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The Origin of Fumarolitic Andradite at Menoyre, France and Fant'Ale, Ethiopia

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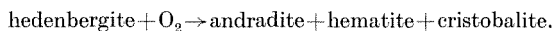
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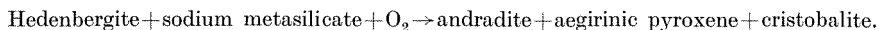
Abstract. Recent discoveries of fumarolitic andradite in alkaline or peralkaline trachytes (Menoyre, Cantal, France, and Fant'Ale, Ethiopia) are interpreted genetically.

The andradites were formed from the constituents of pyroxene, always calcic and iron-rich in these rocks. The elements Ca and Fe were fixed on the surface of fractures by late fumaroles of high oxidizing capacity.

The following reaction can be established at Menoyre:



In a hyperalkaline medium, which is the case for the trachyte of Fant'Ale, the reaction is:



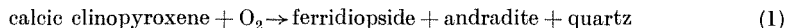
Introduction

Fumarolitic garnets developed on the fracture surfaces of two trachytic massifs at Menoyre, Cantal, France and at Fant'Ale, Ethiopia, have already been described (Varet, 1967, 1969a). In both examples, the minerals belong to a late crystallization which occurred after the solidification of a viscous lava dome (Fig. 1). These minerals are not found *in* the rock, but are always located on fracture surfaces or, as at Menoyre, also in cavities near these areas (Fig. 2). Their origin is due to the circulation, at near atmospheric pressure, of high-temperature fumaroles (above 700° C) in these fractures, probably during the cooling of the dome.

These conclusions (Varet, 1967) are deduced from the mineralogical association (hematite + andradite) found in the cavities of the trachyte of Menoyre, and from the location of the garnets.

The origin of the elements constituting these andradites (analyses given on Table 1) remained to be determined. Even though silica in the saturated trachytes is free, probably not all calcium, iron, titanium and manganese were brought in by the fumaroles; their origin must be sought *in situ*.

Recent work by Huckenholz (1969a) has drawn attention to the transformation of calcic clinopyroxene into andradite according to the following reaction:



We are here concerned with further study of the relations between andradites and the ferromagnesian minerals of the trachytes.

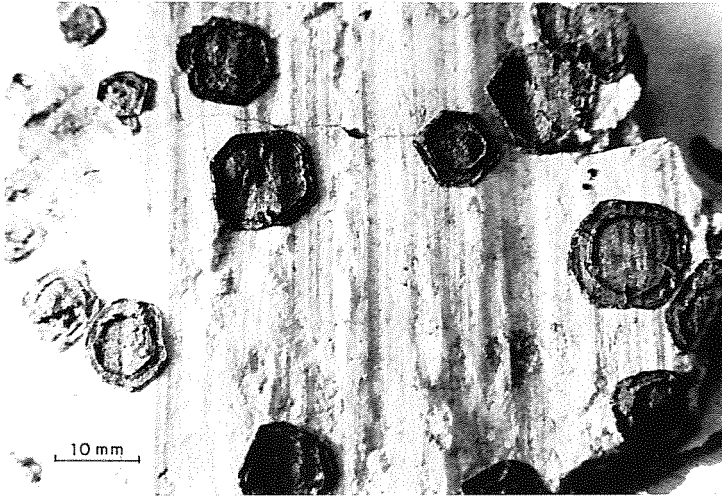


Fig. 1. Andradite crystals developed on a fracture shelf of the dome at Menoyre. Note the lineations contemporaneous with the solidification of the dome, and the later garnets surrounding these structures

