

## Vanadian garnets in calcareous metapelites and skarns at Coat-an-Noz, Belle-Isle-en-Terre (Côtes du Nord), France

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### ABSTRACT

V-rich garnets belonging to the grossular-goldmanite ( $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$ ) series are found within metamorphosed calcareous metapelites. These metapelites are derived from euxinic sediments, and their composition is similar to that of unmetamorphosed Silurian black shales. All garnet compositions in the range  $\text{Gol}_0$  to  $\text{Gol}_{68}$  are represented, and the solid-solution series is a continuous one. Complex sector zoning is observed. Associated clinopyroxenes and actinolites show significant V contents. In skarns developed from similar metapelites, goldmanite-rich garnets form the cores of crystals surrounded by grossular overgrowths. The crystallization of goldmanite seems to be controlled by the bulk chemical composition of the original sediments.

### INTRODUCTION

Calcic garnets belonging to the goldmanite-grossular series have been found in the course of a mineralogical study of Paleozoic metasedimentary rocks containing scheelite mineralization. These formations are part of a small Paleozoic basin situated 50 km to the north of the large Châteaulin basin in Brittany, France. The boreholes were made through tungsten-mineralized skarns near the Belle-Isle-en-Terre locality, Coat-an-Noz (Fig. 1), a few kilometers west of the city of Guingamp (Côtes du Nord). The vanadiferous garnets are found in calcareous metapelites and scheelite-bearing skarns. The object of the present paper is to describe these V-rich garnets as well as other coexisting vanadian silicates.

### GEOLOGIC DESCRIPTION OF THE SERIES

V-rich garnets are found in the upper levels of the Coat Losquet formation. This stratigraphic unit is approximately 200 m thick and comprises centimeter- to meter-thick beds of alternating black shales (infrequently calcareous), sandstones, and subordinate limestones. Because of metamorphic recrystallization and the absence of fossils, the age of these euxinic and calcareous formations can be determined only by comparison with sedimentary series from the nearby Châteaulin basin (Sagon, 1976). Two similar series are present in the Châteaulin basin, namely the Upper Silurian (Ludlow) and the Lower Devonian (Coblencian). Hirbec (1979), however, has given a Coblencian age for the Coat-an-Noz formations, an attribution confirmed by chemical analyses. The Coat-an-Noz formations rest unconformably on the Cambrian Loc-Envel orthogneiss (Andriamarofahatra and La Boisse,

1988). It includes a lower unit of white orthoquartzites (20 to 50 m thick) and a middle unit of black pelitic schists (300 m thick). The Coat Losquet formation itself is overlain by a series of tholeiitic metabasalts and metagabbros (Foz formation).

The stratigraphic units described above have been transformed by regional metamorphism and by thermal metamorphism from Hercynian granites. The regional metamorphism is attested to by the development of andalusite, staurolite, and almandine within pelitic rocks, of hornblende and plagioclase (andesine) in amphibolites, of cummingtonite in Fe-rich or manganiferous metapelites, and of andalusite and calcic plagioclase (bytownite to anorthite) within calcareous metapelites.

Contact metamorphism in the northern part of the area is spatially related to the Plouaret Hercynian granite. The Plouaret granite is associated with known lead-zinc (copper), arsenopyrite-gold, and uranium mineralization, whereas tungsten has not been reported. The wide zone known to the south is attributed to a hidden granite cupola, with the Quintin granite cropping out 10 km south of the Coat-an-Noz area. More specifically, its evolved facies are associated with cassiterite, wolframite, scheelite, and bismuth showings, similar to the Coat-an-Noz association in which, however, tin remains unknown (Chauris, 1983, 1986).

V-rich garnets (Fig. 2) and clinopyroxene occur as undeformed porphyroblasts in some of the Coat-an-Noz metamorphic calcareous metapelites. Textural evidence suggests that they are the product of contact metamorphism. Nonoriented biotites are also widely developed at the same stage in various rock types such as impure marbles, calc-schists, and some metapelites.

