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Mineralogia. — *Preliminary investigation on garnets from granitic and migmatic rocks of the Argentera Massif, Maritime Alps.*

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dal Socio G. SCHIAVINATO.

RIASSUNTO. — I granati dei graniti centrali del Massiccio dell'Argentera e delle anatessiti incassanti del Mt. Pélago hanno colore rispettivamente rosa e rosso bruno e appaiono ampiamente sostituiti da minerali leucocrati. In qualche caso, tuttavia, il granato dei graniti conserva l'originario abito idiomorfo completamente intatto. Il granato delle anatessiti a differenza di quello dei graniti è quasi sempre cloritizzato. Dallo spigolo della cella elementare, dalle intensità di alcuni particolari effetti di diffrazione di raggi X ottenuti da polveri e dagli spettri di raggi X per eccitazione elettronica ottenuti mediante analisi in dispersione di energia, i granati studiati risultano essere soluzioni solide di tipo alspitico. In particolare, mentre il granato dei graniti centrali è costituito da proporzioni quasi eguali dei termini puri almandino e spessartina, nel granato delle anatessiti del Mt. Pélago l'almandino prevale sulla spessartina. Da osservazioni ottiche, dall'aspetto delle righe di diffrazione di raggi X e dalle immagini in scansione di raggi X mediante analisi in dispersione di energia, sia i granati dei graniti che quelli delle anatessiti non sono risultati essere zonati.

INTRODUCTION

Granitic and migmatic rocks of the Argentera Massif, Maritime Alps, quite frequently exhibit garnet (Malaroda and Schiavinato, 1957). Even if the amount of this mineral is rather small, Malaroda (1970) stated the advisability of using a special symbol to indicate its occurrence in the 1 : 50,000 geological map of this massif.

As the study of other minor constituents, particularly zircon, has already given interesting results for mineral- and petrogenesis of this massif (Pupin, Boucarut, Turco and Gueirard, 1968; Pupin and Turco, 1974), a suitable study for garnet has also been undertaken. Its purpose is to investigate the garnet from the central granites and the Mt. Pélago anatexites, the latter having a regional petrological interest both because of their surface outcrop and because they are in contact with the aforementioned granites (Blasi and Schiavinato, 1968; Blasi, 1971).

The present paper reports the results of preliminary studies conducted on this mineral. These give information on the morphological aspect and the distribution of the garnet in the host rocks, along with X-ray diffraction and electron microprobe data useful for characterizing and distinguishing the garnet occurring in the granites from that contained in the anatexites.

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EXPERIMENTAL

Mineral separation. Because of the relatively large amounts of whole rock needed for garnet separation, the material crushed, sieved, and freed of dust and strongly magnetic grains was first run through the Carpcio high-intensity wet magnetic separator at 1.5 A for rapidly removing the light fraction in the $-80 + 120$ or, if necessary, in the $-120 + 230$ mesh A.S.T.M. size-range. The magnetic concentrate was then run through the Frantz isodynamic magnetic separator at 0.3 A with a forward slope of 25° and a side slope away from the operator of 15° , to separate the fraction richer in garnet. This was then centrifuged in methylene iodide ($G = 3.325$) and the garnet sunk to the bottom of the tube was separated after rapid freezing. For this procedure the bottom end of the tube containing the garnets was immersed in a saturated solution of solid CO_2 in acetone. Freezing of the part containing the garnets facilitated the removal of the floating fraction and the recovery of the heavy liquid. The garnet obtained in this way was further purified by hand-picking.