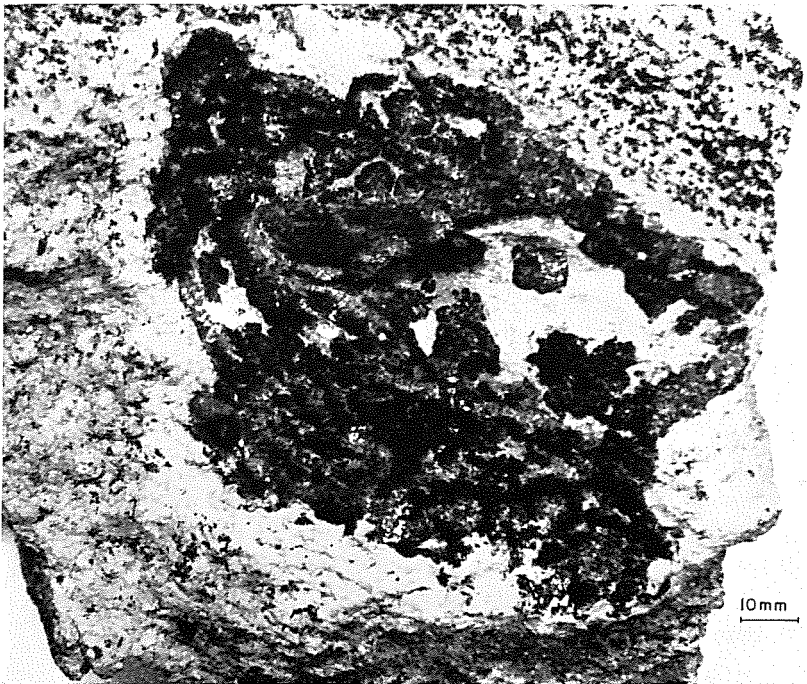


Fig. 2. Andradite crystal in cavities in the trachytic dome at Menoyre. Note the association andradite+hematite in the cavities, and the lighter-coloured trachyte in contact with the garnets (approximately 1 cm)

Table 1. *Chemical and physical data on fumarolitic garnets*

	g 1	g 2a	g 2b	
Chemical analysis				
SiO ₂	35.9	35.33	33.89	
TiO ₂	0.8	1.87	1.51	
Al ₂ O ₃	0.5	0.94	1.14	
Fe ₂ O ₃	29.0 ^a	26.59	30.47	
FeO		0.12	0.19	
MnO	1.9	0.31	0.26	
MgO	0.0	0.00	0.00	
CaO	30.0	31.27	30.45	
Na ₂ O		0.71	0.43	
K ₂ O		0.52	0.34	
P ₂ O ₅		0.28	0.82	
H ₂ O		2.48	1.16	
	98.1	100.41	100.66	
Structural formula calculated on the basis of 24 (0)				
Si	6.15	6.09	5.805	} 6.00
Ti	0.11	0.228	0.194	
Al	0.11	0.191	0.229	} 4.00
Fe ^{'''}	3.74	3.440	3.775	
Ca	5.52	5.779	5.587	} 5.65
Mn	0.23	0.046	0.034	
Mg	0.00	0.000	0.000	
Fe	0.00	0.016	0.028	
Mol % end members				
Andradite	93.2	92.9	94.1	
Melanite	2.8	6.1	4.8	
Spessartine	4.0	0.8	0.6	
Almandin	0.0	0.2	0.5	
Physical properties				
n	1.890 ± 0.005	1.850 ± 0.005	1.850 ± 0.005	
a ₁	12.06 ± 0.01	12.09	11.96	
a ₂	12.02 ± 0.05	12.00	11.97	

^a all Fe as Fe₂O₃.

g 1 Andradite of Fant'Ale, microprobe analysis (H. Bizouard).

g 2a Andradite of Menoyre (fracture) (Varet, 1967).

g 2b Andradite of Menoyre (cavities) (Varet, 1967).

N.B. The hypothesis that (2a) and (2b) might be hydrogarnets had to be discarded (Varet, 1967).

a₁ measured on K α Co diffractograms with 400, 420, 422, 611, 444, 640 and 800 reflections.

a₂ calculated (MacConnel, 1966).

1. The Trachyte

The trachyte at both localities is highly feldspathic (80 to 90% modal anorthoclase) and very slightly oversaturated (Table 1) with either modal tridymite or modal quartz.