### CHEMICAL COMPOSITION OF THE METAMORPHIC ROCKS

Bulk chemical analyses including trace elements were performed using an automated 1400 Philips X-ray fluorescence spectrometer.  $Fe^{2+}/Fe^{3+}$  ratios and weight loss on ignition (L.O.I.) were determined by wet-chemical methods. Three of the four black calcareous metapelites analyzed (Table 1), contain V-rich garnets, and their analyses show between 894 and 2021 ppm V (CAN8, CAN16, CAN147). The fourth specimen (CAN13) closely associated with the three others, does not contain any garnet. Though it contains a significant amount of V (450 ppm), its low CaO content (0.56 wt% as opposed to 5–13 wt%) appears to be a reasonable explanation for the absence of garnet. The V-rich metapelites also have a remarkable Mo (100–200 ppm) and high Ni (100–200 ppm) contents. The high V content of these rocks is similar to that of unmetamorphosed Silurian black shales in Brittany (Dabard and Paris, 1986). These trace-element concentrations attest to the euxinic character of these sedimentary rocks. The high  $K_2O$  content and L.O.I. of CAN147 and CAN13, respectively, are due to alteration phenomena—late-stage K-feldspathization for the former specimen, and intense sericitization for the latter one.

Two different types of skarn have also been analyzed (Table 1). Sample CAN58 (type 1) contains numerous garnets with V-rich cores, scheelite, and sulfides. Specimen CAN108B (type 2) contains homogeneous V-free garnets and no sulfides. Both developed from calcareous

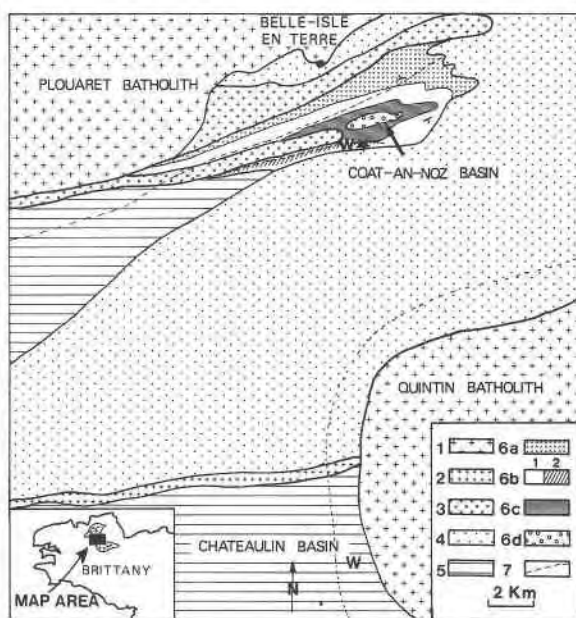


Fig. 1. Simplified geologic map and location of the Coats-an-Noz formation. 1, granite; 2, microgranite; 3, Cambrian Loc Envel gneiss; 4, Brioverian basement; 5, undifferentiated Paleozoic formations; 6, Coats-an-Noz formations (after Hirbec, 1979); 6a, Foz formation; 6b, Coat Losquet formation; 6c, Loch Du formation; 6d, Coat-an-Hay formation; 7, limit of contact metamorphism; W, tungsten mineralization; solid star, borehole location.

