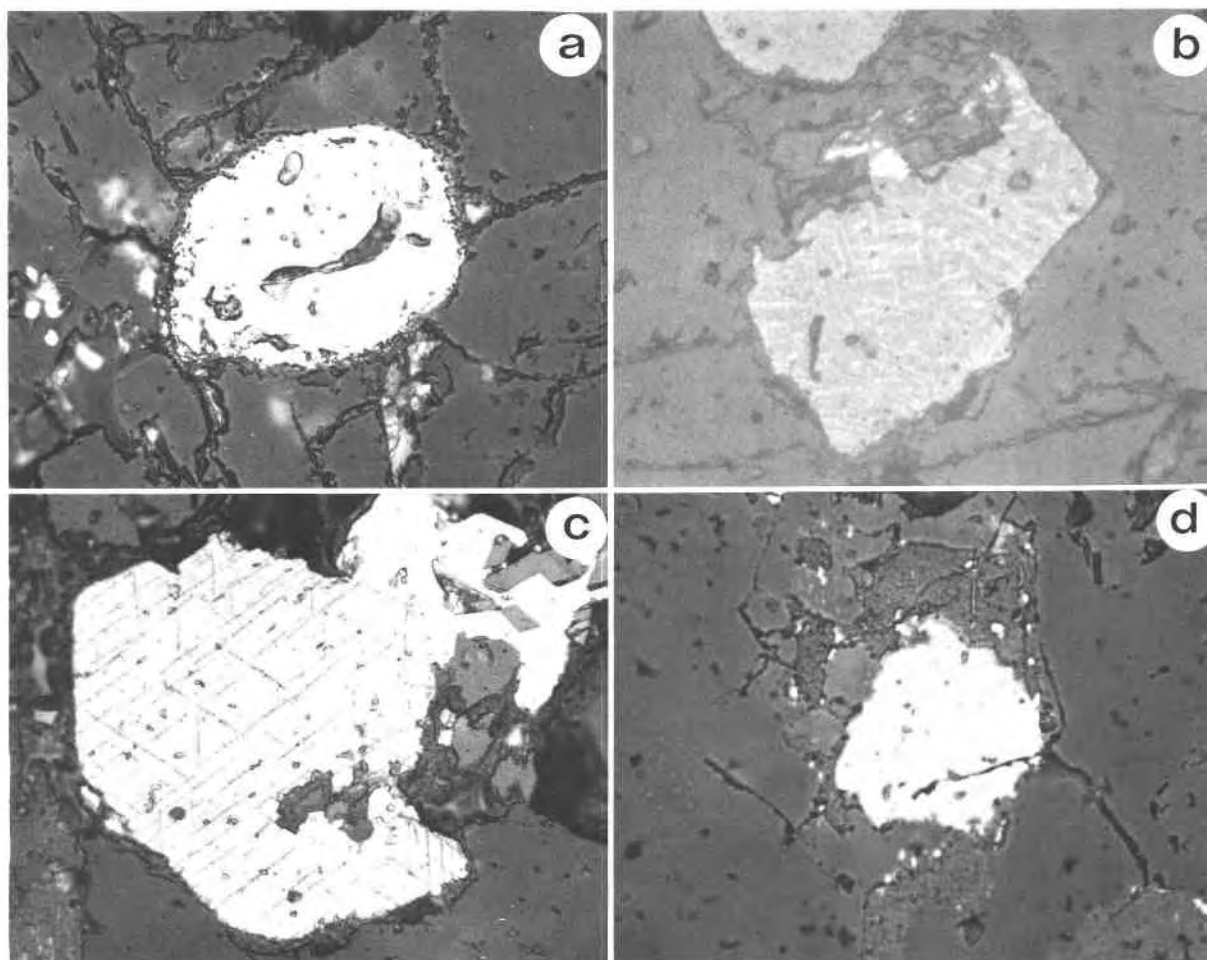


Fig. 1. (a) Inclusion of titanomagnetite (light gray) in sanidine (dark gray); note the titanohematite rim (white) around titanomagnetite. Plane-polarized reflected light; field of view 300  $\mu\text{m}$ . (b) Oxidized aluminous spinel in the groundmass. Plane-polarized reflected light; field of view 400  $\mu\text{m}$ . (c) Groundmass titanohematite (white) containing relict titanomagnetite (medium gray) and a  $\{111\}$  pseudobrookite intergrowth (dark gray). Plane-polarized reflected light; field of view 500  $\mu\text{m}$ . (d) Symplectite-like intergrowth between titanohematite (white) and secondary pseudobrookite (medium gray). Plane-polarized reflected light; field of view 500  $\mu\text{m}$ .

### PETROGRAPHY OF THE GROUNDMASS

The groundmass of the ejectum is layered and is composed, in order of decreasing abundance, of sanidine, Ti-rich phlogopite, Fe-Ti oxides, spinel, titanite, rare zircon, and possibly anatase. The layering is marked by parallel bands that contain vugs (less than 4 mm in diameter). Close to the vugs, sanidine is well-developed as large crystals more than 500  $\mu\text{m}$  in length. The vug-rich layers alternate with fine-grained matrix.

Ti-rich phlogopite, Fe-Ti oxides, and spinel are concentrated preferentially in the fine-grained matrix. They occur as inclusions within sanidine or as interstitial grains. The Fe-Ti oxide minerals vary according to their occurrence in the rock. The inclusions in sanidine consist of titanomagnetite containing more than 20 mol% ulvöspinel in solid solution (Table 1). Pure titanomagnetite is rarely preserved. Most inclusions are connected to the