X-ray data. The unit cell parameter was determined by X-ray powder photographs using Mn-filtered Fe-radiation. The sample 0.3 mm in diameter was mounted in a Philips camera 114.6 mm in diameter, in which the film was placed in the Straumanis's asymmetric position. To obtain 2θ values and intensity data each photograph was read three times with a Wooster microdensitometer Mark III Mod 3 used in the following setting: aperture 0.5 mm in diameter, wedges of densities 0-2 or 0-3, Y-D ratio 1, speed control 4, D-Chart ratio 5. The three different readings for each sample were reduced to 2θ mean values corrected for film shrinkage by means of a Fortran IV program prepared for this purpose. The output data of this program formed the input to the Burnham's (1962) LCLSQ program, which was used to carry out the least squares refinement of the unit cell parameter. This program was set to correct each observation for systematic errors due to specimen absorption and camera eccentricity. Correction for film shrinkage was not included, since it had been applied during the reduction of reading data to mean 2θ values. These systematic error terms in the LCLSQ program are of the form $g(\theta)X$, where $g(\theta)$ is a trigonometric function of θ , and X is a systematic correction term whose value is initially unknown and must be refined simultaneously with the lattice constants by the least squares procedure. As the function $g(\theta)_{abs} = (4 \sin 2\theta/\lambda^2) \cos^2 \theta$ is used for correcting specimen absorption in this program, an optional subroutine was programmed with the function $g(\theta)_{abs} = (4 \sin 2\theta/\lambda^2) (\cos \theta + \sin 2\theta/2) / 2$. This is more appropriate in this specific case, because it includes the well-known function of Nelson and Riley (1945) and Taylor and Sinclair (1945). For the eccentricity error, the function included in the program, i.e. $g(\theta)_{ecc} = (4 \sin 2\theta/\lambda^2) \sin 2\theta$, was used. Use was made of the radiation $\lambda = 0.193728$ nm, where the doublet $K\alpha_1/K\alpha_2$ was unresolved; in the opposite case, use was made of $\lambda = 0.193597$ nm for the reflections due to $K\alpha_1$ radiation, while those due to $K\alpha_2$ were discarded because they were too weak to give a good reading. Unit weight was assigned to each observation.

Electron microprobe data. Microprobe investigations were carried out with a Jeol JXA-50A electron probe microanalyzer on carbon-coated polished mounts. Spectra from energy dispersive analysis (EDA) of X-rays with electron excitation were obtained by means of a Canberra lithium-drifted silicon detector (Si(Li)-detector) and a Silena 1,024-channel analyzer with analytical conditions maintained throughout. The accelerating voltage was 25 kV, the sample current was 2×10^{-10} A, the field scan had a magnification of $1,200\times$, the multichannel analyzer (MCA) operated at a fixed preset livetime of 100 seconds with a 10 eV/channel, and the vertical full scale of spectra recordings was 4×10^8 counts. X-ray scanning pictures by the EDA system for AlK, SiK, CaK α , MnK α , FeK α + MnK β_1 , and FeK β_1 , as well as the corresponding secondary electron (SE) images of polished mounts, were taken at 25 kV accelerating voltage.

Scanning electron microscope data. SE pictures were taken with a Stereoscan Cambridge SEM on euhedral garnet grains coated with a vacuum-deposited Pt-10% Au alloy at 30 kV accelerating voltage.

GENERAL FEATURES OF THE ARGENTERA GARNETS

Garnet from central granites. The central granites of the Argentera Massif (fig. 1) include the following main intimately associated petrographic types: (a) medium-grained, (b) medium- to coarse-grained with K-feldspar megacrysts, and (c) medium- to fine-grained granitic rocks (Malaroda and Schia-