TABLE 1. Chemical analyses (wt%) of Coats-an-Noz metapelites and skarns

	CAN147	CAN16	CAN8	CAN13	CAN58	CAN108B
SiO <sub>2</sub>	55.25	54.69	43.28	47.18	37.31	42.94
TiO <sub>2</sub>	0.77	0.56	0.92	0.93	0.58	0.46
Al <sub>2</sub> O <sub>3</sub>	19.86	16.09	25.41	25.44	16.55	14.92
Fe <sub>2</sub> O <sub>3</sub>	2.79	4.95	2.56	2.96	7.30	2.99
FeO	2.17	4.54	2.52	4.84	7.77	3.16
MnO	0.08	0.08	0.08	0.07	0.84	0.26
MgO	2.19	1.86	3.03	4.49	1.84	2.05
CaO	5.22	8.45	13.22	0.56	20.92	26.34
Na <sub>2</sub> O	0.41	0.11	0.65	0.13	tr.	tr.
K <sub>2</sub> O	5.60	3.15	2.81	5.95	0.03	0.02
P <sub>2</sub> O <sub>5</sub>	0.21	0.24	0.15	0.13	0.24	0.18
L.O.I.	4.51	5.45	4.58	7.67	6.53	5.09
Sum	99.06	100.17	99.21	100.35	99.91	98.41
Ba	831	104	227	1491	<15	<15
Cu	289	475	176	125	661	12
Rb	426	143	146	439	<10	<10
Sr	446	336	752	82	62	20
Y	30	62	33	26	77	39
Nb	<10	11	15	24	12	10
Zr	192	94	95	131	143	81
Co	15	19	11	25	11	10
Ni	120	234	100	79	211	153
Cr*	147	133	140	145	166	112
V	2021	1745	894	446	2433	1283
Zn	433	1981	34	124	246	180

Note: CAN 147: CZ61, level 208.8 m; garnet + K-feldspar + sphene ± pyrite ± sericite. CAN16: CZ20, level 163.3 m; diopside + garnet ± quartz + sphene + pyrite + arsenopyrite ± epidote ± chlorite ± prehnite ± sericite. CAN8: CZ20 level 153.8 m; plagioclase (An<sub>60</sub>) + clinopyroxene + garnet + sphene + pyrite + arsenopyrite ± actinolite ± epidote ± chlorite ± prehnite. CAN13: CZ20, level 157.4 m; muscovite + chlorite (after biotite) + ilmenite + pyrite ± sericite. CAN58: CZ20 level 166.1 m; garnet ± epidote ± calcite ± siderite ± chlorites ± quartz ± scheelite ± sulfides. CAN108B: CZ45 level 241.3 m; garnet ± epidote ± calcite ± siderite.

\* ICP determination (Geology Department of St. Etienne School of Mines).