Table 2. *Chemical analysis of pyroxenes from fumarolitic Andradite-bearing trachytes*

	pla	plb	p2
SiO ₂	—	—	52.7
TiO ₂	0.3	0.3	0.54
Al ₂ O ₃	—	—	1.83
Fe ₂ O ₃		29.4 ^b	
FeO	29.4 ^a		10.0 ^a
MnO			0.9
MgO	0.8	1.6	12.0
CaO	18.8	8.2	22.4
Na ₂ O	0.4	6.2	0.84
K ₂ O			
P ₂ O ₅			
H ₂ O +			
			101.2

Structural formula, calculated on the basis of 6 (O)

Si	1.99	1.99	1.960	} 2.00
Al	—	—	0.040	
Ti	0.01	0.01	—	
Fe'''	—	—	—	} 2.05
Al	—	—	0.076	
Ti	—	—	0.017	
Fe'''	—	0.98	—	
Fe''	1.10	—	0.311	
Mn	—	—	0.029	
Mg	0.05	0.10	0.666	
Ca	0.83	0.39	0.892	
Na	0.02	0.53	0.062	

Molecule % end-members (following Yoder and Tilley, 1962)

Ac	0.02	0.53	0.06
Tsch	0.10	—	0.08
Hd	0.83	0.37	0.26
Di	0.05	0.10	0.60

p 1a Hedenbergite from area in trachyte grey } Fant'Ale
 p 1b Aegirinic pyroxene in beige area in trachyte }

N.B. 1a Microprobe analysis (H. Bizouard). Total Fe as FeO.

1b Microprobe analysis (H. Bizouard). Total Fe as Fe₂O₃.

1a and 1b: Si assumed in structural formula.

p 2 Pyroxene from trachyte at Menoyre (microprobe analysis by T. Frisch).

^a Total Fe as FeO.^b Total Fe as Fe₂O₃.

At Menoyre, the anorthoclase phenocrysts have oligoclase cores and the rock is just saturated. At Fant'Ale no plagioclase is discernible and the rock is over-saturated. The associated ferromagnesian mineral (10% modal) is a calcic pyroxene (Ca₄₁₋₄₈; Fe₅₅₋₁₄, Mg₂₋₃₇) (Table 2). This mineral may be replaced by a biotite-amphibole association at Menoyre and by aegirine at Fant'Ale.

The chemical analyses of these rocks (Table 3), show that they are alkaline to peralkaline trachytes (normative aegirine at Menoyre, normative sodium metasilicate at Fant'Ale).

Table 3. *Chemical analysis of the alkaline trachytes containing fumarolitic andradite*

	1	2	C.I.P.W. Norm			
			1	2		
SiO ₂	62.74	63.30	Q	4.10	8.67	
TiO ₂	0.03	0.46	Or	33.26	21.86	
Al ₂ O ₃	14.01	12.33	Ab	40.72	42.82	
Fe ₂ O ₃	6.33	5.26	An			
FeO	0.10	0.20	Ac	9.06	15.22	
MnO	0.05	0.19	Wo	7.93	1.79	
MgO	0.10	0.12	Di {	wo	0.29	0.35
CaO	3.97	1.12		en	0.25	0.30
Na ₂ O	6.03	9.30	Mt	0.40		
K ₂ O	5.63	3.70	He	2.92		
P ₂ O ₅	0.00	0.13	Il	0.06	0.83	
H ₂ O ⁻	0.35	0.62	Sph		0.06	
H ₂ O ⁺	0.31	2.66	Ns		4.32	
			Ap		0.31	
Total	99.65	99.79				

1 Trachyte from Menoyre, France (Brousse and Varet, 1967).

2 Pantelleritic trachyte from Fant'Ale, Ethiopia; new analysis.

Late crystallization of andradite seems to be characteristic of hyperalkaline rocks, such as trachytes, phonolites and nephelinic syenites (Varet, 1969a)¹.