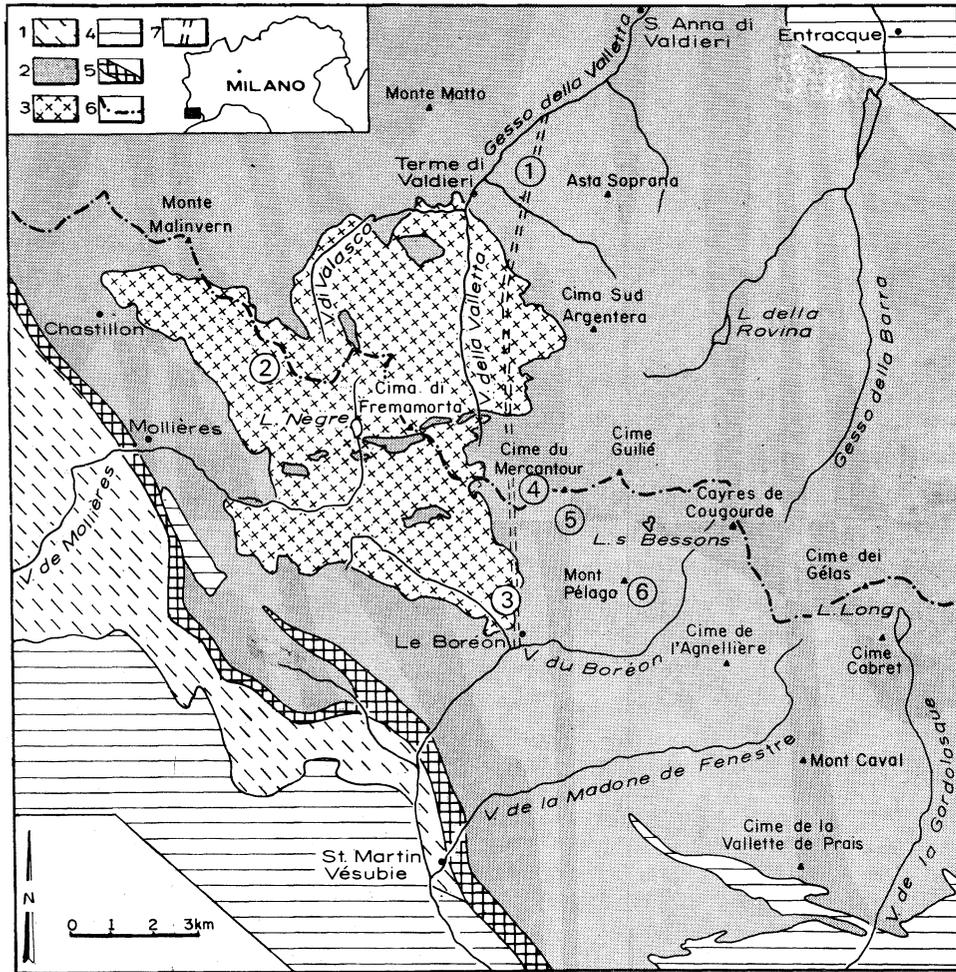


Fig. 1. - Geological sketch of the Argentera Massif, Maritime Alps, and locations of the specimens studied. 1 Tinée Complex; 2 Malinvern-Argentera Complex; 3 Central Granites; 4 Sedimentary Cover; 5 Ferriere-Mollières Mylonites; 6 Italo-French frontier; 7 Planned Ciriégia road tunnel. (Geology from Malaroda, 1970; Faure-Muret, 1955; Blasi, 1971).

vinato, 1957). The dominant constituents are quartz, K-feldspar, and acid plagioclase in a subequal amount. Frequently chloritized biotite, muscovite, garnet, nodules of quartz + pinitized cordierite are subordinate along with minor apatite and zircon.

Incidentally, as the occurrence of cordierite together with that of garnet can be of particular interest in providing an explanation for the genesis of the granitic rocks, it is here emphasized that these nodules are more widely abundant than is apparent at this stage⁽¹⁾.

It is the fine- and medium-grained central granites that commonly exhibit garnet. Boucarut (1967), confirming the observations of Faure-Muret (1955), reports that garnet occurs principally at the top of the central granites, along a marginal portion, for a thickness of about 100 m, irrespective of whether the granites are medium- or fine-grained. As garnet can be very small in size, however, it is most probable that its occurrence in central granites is more frequent than now appears from the geological maps.

It is pink-coloured and in a thin section appears substituted, sometimes strongly, by quartz or other leucocratic constituents (fig. 2). However, garnet from fine-grained central granites encountered after a tunnelling progress of 1,060 m along the Italian exploratory trench of the planned Ciriegia road tunnel (fig. 1), keeps the former euhedral morphology completely intact (figs. 3 *a-c*).

As also ascertained by Compagnoni, Lombardo and Prato (1974), garnet from central granites hardly ever gives rise to breakdown products.

Garnet from Mt. Pélago anatexites. Mt. Pélago anatexites, in the French sector of the Argentera Massif, outcrop in the middle part of V. du Boréon and also occur partially in the V. de la Madone de Fenestre (Blasi, 1971).

These migmatites can be considered among the most highly granitized rocks of this massif, and appear different from other anatexites due to their mineralogical composition, which is similar to that of central granites, but with which they show cross-cutting relationships.