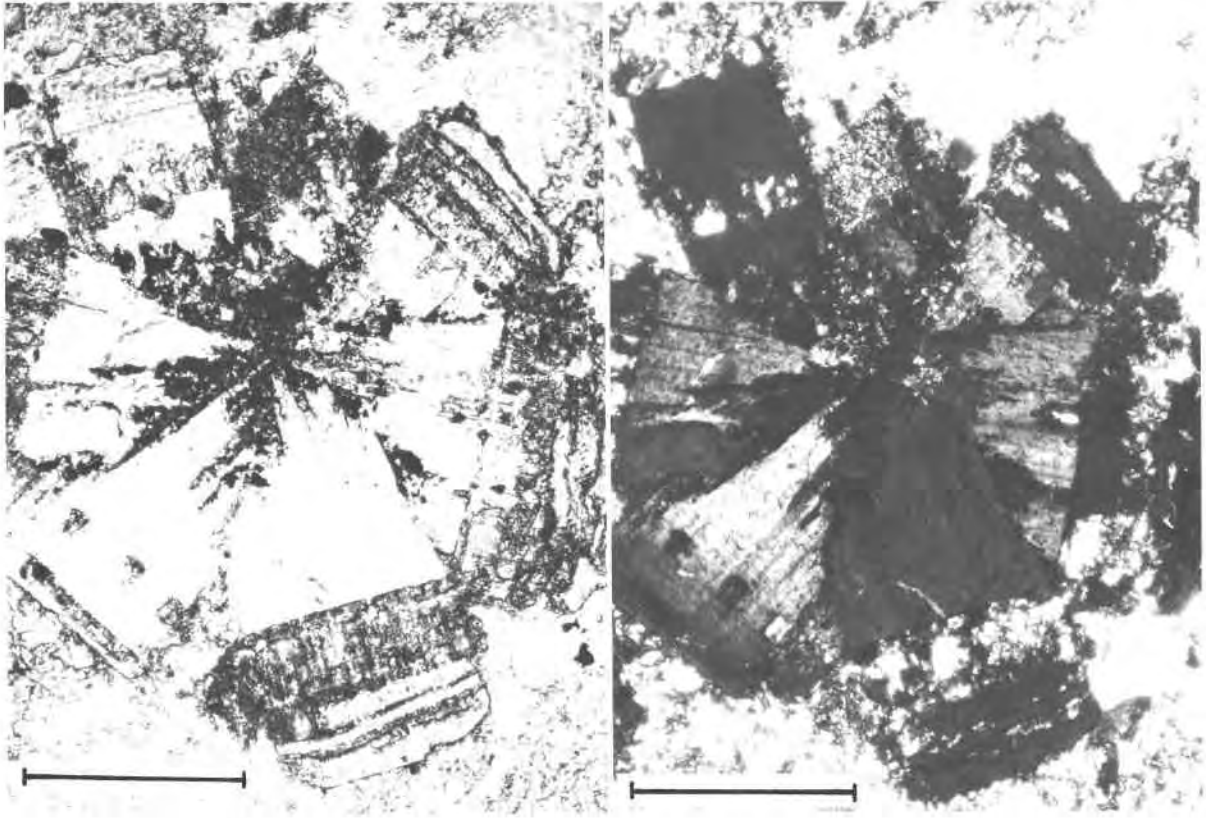


Fig. 2. Idiomorphic zoned goldmanite-rich garnet showing anisotropic sectors. Plane-polarized light (left) and crossed Nicols (right). Contiguous sectors have different optical orientation, whereas opposed sectors have identical optical properties. The profiles in Fig. 5 were obtained on this particular garnet, following the longest crystal diameter from top left to bottom right. Length of bar is 0.2 mm.

V-rich metapelites. Their V content is 2433 and 1283 ppm, respectively.

When skarn compositions are compared to those of the calcareous metapelites, it appears that Al, Ti, P, Zr, and probably Mg behaved as inert components during skarn development. Small amounts of Mn and larger amounts of Fe (CAN58, Table 1) were probably added while conspicuous amounts of Si, K, Ba, Rb, Sr, and Na were subtracted by percolating fluids. The CaO increase from metapelites (5–13 wt%) to skarns (21–26 wt%) suggests a substantial addition of Ca directly related to skarn formation.

#### MINERAL ASSOCIATIONS IN THE CALCAREOUS METAPELITES

Quantitative analyses were performed using a CAMECA CAMEBAX electron microprobe (Geology Department, Paris School of Mines, Fontainebleau). Accelerating voltage was 20 kV, and specimen current was 15 nA. The standards used (followed by counting times in seconds) were F, fluorite (36 s); Cl, chlorapatite (24 s); Mg, periclase (24 s); Al, corundum (12 s); Na, albite (24 s); Si, olivine (12 s); K, orthoclase (24 s); Ca, wollastonite (12 s); Ti, rutile (24 s); Fe, hematite (24 s); Mn, MnO (12 s); Cr, Cr<sub>2</sub>O<sub>3</sub>

(24 s); V, vanadium metal (24 s); and Y, yttrium metal (24 s). Cr<sub>2</sub>O<sub>3</sub> was corrected for VK<sub>β</sub> interference.

The metapelites are composed of plagioclase (An<sub>80</sub> to An<sub>92</sub>), pyrite, arsenopyrite, sphene, very conspicuous garnets (5 vol%), and uncommon clinopyroxene. Retrograde minerals include actinolite with finely prismatic to fibrous habit, chlorite commonly replacing clinopyroxene, and epidote as rounded porphyroblasts or forming a rim around the sulfide grains. Prehnite or zeolites may also be found. Carbonaceous matter is ubiquitous.