2. Observational Difficulties

At Menoyre one cannot observe the mineralogical relations of the garnets with the trachyte that bears them. The fractures, areas favorable for the circulation of fumaroles, were also areas favored by circulating meteoric solutions. Thus the fracture shelves bearing the garnets are altered (e.g. feldspars changed to clay) to a depth of 0.5 to 5 mm in the rock (Varet, 1967), so that no observation of the relations between the garnets and the lava is possible. We can only note that the areas around the garnets are lighter than the unaltered lava (Fig. 2).

The samples collected at Fant'Ale, coming from a younger massif that has not undergone such intense alterations, allow us to draw more precise conclusions. Like those of Menoyre, the garnets at Fant'Ale have grown on the surface of beige-coloured trachyte slabs. Every garnet is surrounded by a white area (Fig. 3) in the trachyte.

3. Description of the Trachyte-Garnet Contact

A thin section cut normal to the rock surface² shows the relations between the minerals of the trachyte and the garnet (Fig. 5). In addition, an X-ray diffraction study was made on the bulk rock and on some separated mineral phases.

¹ Lacroix (1907) described crystallization of andradite on the surface of diopsidic inclusions at Vesuvius. He also noted that the garnets appear to have formed at the expense of calcic pyroxene.

² Obtaining a thin or polished section of the surface of a rock is a very difficult task. It was made possible by embedding the rock in "Araldite" in *vacuo* before making the thin section. Thanks to this technique (Method of C. Chauvet, Orsay), sections of extremely fragile materials can be made.



Fig. 3. Andradite crystals developed on the fracture surfaces in the pantelleritic trachyte at Fant'Ale. Note the white area surrounding the garnet

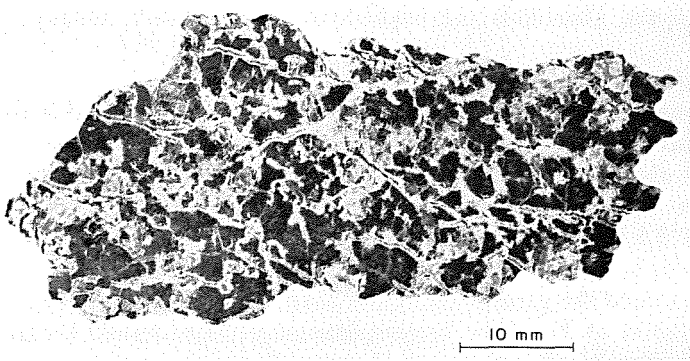


Fig. 4. Photograph of the trachyte at Fant'Ale. Note the lattice-like structure, light areas (*Area 2* in the text) correspond to the fracture planes of the trachyte, grey areas (*Area 1*) pre-date *Area 2*

a) *The trachyte* presents a lattice-like appearance, with beige areas surrounding greyish areas (Fig. 4). As noted by Gibson (1967 and pers. comm.), the trachyte is inhomogeneous and shows different ferromagnesian mineral assemblages.

In the grey areas (*Area 1*) there occur, besides anorthoclase, minor fayalite (apparently out of equilibrium) and green hedenbergite (analysis on Table 2) mostly surrounded by hematite and ilmenite.

In beige areas (*Area 2*), a brown pyroxene with strong birefringence is present in addition to anorthoclase. Opaque minerals do not appear in these areas³.

³ This observation is in agreement with those made by Upton (1960) and MacDonald (1966), who both noted the incompatibility of aegirine and iron oxides in hyperalkaline rocks.