intergranular medium by fracture planes and exhibit an incipient replacement rim of titanohematite (Fig. 1a). Titanohematite also occurs as parallel blades along the  $\{111\}$  cleavage plane of titanomagnetite. Where enclosed in sanidine, spinel has a composition between hercynite and pleonaste (Table 1). Phlogopite occurs as single, euhedral crystals.

Where they occur interstitially, phlogopite, spinel, and Fe-Ti oxides have been strongly oxidized. Phlogopite forms polycrystalline aggregates with hematite selvages lying on the basal cleavage plane. The spinel becomes red in transmitted light, probably because of the presence of numerous, small hematite blades (Fig. 1b). The oxidation sequence involving Fe-Ti oxides is similar to that described in detail for subaerially extruded basaltic lava flows (e.g., Haggerty, 1976). Residual titanomagnetite remains in the core of euhedral grains that now consist of titanohematite; an original  $\{111\}$  fabric outlined by dark gray

**TABLE 1.** Chemical analyses of the oxides in the groundmass

	05Psb	15Psb	14Hm	04Tm	13Her
TiO <sub>2</sub>	38.38	44.36	1.52	7.4	0.42
V <sub>2</sub> O <sub>5</sub>	0.30	0.03	0.16	0.31	0.13
Al <sub>2</sub> O <sub>3</sub>	1.67	1.36	6.78	1.45	46.82
Cr <sub>2</sub> O <sub>3</sub>	0.29	0.27	0.58	0.40	0.17
Fe <sub>2</sub> O <sub>3</sub>	55.90	44.01	88.16	51.18	16.02
FeO	—	7.31	0.93	36.6	28.83
MgO	2.39	0.90	—	0.57	6.51
MnO	0.30	0.52	0.47	0.73	0.88
CaO	—	0.07	0.17	0.04	0.08
Total	98.61	99.66	100.4	100.06	100.60
Ti <sup>4+</sup>	2.251	2.624	0.059	1.703	0.074
V <sup>5+</sup>	0.015	0.002	0.006	0.630	0.020
Al <sup>3+</sup>	0.153	0.126	0.416	0.523	12.937
Cr <sup>3+</sup>	0.018	0.017	0.024	0.097	0.032
Fe <sup>3+</sup>	3.281	2.605	3.425	11.785	2.823
Fe <sup>2+</sup>	—	0.481	0.040	9.366	5.645
Mg <sup>2+</sup>	0.178	0.106	—	0.260	2.275
Mn <sup>2+</sup>	0.020	0.035	0.021	0.189	0.175
Ca <sup>2+</sup>	—	0.006	0.009	0.013	0.020