#### Garnets

The garnets (Table 2) with their yellow (V-poor) to green (V-rich) coloring and beautiful sector zoning are very conspicuous in thin section. Their morphology is similar (Fig. 2) to that reported by Filippovskaya et al. (1972). They show large variations in birefringence, and contiguous sectors have different optical orientation whereas opposed sectors have an identical one (Fig. 2). This sector zoning is a common feature of grossular garnets and garnets from skarns and has recently been attributed (Allen and Buseck, 1988) to the growth ordering of trivalent and divalent elements, and possibly OH, within triclinic sectors. The unusual composition of these

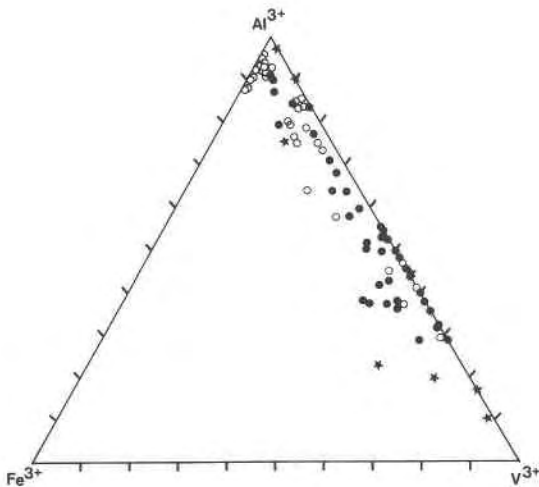


Fig. 3. An  $\text{Al}^{3+}$ - $\text{V}^{3+}$ - $\text{Fe}^{3+}$  diagram showing Coat-an-Noz garnet compositions. Solid circles, metapelites; open circles, skarns; solid stars, V-bearing garnets from the literature (Badalov, 1951; Moench and Meyrowitz, 1964; Shepel' and Karpenko, 1970; Filippovskaya et al., 1972; Jobbins et al., 1975).

garnets (Table 2) can be described as a solid solution of two end-members (Fig. 3), goldmanite ( $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$ ) and grossular. The cell parameter of a goldmanite specimen (analysis 7, Table 2) has been calculated as  $11.971(2)$  Å (determined with a Gandolfi camera), in agreement with its position in the solid-solution series (Fig. 4). There is also a small admixture of two other end-members, almandine (<9 mol%) and andradite (<11 mole%). The V content of the garnets appears to be related to the bulk composition of the rock as exemplified by specimen CAN147 (2021 ppm), which contains garnets with  $\text{V}_2\text{O}_3$  contents ranging from 14.6 to 21.3 wt%, and specimen CAN8, which, with only 894 ppm V, hosts garnets containing 3.7 to 4.8 wt%  $\text{V}_2\text{O}_3$ . The V content of the bulk