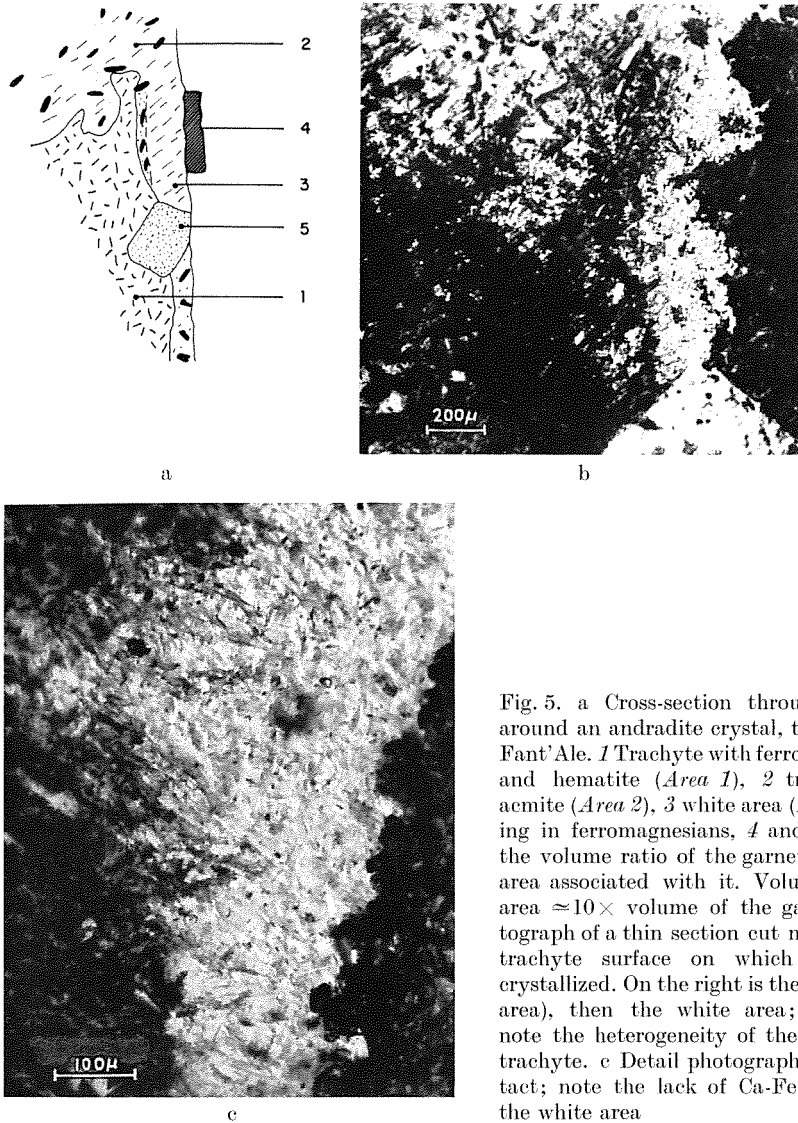


Fig. 5. a Cross-section through the area around an andradite crystal, trachyte from Fant'Ale. 1 Trachyte with ferrohedenbergite and hematite (*Area 1*), 2 trachyte with aegirite (*Area 2*), 3 white area (*Area 3*), lacking in ferromagnesian, 4 andradite. Note the volume ratio of the garnet to the white area associated with it. Volume of white area $\approx 10 \times$ volume of the garnet. b Photograph of a thin section cut normal to the trachyte surface on which the garnet crystallized. On the right is the garnet (dark area), then the white area; on the left note the heterogeneity of the surrounding trachyte. c Detail photograph of the contact; note the lack of Ca-Fe minerals in the white area

The pyroxene may reach 3 mm in size, is poikilitic and obviously crystallized late. Its X-ray diffraction pattern indicates (Nolan and Edgar, 1963) aegirine (reflexes 110 and 021 are very intense, 311 is lacking) but chemical analysis (Table 2) shows it to be aegirinic pyroxene.

The assemblage with aegirinic ferrohedenbergite is a later one than that with hedenbergite (Fig. 3). The association is found in the movement areas of fracture surfaces, as well as on joint surfaces of the rock on which garnets develop. The ferrohedenbergites reach large sizes in those areas favourable for the circulation of fumaroles.

The association hedenbergite-Fe-Ti oxyde, on the other hand, occurs in the most massive parts of the dome flow.

The assemblage aegirinic ferrohedenbergite-anorthoclase is probably the result of the transformation *in situ* of the hedenbergite-bearing assemblage.

b) *The White Area (Area 3)*. The thin section (Fig. 5) shows a rather sudden change from the beige-coloured, unaltered trachyte (*Area 2*) to the white area (*Area 3*) surrounding the garnets. The white area, situated wherever the garnet is in contact with the trachyte (Fig. 3), is 0.5 to 2 mm thick. In general, its thickness seems to be approximately equal to that of the radius of the garnets, which is never more than 1 mm. The ratio of the volume of the white area to that of the garnet is therefore near 8 or 10 (Fig. 5).