The most important minerals are K-feldspar, plagioclase and quartz in a subequal amount; biotite, muscovite, garnet, fibrolite, nodules of quartz + fibrolite, nodules of quartz + cordierite are subordinate constituents, together with minor apatite and zircon (Blasi and Schiavinato, 1968; Blasi, 1971).

(1) In addition to the occurrence described by Blasi and Schiavinato (1968), cordierite nodules have been encountered in the central granites of the Argentera Massif in the following localities: (*a*) On the west side of the V. della Valletta from the confluence with the V. di Valasco to the Gias delle Mosche; here one can observe all the intermediate steps between nodules of quartz + cordierite and little nodules consisting exclusively of quartz, the latter having already been described by Malaroda and Schiavinato (1957). (*b*) About 1.2 km to the north of the Cima di Fremamorta, on the outskirts of the lakes of the same name, particularly along the east side of the principal lake, where the granitic rocks seem to be spattered with quartz + cordierite nodules of different sizes. (*c*) North of Lac Nègre, at an altitude of about 2,400 m, where a minor aplitic body emplaced in medium-grained granites exhibits a large number of quartz + cordierite nodules and nodules of quartz alone. (*d*) In the granitic rocks, perhaps apophyses of the Argentera central granites, encountered for more than 1,000 m in a tunnel excavated in 1972 by the firm Mazzoli, of Bolzano, on the north-western side of Lago della Rovina during work on the Chiotas Dam.

Biotite is usually chloritized, fibrolite is muscovitized and cordierite is pinitized. The garnet, unlike that of the central granites, always tends to break down into chlorite.

In Mt. Pélago anatexites, garnet also occurs in small amounts; usually it is pinkish-red in colour, darker than garnet from granitic rocks, and, in thin section, appears strongly replaced by leucocratic minerals (figs. 4-5).

UNIT CELL EDGE

Irrespective of separation procedures used for the garnet investigated, all the X-ray powder patterns show up, although very weakly, the two strongest lines of quartz. In addition, some powder photographs show the strongest line of albite, and others of garnets from anatexitic rocks exhibit a line

TABLE I

Unit cell edges of garnets from the Argentera Massif.

Rock type	Granites			Anatexites		
	472	To87	26364	3866	5570	1766
Sample No. referred to in fig. 1	1	2	3	4	5	6
a (nm)	1.15713 ±.00012	1.15681 ±.00009	1.15717 ±.00019	1.15369 ±.00008	1.15432 ±.00005	1.15382 ±.00007
X_{abs} (*)	.00143 ±.00063	.00030 ±.00028	.00084 ±.00077	.00022 ±.00029	.00025 ±.00018	.00049 ±.00022
X_{ecc} (**)	.00059 ±.00056	.00004 ±.00031	.00025 ±.00074	.00019 ±.00029	.00062 ±.00019	.00002 ±.00023
$SQRSG$ (nm ⁻²) (***)	.022	.020	.036	.017	.012	.015
Ref (+)	12/17	16/17	13/17	14/17	15/17	16/17
NV (++)	3	3	3	3	3	3
DF (+++)	9	13	10	11	12	13

Sample locations are given in the appendix.

(*) Systematic correction term for absorption.

(**) Systematic correction term for eccentricity.

(***) Estimated standard error of unit weight observation of Q.

(+) Number of lines used in the refinement/number of input diffraction lines.

(++) Number of varied parameters.

(+++) Degrees of freedom.

($d = 1.05$ nm) tentatively referred to as palygorskite. These effects indicate that the inclusions in these garnets must be appropriately taken into account when conducting physical or chemical investigations on the whole separated fractions.

Table I gives the values of the refined unit cell edge for three garnets from the central granites and for as many garnets from the Mt. Pélago anatexites (cf. fig. 1).

To give a measure of the influence of the systematic error terms in the refinements, the nondimensional values of correction terms for absorption, X_{abs} , and for eccentricity, X_{ecc} , are also given in Table I as obtained from the least squares procedure. These values show that the parameter X_{abs} is greater than X_{ecc} , except in specimen No. 5.