rock may thus serve as a guide to the composition of the garnets; for instance, sample CAN16 is intermediate both in bulk-rock V content and V content of the garnets. Other trace-element contents are variable.  $\text{Y}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  in the garnets vary between 0 and 0.6 and 0 and 1.33 wt%, respectively, and these two elements show no apparent correlation with the V content. The Ti content, which is high for garnets unrelated to alkaline rocks, varies between 0.54 and 1.27 wt%  $\text{TiO}_2$  and is correlated with  $\text{Fe}^{3+}$  and less distinctly with V content. The Coat-an-Noz garnets contain some F (0.2 to 1.3 wt% F) unlike other V-rich garnets described in the literature (Badalov, 1951; Gubelin and Weibel, 1975; Moench, 1962; Moench and Meyrowitz, 1964; Shepel' and Karpenko, 1970; Filippovskaya et al., 1972) but similar in this respect to grossulars described in calc-silicate rocks (Valley et al., 1983). The structural formulae, as well as the garnets' conspicuous birefringence, suggest a significant OH content. Individual crystals may appear to be optically homogeneous but commonly show compositional variations. A polyhedral central sector is relatively homogeneous with compositions between 11 and 16 wt%  $\text{V}_2\text{O}_3$  and an outer zone with alternating goldmanite-rich ( $\text{V}_2\text{O}_3$  from 13.1 to 17 wt%) and goldmanite-poor ( $\text{V}_2\text{O}_3$  from 8 to 12.5 wt%) zones (Fig. 5). Commonly the centers of the garnets are V-rich compared to the borders, and the contrasting behavior of V between the center part and the outer parts of the crystals is followed by other elements such as Al, Ti, Cr, Y, Ca, Fe, Mn, and Mg. Chemical profiles (Fig. 5) of the crystal in Figure 2 show the following relationships: (1) Contrasting patterns exist for the core and the rim of the crystals. For most elements, a jagged profile corresponds to the outer zone, whereas the center shows a flat pattern. (2) The center zone is V-, Ca-, Ti-, an Mg-rich relative to the rim. (3) Most variations correspond to known garnet substitution schemes as evidenced by a strong inverse correlation between V and Al.

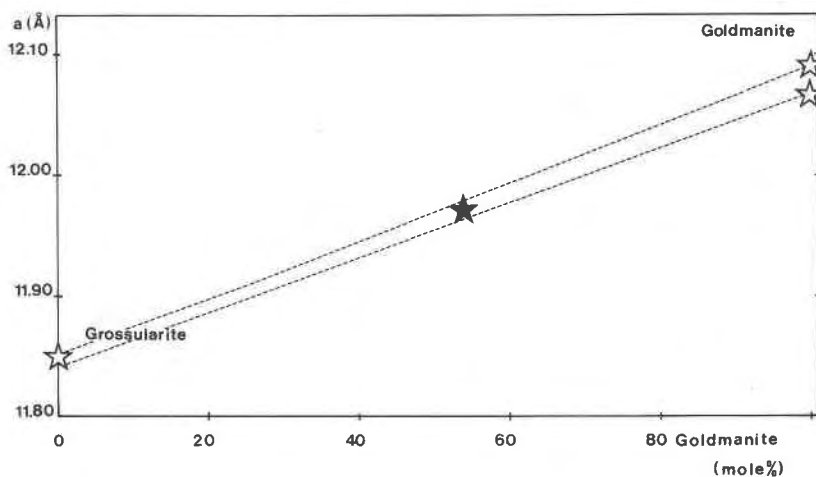


Fig. 4. Variation goldmanite cell-dimension (Å) as a function of composition (goldmanite mol%). Solid star, Coat-an-Noz garnet; open stars, end-members goldmanite (Mill', 1964; Strens, 1965) and grossularite (Skinner, 1956).