Microscopic study reveals a lack of ferromagnesian minerals in this area. This is confirmed by X-ray study, which clearly indicates that only anorthoclase and cristobalite are present.

The feldspathic matrix seems to have remained intact inside the white area, although the glassy phase appears to be more developed in this area than in the unaltered trachyte (Areas 1 and 2).

c) *The garnets* occur in the white areas. The fact that the large garnets include feldspar microlites (Fig. 4) confirms that they have formed later. The garnet does not show the unusual birefringence observed by Lacroix (1901) in certain melanites.

Petrologic Interpretation

A. The Formation of Pyroxene

The finding of andradite in hyperalkaline rocks is not new (Zedlitz, 1933; Knop, 1877 and other references given by Huckenholz, 1969).

Generally, whether they are saturated (trachytes, pantelleritic rocks) or under-saturated (agpaitic phonolites), the host rocks possess more alkalis than alumina. *Iron is essentially in the ferric state*. They possess *very little magnesium*, because of their high degree of differentiation, but contain a significant amount of *calcium*.

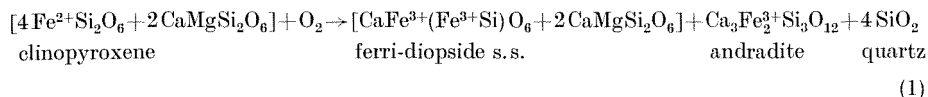
The consequences of this chemical composition are the following:

1. The alumina is not sufficient to fix all the alkalis in the feldspars, so that:
 - (a) the alkalis enter other silicates, e.g. acmite,
 - (b) the calcium does not form plagioclase, being consumed in the formation of pyroxene and garnet.
2. The high degree of oxidation of the iron makes the formation of a significant amount of normative acmite possible.
3. The calcium combines with the remaining ferrous iron and with the minor magnesium in the clinopyroxenes. The latter are therefore hypercalcic, and normative wollastonite appears in these rocks (Table 1). This has already been observed in the pyroxenes of the phonolites and alkaline trachytes of Cantal (Varet, 1969b). As a result, we find pyroxene that is generally very calcic, rich in ferric iron, and slightly aegirinic.

At Fant' Ale, two generations of pyroxenes were observed. The first generation corresponds to conditions of crystallization with relatively low oxygen pressure, and is essentially hedenbergite (Yoder and Tilley, 1962). The second corresponds to higher fO₂ conditions, sodium entering the ferric silicate. This condition may be due to the circulation of fumaroles with a high oxidizing capacity, mobilizing the alkalis and passing through the fracture areas of the rock.

The oxygen pressure being sufficiently high, some kind of combination of calcium with ferric iron becomes necessary, and andradite can appear.

Thus reaction (1) experimentally established by Huckenholz (1969a) is verified in nature:



B. The Pyroxene-to-Andradite Transformation

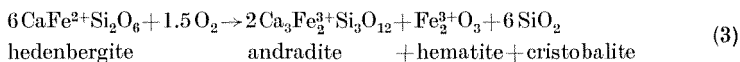
In the fractures of the trachytic dome (under atmospheric pressure), high temperature fumaroles circulated after solidification of the dome. The association of andradite with hematite at Menoyre indicates a temperature of crystallization above 700° C (Varet, 1967). On the other hand, the temperature must, of course, be lower than the melting point of the trachyte. The fumaroles must have had a high oxidizing capacity, as is evident from the mineralogic transformations and the presence of hematite associated with the garnet at Menoyre.

The relations at Fant' Ale demonstrate that the pyroxene has disappeared from the area around the garnet. So we may postulate a process in which certain elements from the pyroxene have entered the garnet.