From Table I it can be deduced that: (a) garnets from granites have unit cell edge values very close to each other, and this also occurs even in garnets from anatexites; (b) unit cell edge values of garnets from granites are clearly greater than those of garnets from anatexites.

If the unit cell edge reference values for garnet end-members (cf. Skinner, 1956) and the solid solution field in the common natural garnets are taken into account, garnets from both granitic and anatexitic rocks in Table I can probably be interpreted as pyralspitic members. On this assumption, one can suspect that the difference between them is due to the fact that in garnet from granitic rocks there is a greater content of divalent cations with higher ionic radius.

X-RAY INTENSITIES

The principal features for the crystal structure of a silicate garnet with space group symmetry $Ia3d(230)$ are summarized as follows:

general structural formula (Geller's (1967) notation)	{ X_3 }	[Y_2]	(Z_3)	O_{12}
common cations in silicate garnets	Mg ²⁺ , Fe ²⁺ , Mn ²⁺ , Ca ²⁺	Al ³⁺ , Fe ³⁺ , Cr ⁵⁺	Si ⁴⁺	
coordination to oxygen	8	6	4	
type polyhedron	triangular dodecahedron (distorted cube)	octahedron	tetrahedron	
space group position	24c	16a	24d	96h
point symmetry	222	$\bar{3}$	$\bar{4}$	1

All the atoms occupy special positions except oxygen, which depends on three variable structure parameters x, y, z . Although in the silicate garnets the atomic coordinates of oxygen are subject to variation according to chemical composition (Novak and Gibbs, 1971), for our purposes these parameters can be considered as constant to a first approximation. This is in line with Quarenì and De Pieri (1966), who suggested that in practice the trigonometric parts of the structure factors can be considered as constant.

Consequently, if we take into account that usually the Si atom is not easily substituted in silicate garnets, some appropriate structure factors can be used to a first approximation as a function of the scattering power of the atoms in the c and a sites. This is done in a similar manner to other physical properties related to composition and with the well-known limitations involved (cf. Fenoglio and Rigault, 1960; Ferraris and Franchini Angela, 1970; Franchini Angela and Ferraris, 1971).

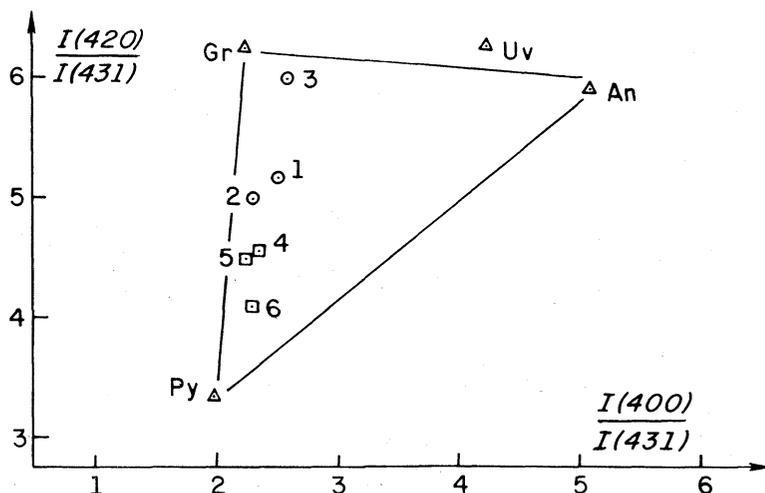


Fig. 6. - $I(420)/I(431)$ versus $I(400)/I(431)$ for garnet from granitic rocks (circles) and anatectic rocks (squares) of the Argentera Massif. Triangles are for reference garnets from Borg and Smith (1969).

As a less time-consuming alternative, instead of the structure factors, the integrated intensities were used. In particular, it was found that the following appropriate lines in the front reflection region could be used: (a) 400, the intensity of which receives a contribution from O, Z, Y and X atoms; (b) 420, which receives a contribution from O, Z and X atoms; (c) 431, which, in the Argentera garnets, is the strongest reflection controlled only by O atoms, and can accordingly be used as an internal standard. The last reflection in the garnets investigated is much more intense than 741, which is used for andradite by Quarenzi and De Pieri (1966).