TABLE 2. Representative electron-microprobe analyses of vanadian garnets

	CAN8 1	CAN16 2	CAN147 3	CAN14 4	CAN14 5	CAN14 6	CAN147 7	CAN58 8	CAN58 9
SiO <sub>2</sub>	38.18	37.39	36.35	35.87	38.00	37.37	36.60	37.40	39.00
TiO <sub>2</sub>	1.07	0.81	0.77	0.54	0.57	0.87	1.03	1.12	0.49
Al <sub>2</sub> O <sub>3</sub>	16.81	17.71	5.87	7.11	14.73	11.17	7.66	8.09	20.12
Cr <sub>2</sub> O <sub>3</sub>	0.15	<0.05	0.15	0.38	0.46	0.29	0.29	0.09	<0.05
V <sub>2</sub> O <sub>3</sub>	4.77	4.64	21.31	16.62	7.90	12.10	17.14	16.99	0.14
Y <sub>2</sub> O <sub>3</sub>	0.37	0.06	0.20	0.24	0.08	0.19	0.24	<0.05	<0.05
FeO*	2.80	2.32	2.08	5.26	2.36	2.41	2.24	2.70	5.24
MnO	1.03	0.48	0.78	1.58	0.57	0.45	0.73	0.91	1.04
MgO	0.05	0.06	0.18	0.18	0.06	0.14	0.23	0.14	<0.05
CaO	33.82	35.35	32.70	30.35	34.66	33.99	33.01	32.63	34.09
F	0.39	1.30	<0.05	0.84	0.25	0.30	0.52	0.25	0.71
O ≡ F	-0.16	-0.55	—	-0.35	-0.11	-0.13	-0.22	-0.11	-0.30
H <sub>2</sub> O**	—	0.64	0.69	0.06	—	—	0.15	—	—
Sum	99.28	99.57	101.08	98.62	99.53	99.15	99.47	100.21	100.38
Si	5.939	5.704	5.815	5.874	5.918	5.944	5.893	6.006	5.908
Ti	0.125	0.093	0.093	0.067	0.067	0.104	0.125	0.135	0.056
Al	3.082	3.184	1.107	1.372	2.704	2.094	1.454	1.531	3.592
Cr	0.018	—	0.019	0.049	0.057	0.036	0.037	0.011	—
V	0.595	0.568	2.733	2.182	0.986	1.543	2.213	2.188	0.017
Y	0.031	0.005	0.017	0.021	0.007	0.016	0.021	—	—
Fe <sup>3+</sup>	0.023	0.057	—	0.242	0.113	0.102	0.027	—	0.279
Fe <sup>2+</sup>	0.341	0.239	0.278	0.478	0.194	0.218	0.275	0.363	0.385
Mn	0.136	0.062	0.106	0.219	0.075	0.061	0.100	0.124	0.133
Mg	0.012	0.014	0.043	0.044	0.014	0.033	0.055	0.034	0.005
Ca	5.637	5.778	5.605	5.325	5.783	5.792	5.695	5.614	5.533
F	0.192	0.627	—	0.435	0.123	0.151	0.265	0.127	0.340
OH	—	0.555	0.741	0.068	—	—	0.162	—	—
Goldm	14.6	14.0	68.0	54.0	24.4	37.9	54.2	53.5	0.4
Andr	3.6	3.7	2.3	7.6	4.5	5.1	3.7	3.3	8.3
Uvar	0.5	—	0.5	1.2	1.4	0.9	0.9	0.3	—
Gros	76.6	79.7	25.2	27.3	67.0	54.1	38.1	38.3	84.1
Alm	5.6	3.9	4.6	7.9	3.2	3.6	4.5	5.9	6.4
Pyro	0.2	0.2	0.7	0.7	0.2	0.5	0.9	0.6	0.1
Spes	2.2	1.0	1.8	3.6	1.2	1.0	1.6	2.0	2.2

Note: Atom proportions based on 10 cations ([8] and [6] sites) and 12 oxygens. OH calculated using  $6 - \text{Si} = (\text{OH} + \text{F} + \text{Cl})/4$  (see Valley et al., 1983).

\* Total Fe as FeO.

\*\* Calculated to be equivalent to OH.

Antipathetic variations between Cr and Ti on one hand and Mn, Fe, and Ca on the other hand are noteworthy.

In a review of the various types of zoning in garnets (Tracy, 1982) the zoning of the goldmanite-rich garnets described above would be characterized as growth zoning and, at the rim, as discontinuous. The discontinuous zoning is interpreted as being due to either changes in the buffering paragenesis, perhaps caused by the resorption of a phase through reaction, or polymetamorphism. The very complicated and recurrent type of zoning found in Coat-an-Noz has, however, no equivalent among the cases mentioned by Tracy. The abrupt changes seem too numerous to be reasonably assigned to the disappearance of a succession of reacting minerals.

These chemical variations allow some tentative conclusions to be made concerning the physical environment in which these garnets grew. There is no reason to suspect that the central and external zones of the crystals grew under widely differing temperature conditions. Elements such as Cr and Y that are reputed to enter readily into the garnet structure are all but absent in the crystal cores, whereas they occur in the external zone. The abrupt variations observed cannot be the result of diffusion effects.