Even though such a conclusion may be presumptuous, let us note that the volume ratio of the garnet to its surrounding area (1/10) is not incompatible with the volumetric equation (cf. Fig. 4)⁴:



Thus the transformation proposed by Huckenholz (1969a) is replaced for the trachyte at Menoyre by the following generalized reaction:



Hematite is present near or within the area affected by this oxidation at both Menoyre and Fant' Ale.

In a hypersodic environment where (Na+K) > (Al+Fe³⁺), as is the case at Fant' Ale, the ferric iron is not always stable as hematite, and may combine again with free sodium silicate to produce an aemitic pyroxene (Bailey and Schairer, 1966; Bailey, 1969). On the other hand, at Menoyre this reaction is not realized as (Na+K) < (Al+Fe), even though the trachyte is peralkaline.

⁴ i.e. the original rock (*Area 1*) contained about 10% pyroxene, whereas it is completely absent from the white areas (*Area 3*) surrounding the garnet.

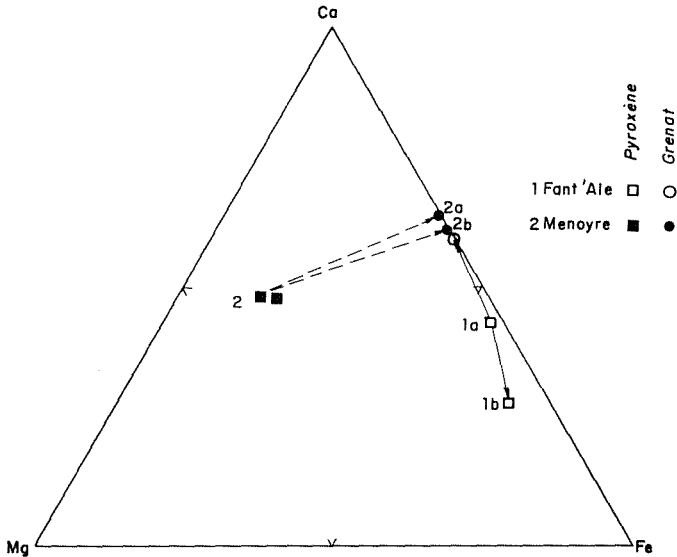
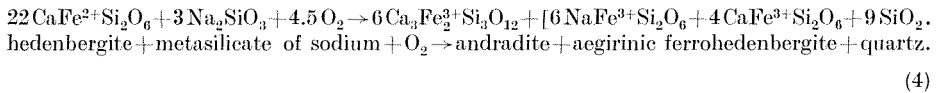


Fig. 6. Ca-Mg-Fe diagram showing the compositions of the pyroxenes and the associated garnets in the trachytes. Note that the hedenbergite is situated between the aegirinic ferrohedenbergite and the andradite (Fant'Ale)

Reaction (3) may thus be modified for hypersodic conditions as follows:



Further deductions or attempts to compare the composition of the pyroxenes and associated garnets are difficult, since this is a fumarolitic transformation, in which some elements were brought in whereas others were removed. In fact they are not co-existing minerals, but two distinct phases formed at different times under different conditions in an open system. Element partitioning between andradite and pyroxene (Huckenholz, 1969, p. 227) is not of significance in this case. But the comparison is interesting (Fig. 6), especially considering that the points representing hedenbergite, andradite and aegirite in the trachyte at Fant'Ale are nearly co-linear.

Conclusion

The origin of the fumarolitic garnets of Fant'Ale and of Menoyre appears to provide a natural verification of the experimental results of Huckenholz (1969a). Circulation of highly oxidizing, high-temperature fumaroles in fractures is obviously important for the crystallization of the garnets. However, it is clear that the elements making up the garnets were not all brought in by the fumaroles. On the contrary, the fumaroles found most of these elements *in situ*, namely in pyroxene already present. Breakdown of the pyroxene by the oxidizing action of the fumaroles results in the formation of andradite, which is deposited on the fracture surfaces. Hematite and cristobalite may form if the environment is not

excessively peralkaline, whereas hematite may be replaced by an acmitic pyroxene in a hyperalkaline medium.

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