Note: Psb = pseudobrookite; Hm = hematite; Tm = titanomagnetite; Her = hercynite. Structural formulae of pseudobrookite, hematite, titanomagnetite, and hercynite calculated on the basis of 10, 6, 32, and 32 oxygens, respectively. Fe<sup>3+</sup> calculated assuming stoichiometry.

irregular pseudobrookite lamellae is still evident in Figure 1c. More commonly, the original titanomagnetite is fully replaced by titanohematite or by graphic intergrowths of titanohematite, secondary pseudobrookite, and minor rutile (Fig. 1d). There, pseudobrookite shows excess Fe<sub>2</sub>TiO<sub>5</sub> (Table 1), a feature that is typical of secondary pseudobrookite formed by direct decomposition of titanomagnetite (Haggerty, 1976).

### EXPERIMENTAL METHODS

The X-ray powder-diffraction patterns of osumilite and the associated pseudobrookite-group mineral were obtained by means of a Gandolfi camera with Ni-filtered Cu K $\alpha$  radiation. Indexing was made by comparison with the respective JCPDS cards, and least-square refinement of the unit-cell parameters was performed by the computer program LSQ82 (Hubbard et al., 1982). Chemical analyses were performed on the WDS-EMP CAMEBAX of Museum National d'Histoire Naturelle in Paris. The counting time on peak and background was 6 s at 15 kV of acceleration voltage and a beam current of 10 nA. The standards used were natural orthoclase (K), albite (Si, Al, Na), forsterite (Mg), wollastonite (Ca), rutile (Ti), chervite (V), and synthetic HfO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>.

### MINERAL CONTENTS OF THE VUGS

The vugs walls are covered by transparent sanidine; twinned, red-orange titanite; and hematite plates. Osumilite occurs as rare, transparent, light-blue, flattened hexagonal prisms. The maximum dimension of the crystals never exceeds 0.2 mm. Pseudobrookite forms semiradial aggregates of translucent, acicular prisms free of other Fe-Ti oxides (up to 3 mm in maximum dimension). The prisms are characterized by sharply defined, lustrous faces of deep-brown color. Straight extinction has been ob-

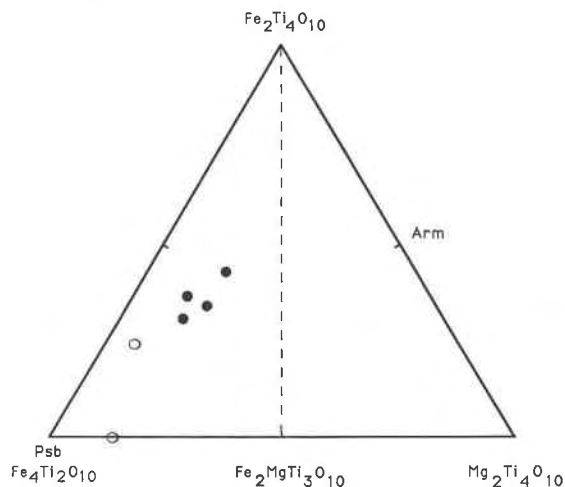


Fig. 2. Classification diagram for the pseudobrookite group minerals. Full circles = pseudobrookite in the vesicles; open circles = pseudobrookite in the groundmass. Psb = pseudobrookite and Arm = armalcolite. Data points from Tables 1 and 2.

served. Pseudobrookite and osumilite are intimately associated; commonly, pseudobrookite crystals have grown over osumilite or vice versa.

### Pseudobrookite

The refined cell parameters of pseudobrookite (*Bbmm*) are (in Å)  $a = 9.751(2)$ ,  $b = 9.956(1)$ ,  $c = 3.720(1)$  and  $V = 361.1(1)$  Å<sup>3</sup>. These values differ from the data of Akimoto et al. (1957) by a slightly smaller  $a$  parameter and volume.