Fig. 6 is a plot of $I(420)/I(431)$ vs. $I(400)/I(431)$ for the representative points of the Argentera garnets:

Sample No. (cf. Table 1)	1	2	3	4	5	6
$I(420)$	5.2	5.0	6.0	4.5	4.5	4.1
$I(431)$						
$I(400)$	2.5	2.3	2.6	2.4	2.2	2.3
$I(431)$						

and, as a reference, for the values of grossularite, pyrope, andradite and uvarovite obtained from the $I(\text{Int})$ calculated by Borg and Smith (1969) on the basis of the structural data supplied by Prandl (1966), Gibbs and Smith (1965), Quareni and De Pieri (1966), and Novak and Gibbs (1968, quoted as a personal communication in Borg and Smith, 1969).

In fig. 6 the garnets of the Argentera Massif appear distributed near to the line that joins the reference points for pyrope and grossularite. Considering the parameter $I(420)/I(431)$, it can be deduced that the garnet from granitic rocks is different from that of anatexitic rocks in the atom occupancies of the c sites. From the parameter $I(400)/I(431)$ it can be deduced that garnets from both granitic and anatexitic rocks would have occupancies in the a sites giving a similar effect.

COMPOSITIONAL ZONING

Recent work by Edmunds and Atherton (1971), De Pieri and Galetti (1972), Emiliani and Venturelli (1972), Anderson and Buckley (1973), Béthune, Laduron and Bocquet (1975), Råheim (1975), reviewing the extensive literature on compositional zoning in garnets have discussed some possible growth models concerning this phenomenon.

While for the garnet of metamorphic rocks compositional zoning is widely proved, for garnet occurring in granitic rocks this effect appears more rare or sometimes uncertain (cf. for instance Callegari, 1966; Leake, 1967; Emiliani and Zeda, 1974).

As zoning in garnet is very important to an explanation of the genesis of this mineral and of the host rocks, suitable research has been undertaken to ascertain its occurrence in garnet from the Argentera Massif.

Optical studies have not identified any of the elements that usually lead to suspicion of this effect. This is supported by the following data: (a) The leucocratic constituents usually replace garnet in a completely irregular way, and it is statistically rare to find atoll garnets, although this peculiar replacement has been observed in garnet from anatexitic rocks (fig. 5), rather than in garnet from granitic rocks. Incidentally, the existence of an atoll replacement can be caused in a zoned garnet by the attack of the unstable inner zone through some breach of the rim (b) The breakdown effects, occurring in practice only in garnet from anatexites, appear irregularly distributed (c) Colour variations between core and rim, or an arrangement of inclusions similar to that encountered in many zoned garnets have not been observed.

On the basis of X-ray diffraction photographs, all the garnets investigated here show sharp lines in the forward reflection region as well as well-resolved doublets $K\alpha_1$, $K\alpha_2$ in the high 2θ region. As the reflections tend not to be diffuse, poorly resolved or split, zoning or coexistence of different phases are confirmed as not appearing in the garnets studied.

In order to check the results of these observations, microprobe investigations were also carried out. First of all, for garnets from granitic rocks

(specimen To87) and anatexitic rocks (specimen 5570) X-ray spectra were obtained by the EDA system and these appear quite significantly different (figs. 7 and 9). From these spectra it can be deduced that the more abundant elements are Al, Si, Mn, and Fe. With the same AlK/SiK ratio, in garnet from granites counts for $MnK\alpha$ and $FeK\alpha + MnK\beta_1$ are in subequal amounts, while in garnet from anatexites, the counts for $MnK\alpha$ are less than those for $FeK\alpha + MnK\beta_1$. In garnet from anatexites a small amount of Mg and Ca occurs, while in garnet from granites Mg is not present, and Ca appears in a slightly greater amount.

After identification and evaluation of the element occurrence in the samples investigated, X-ray scanning pictures by the EDA system were taken showing element distributions that were very uniform for garnets of both granitic and anatexitic rocks (figs. 8 *b-g* and 10 *b-g*).

In garnet from central granites - apart from some inclusions of quartz visible even in the SE picture (fig. 8 *a*) - it may be observed that only Ca distribution appears a little irregular (fig. 8 *d*). In order to avoid ambiguity due to the overlap $FeK\alpha + MnK\beta_1$ (cf. Reed, 1975; Smith, 1976), X-ray scanning pictures for $FeK\beta_1$ were also taken (figs. 8 *g* and 10 *g*).