Like most terrestrial pseudobrookites, the pseudobrookite that occurs in vugs shows ternary solid solution among pseudobrookite, the unnamed FeTi<sub>2</sub>O<sub>5</sub> end-member, and the unnamed MgTi<sub>2</sub>O<sub>5</sub> end-member. It differs from the pseudobrookite in the groundmass by higher FeTi<sub>2</sub>O<sub>5</sub>, MgTi<sub>2</sub>O<sub>5</sub>, and Al<sub>2</sub>TiO<sub>5</sub> contents (Fig. 2, Table 2). Moreover, it contains more than 0.1 V atoms per formula unit. To our knowledge, this is the highest value reported so far for the pseudobrookite-group minerals.

Pseudobrookite end-members correspond to the general formula X<sub>4</sub>Z<sub>2</sub>O<sub>10</sub>. For the end-members containing divalent ions, the general formula is Y<sub>2</sub>Z<sub>4</sub>O<sub>10</sub>. The position of X may be occupied by trivalent ions, Y by divalent ions, and Z by tetravalent ions. Without any information on which site V is localized, we may assign two possible formulae, both of which correspond to the intermediate phase named "kennedyite" (Von Knorring and Cox, 1961) and now discredited (Bowles, 1988). The first formula is Y<sub>1±x</sub>X<sub>2±x</sub>Z<sub>3</sub>O<sub>10</sub>, and the second one Y<sub>1±x</sub>X<sub>3±x</sub>Z<sub>2</sub>O<sub>10</sub>. In the second case, V and the excess Ti are considered to be trivalent and to occupy the X sites. In the first case, Ti and V are considered to be tetravalent and pentavalent, respectively. We have preferred the first case in Table 2 because Ti<sup>3+</sup> is stable only under very

**TABLE 2.** Chemical analyses of the pseudobrookite (Psb) in the vugs

	02Psb	04Psb	05Psb	06Psb
TiO <sub>2</sub>	47.96	44.81	46.81	45.63
HfO <sub>2</sub>	0.47	0.19	0.22	0.19
V <sub>2</sub> O <sub>5</sub>	4.34	3.93	4.42	4.34
Al <sub>2</sub> O <sub>3</sub>	2.82	2.72	2.70	2.70
Fe <sub>2</sub> O <sub>3</sub>	28.12	36.98	31.79	34.07
FeO	12.78	9.34	11.55	11.04
MgO	3.27	3.07	3.25	2.8
Total	99.76	101.04	100.74	100.85
<b>Number of ions on the basis of 10 oxygens</b>				
Ti <sup>4+</sup>	2.736	2.533	2.647	2.583
Hf <sup>4+</sup>	0.009	0.008	0.005	0.004
V <sup>5+</sup>	0.218	0.195	0.220	0.216
Al <sup>3+</sup>	0.252	0.241	0.239	0.249
Fe <sup>3+</sup>	1.723	2.092	1.799	1.930
Fe <sup>2+</sup>	0.811	0.587	0.726	0.695
Mg <sup>2+</sup>	0.370	0.344	0.364	0.323

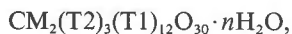
Note: Fe<sup>3+</sup> calculated assuming stoichiometry.

reduced conditions (El Goresy, 1976), a requirement that seems unlikely in this sample (see below). In addition, the choice of V<sup>5+</sup> (which has an ionic radius smaller than that of Ti: 0.54 vs. 0.61 Å; data from Shannon, 1976) is consistent with the smaller of volume of our sample compared with pseudobrookite.

### Osumilite

The X-ray diffraction pattern of osumilite was indexed on the basis of space group *P6/mcc* as given by Miyashiro (1956). The refined cell parameters are (in Å) *a* = 10.095(5), *c* = 14.352(1) and *V* = 1266.7(2) Å<sup>3</sup>; these are in good agreement with the data listed for osumilites from various other localities in Deer et al. (1986, Table 33). The basic feature of the structure of the osumilite-like minerals is a double six-membered ring of (Si,Al)O<sub>4</sub> T1 tetrahedra, laterally and vertically linked by (Al,Fe<sup>3+</sup>,Mg) T2 tetrahedra and (Mg,Fe<sup>2+</sup>,Mn) M octahedra (Miyashiro, 1956; Brown and Gibbs, 1969; Goldman and Rossman, 1978; Hesse and Seifert, 1982; Abraham et al., 1983). The resulting three-dimensional tetrahedral framework should then be classified as a tectosilicate (Brown and Gibbs, 1969; Zoltai, 1960), although Si occurs only in the T1 ring-forming tetrahedra.

The chemical formula, simplified from the more general formula for the milarite-type minerals given in Forbes et al. (1972), may be written as



where T1 = (Si,Al); T2 = (Al,Fe,Mg); M = (Mg,Fe,Mn), and C = (K,Na,Ca). Additional cation sites—located inside the double rings, or side-linking the tetrahedral chains, and partially occupied by alkali ions or water molecules—were established for milarite-type minerals (Ito et al., 1952; Forbes et al., 1972). They are considered to be vacant in the case of osumilite s.s. (Olsen and Bunch, 1970). Several cation substitutions are possible, which are balanced via partial occupancies over the six cation

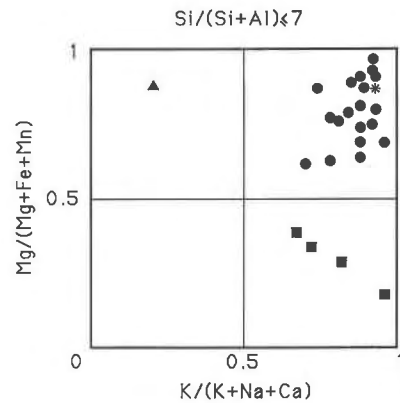


Fig. 3. Classification diagram for osumilites and related minerals. Full squares = Fe-rich osumilites; full dots = Mg-rich osumilites; full triangle = yagiite; star = osumilite (this work). Data points from Table 3 and Deer et al. (1986).

sites and by the yet not-well-determined, but suspected, presence of water inside the structure (Miyashiro, 1956; Schreyer and Seifert, 1967; Brown and Gibbs, 1969).

The microchemical analysis is shown in Table 3. In the calculation of the formula, all the cations have been distributed among the structural sites according to the general formula given in Deer et al. (1986).

The nomenclature of the osumilite group still needs clarification. According to the definition of Bunch and Fuchs (1969), osumilite is characterized by having Si/Al < 7, K > Na, and Fe > Mg, in contrast to yagiite, defined to have Mg > Fe. Problems of classification were discussed by Chinner and Dixon (1973) and Berg and Wheeler (1976), as their osumilites had Mg > Fe. The same applies to osumilite from Latium, as well as to many osumilites from Eifel described by Schreyer et al. (1983). Nevertheless "osumilite-(Mg)" as a separate species of the osumilite group is listed in Fleischer (1987). To avoid confusion, a better definition of osumilite and related minerals is desirable. Beyond any classification purpose, a distinction between Fe-rich osumilite and Mg-rich osumilite is important, for they have different petrological significances (Schreyer et al., 1983), and a simple diagram (Fig. 3) could be useful to distinguish different osumilites.

### PETROGENESIS OF THE OSUMILITE + PSEUDOBROOKITE ASSEMBLAGE

Within the binary, Mg-free system, the lower thermal-stability limit of pseudobrookite-group minerals increases from pseudobrookite (585 °C) to the Fe<sub>2</sub>Ti<sub>4</sub>O<sub>10</sub> end-member (1140 °C) (Haggerty and Lindsley, 1970). For the Mg-bearing system, MgTi<sub>2</sub>O<sub>6</sub> has a thermal stability lower than 700 °C. Since primary pseudobrookite is a multi-component solid solution, its lower thermal-stability limit lies between the above temperatures. However, complicating factors are the effects of V and Al. Nothing is known about V but Al is known to decrease the lower thermal-stability limit of pseudobrookite-group minerals (Kesson