CONCLUDING REMARKS

Garnets from the central granites of the Argentera Massif and the surrounding Mt. Pélago anatexites are pink and dark red in colour respectively, and appear widely replaced by leucocratic minerals, particularly by quartz. In some case, however, garnet from granites preserves the former euhedral habit completely intact.

Breakdown effects are observed in many minerals from both granitic and anatexitic rocks; however, only garnet from anatexites appears almost always chloritized. This leads to the supposition that, unlike garnet from granites, it contains mafic elements in a sufficient amount to give chlorite.

From unit cell edge values, it can be deduced that the garnets investigated are probably pyralispitic members and, on this assumption, it may be suspected that in garnet from granitic rocks there is a greater content of divalent cations with higher ionic radius. This is confirmed by the behaviour of the intensity ratios $I(420)/I(431)$ and $I(400)/I(431)$. Taking into account these results, microprobe data from X-ray spectra by the EDA system permit to point out that garnets from granites are solid solutions of the end-members almandine and spessartite, while the garnets from anatexites are composed of almandine predominating over spessartite.

By optical observations, from the features of the X-ray diffraction lines and from X-ray scanning pictures by the EDA system, the garnets studied do not appear to exhibit the common effect of compositional zoning.

APPENDIX: *sample documentation*

- 1 472. Garnet from fine-grained granite. After tunnelling progress of 1,060 m in the Italian exploratory trench of the planned Ciriugia road tunnel.
- 2 To87. Garnet from fine-grained granite. Altitude 2,460 m, south-east of Testa delle Portette.
- 3 26364. Garnet from medium-grained granite. Altitude 2,200 m in the Serre des Bous, near the contact with the Mt. Pélago anatexites.
- 4 3866. Garnet from Mt. Pélago anatexite. 0.8 km east of the Cime du Mercantour on the Italo-French frontier.
- 5 5570. Garnet from Mt. Pélago anatexite. East side of Cayre Nègre du Mercantour.
- 6 1766. Garnet from Mt. Pélago anatexite. South-east side of Mt. Pélago.

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All computations were carried out on a Univac 1106 computer at the Milan University Computer Center; microprobe studies were conducted as a form of scientific exchange at CISE, Information Study and Experiment Centre, Segrate, Milan; scanning electron microscope pictures were taken at the Central Alps Stratigraphy and Petrography Research Centre, Milan, an institution of the Italian National Research Council, which sponsored this investigation.

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EXPLANATION OF PLATES I-II

PLATE I

- Fig. 2. – Microphotograph of a sub-idiomorphic garnet from granitic rocks showing marginal replacement by leucocratic minerals. Sample To87, plane-polarized light.
- Figs. 3 *a-c*. – Scanning electron micrographs of euhedral garnet grains from fine-grained granites of the Ciriegia tunnel. Sample 472.
- Fig. 4. – Microphotograph of garnet from Mt. Pélago anatexites showing the commonest type of replacement by leucocratic minerals and the breakdown products, principally chlorite. Sample 1766, plane-polarized light.
- Fig. 5. – Microphotograph of garnet from Mt. Pélago anatexites showing a rarer atoll replacement by leucocratic minerals. Breakdown products with formation of prevailing chlorite are also shown. Sample 1766, plane-polarized light.

PLATE II

- Fig. 7. – X-ray oscilloscope spectrum by the EDA system, obtained with Si(Li)-detector for garnet from granitic rocks. Sample To87.
- Figs. 8 *a-g*. – (*a*) SE picture, (*b-g*) X-ray scanning pictures by the EDA system for garnet from granitic rocks. Sample To87.
- Fig. 9. – X-ray oscilloscope spectrum by the EDA system, obtained with Si(Li)-detector for garnet from anatexitic rocks. Sample 5570. Same instrumental conditions used for sample To87.
- Figs. 10 *a-g*. – (*a*) SE picture, (*b-g*) X-ray scanning pictures by the EDA system for garnet from anatexitic rocks. Sample 5570.