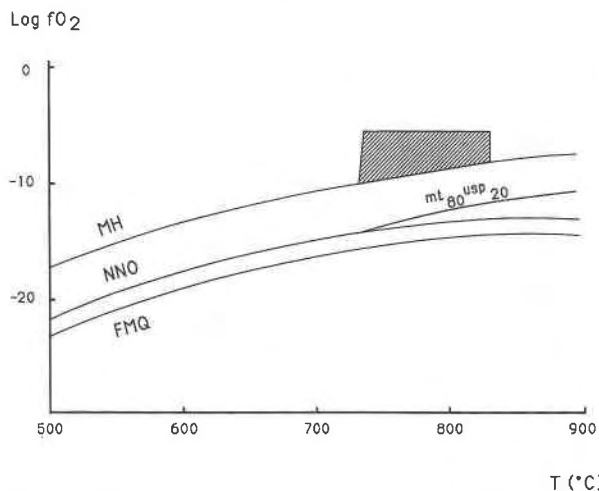


Fig. 4. Plot of  $\log f_{\text{O}_2}$  vs. temperature showing the inferred stability field (hatched area) for the osumilite + pseudobrookite assemblage from the vugs. Abbreviations for solid-solid buffers: MH, magnetite-hematite; NNO, nickel-nickel oxide; FMQ, fayalite-magnetite-quartz; mt = magnetite; usp = ilvospinel (after Lindsley, 1976).

and Lindsley, 1975). Taking into account all these constraints, we may possibly assume that the pseudobrookite that occurs in vugs has formed above 585 °C.  $\text{Fe}_4\text{Ti}_2\text{O}_{10}$ -rich end-members exist only at relatively high values of  $f_{\text{O}_2}$  (Haggerty, 1976). The close association of pseudobrookite with hematite in the vesicles indicates an oxygen fugacity value higher than  $10^{-14}$  atm at 600 °C (Fig. 4).

Osumilite is found in cavities or in the groundmass of rhyolitic and dacitic lavas and in contact-metamorphic xenoliths. Other regional occurrences are in granulites, and osumilite-like phases have been described from meteorites (Fuchs et al., 1966; Bunch and Fuchs, 1969). For all previously reported occurrences, a high- $T$ , but low- $P$  origin is certain, except for granulites, for which a high- $T$ , high- $P$  origin was reported (Grew, 1982; Berg and Wheeler, 1976).

Experimental work on osumilite stability in the system  $\text{K}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  supports the low- $P$  origin for the K-Mg end-members. Schreyer and Seifert (1967) failed to synthesize osumilite above 1-kbar  $P_{\text{H}_2\text{O}}$  and 650–700 °C and observed that both their synthetic and a natural (Sakkabira) osumilite broke down into cordierite + quartz + K-feldspar under the conditions at which they had achieved synthesis, when duration of the experiment was increased. They concluded that natural osumilite may form only metastably under conditions of rapid, nonequilibrium crystallization. More recently, however, Olesch and Seifert (1981) showed that osumilite can be stable at  $P_{\text{H}_2\text{O}} < 0.8$  kbar and concluded that its stability field increases with decreasing water pressure (from 720 °C at  $P_{\text{H}_2\text{O}} = 2$  kbar to at least 850 °C under near-surface, essentially anhydrous conditions). However, the thermal stability of osumilite definitively widens with increasing pressure pro-

TABLE 3. Chemical analysis and crystal-chemical formula for osumilite from Vetralla (Latium, Italy)

$\text{SiO}_2$	60.89
$\text{Al}_2\text{O}_3$	23.40
FeO	1.97
MnO	0.37
MgO	7.77
CaO	0.03
$\text{Na}_2\text{O}$	0.23
$\text{K}_2\text{O}$	3.95
Total	98.61
<b>Number of ions on the basis of 30 oxygens</b>	
T1 site	
Si	10.18
Al	1.82
$\Sigma$	12.00
T2 site	
Al	2.78
Mg	0.22
$\Sigma$	3.00
M site	
Mg	1.72
Fe	0.27
Mn	0.05
$\Sigma$	2.04
C site	
K	0.84
Na	0.07
Ca	0.005
$\Sigma$	0.915

vided  $P_{\text{H}_2\text{O}}$  remains low: Hensen (1977) has achieved its synthesis at 3.5–6.1 kbar, under conditions of low oxygen fugacity only. In natural occurrences, osumilite can be stable up to 900 °C and <9 kbar (Grew, 1982) but, again, essentially under anhydrous conditions.

As the environment responsible for the formation of the samples studied is characterized by conditions of essentially  $P_{\text{H}_2\text{O}} = P_{\text{tot}}$ , as documented by Landi (1987) via the application of the Stormer (1975) and Kudo and Weill (1970) geothermometers, we conclude that our osumilite formed at low pressure. Since the osumilite + pseudobrookite assemblage texturally appears to have formed simultaneously in the vugs, we also consider it reasonable to conclude that it crystallized in the temperature range between 720 and 850 °C at less than 0.8-kbar total pressure and at a  $f_{\text{O}_2}$  higher than that of the magnetite-hematite buffer in agreement with the experimental results of Olesch and Seifert (1981) and Hensen (1977).

Since hematite and pseudobrookite are also the only stable Fe-Ti oxides, it seems likely that the groundmass of our ejectum underwent the same high  $f_{\text{O}_2}$  conditions as the vesicles. According to most authors, deuteric oxidation trends of interstitial Fe-Ti oxides such as those observed in the groundmass of the specimens studied are due to accumulation of a chemically reactive phase rich in  $\text{H}_2\text{O}$  vapor in the intergranular joints. This fluid phase would become oxidizing because of diffusion-controlled  $\text{H}_2$  loss at subsolidus temperatures (Anderson, 1975). Generally, oxidation temperatures of many subaerially extruded basalts are close to 700–750 °C (Haggerty, 1976). The latter temperatures could also pertain to the ground-

mass of the rocks investigated, not only because pseudobrookite is present, but also because it forms graphic intergrowths with hematite, a feature that is related to the very rapid oxidation of titanomagnetite at high temperatures (e.g., Haggerty, 1976). From the similarities of  $f_{O_2}$ - $T$  conditions, we propose that the fluid phase that oxidized the groundmass oxides was also responsible for pseudobrookite and osumilite growth in the vesicles. The compositional features of the vesicle-hosted pseudobrookite suggests that this fluid phase was also vanadium-rich.

### CONCLUSIONS

High oxygen fugacity, rapid crystallization, low- $P$  and high- $T$  conditions may be inferred for the Latian osumilite. These physical conditions of formation (particularly high oxygen fugacity and a rapid crystallization) are also supported by the presence of the associated pseudobrookite-like phase and hematite. The unusual osumilite + pseudobrookite assemblage is related to accumulation of a fluid phase in the vesicles, probably just after the crystallization of the studied ejectum, because of its inferred crystallization temperature range.

Our data are consistent with the experimental results of Schreyer et al. (1983), according to which, as with the structurally related Mg-Fe cordierite series, the  $P$ - $T$  stability range of Mg-rich osumilites is larger than that of the Fe-rich osumilites. Osumilite rich in Mg can form in both high- and low- $P$  environments, but those rich in Fe are restricted to volcanic, near-surface environments.

The Latian occurrence is similar to the occurrence at Eifel, Federal Republic of Germany (Schreyer et al., 1983). The rocks there belong to the well-known alkali-potassic volcanic complex, similar to the Roman Comagmatic Region. The alkali deficiency shown by some analyses of osumilite from Eifel was considered by Schreyer et al. (1983) to be correlated with high  $f_{O_2}$ , possibly according to the substitution  $\square + Fe^{3+} \rightarrow (K,Na) + Fe^{2+}$ . This certainly does not hold true in general, since our osumilite shows a high total alkali content (0.92 per formula unit) though crystallized at high  $f_{O_2}$ .

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