It is concluded that the buffers that controlled the composition of the garnets' cores were strongly altered at a time corresponding to the beginning of growth of the external zone. The compositional fluctuations in the external zone suggest that it grew in a system open to percolating fluids. Thus the zoning of the garnet margin probably records the existence of a fluid phase convecting through the enclosing rocks in response to heat from a granitic intrusion below the level investigated.

### Pyroxenes and amphiboles

The pyroxenes (Table 3) belong to the diopside-hedenbergite series (Hd<sub>10</sub> to Hd<sub>15</sub>). They contain only minor CaVSiAlO<sub>6</sub> (VAT) and NaVSi<sub>2</sub>O<sub>6</sub> (natalyite) substitutions. V is present with values in the range 0.5 to 2.8 wt% V<sub>2</sub>O<sub>3</sub>. A zonation is observed but limited when compared to that of the garnets.

The composition of the actinolites is variable (Table 3), but their V content remains in the range 0 to 3.2 wt% V<sub>2</sub>O<sub>3</sub>. The compositional variability is comparable and is seemingly correlated with that shown by clinopyroxenes.

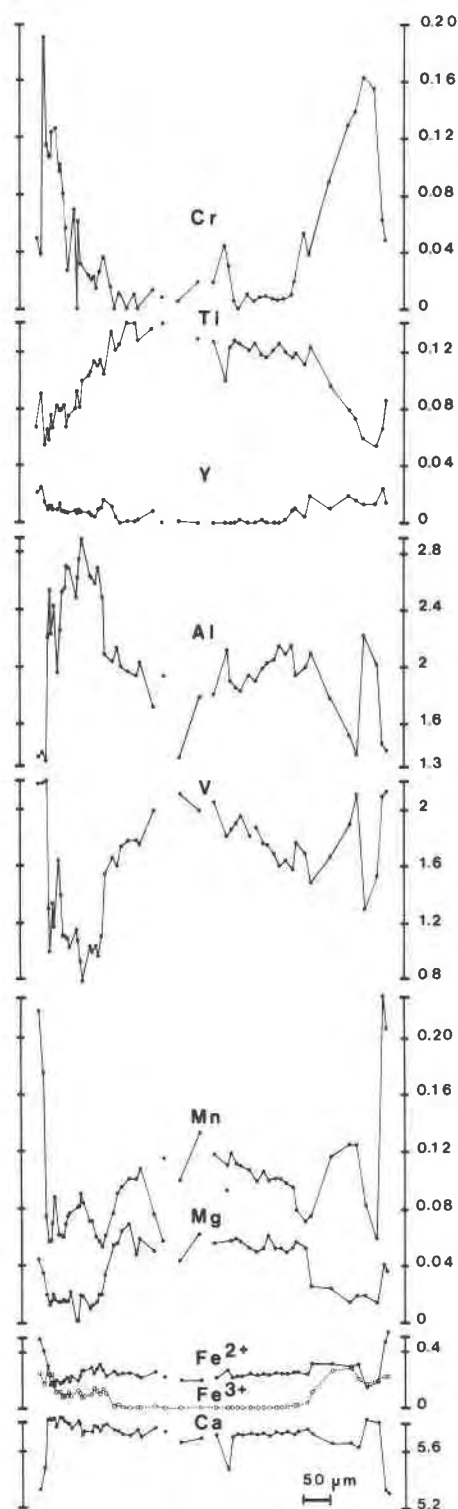


Fig. 5. Trace- and major-element variations (expressed as atoms per formula unit) across the garnet crystal shown in Fig. 2.

TABLE 3. Representative electron-microprobe analyses of V-bearing clinopyroxenes and actinolites

	CAN8 1	CAN14 2	CAN106A 3	CAN108 1	CAN7B 2
SiO <sub>2</sub>	53.50	53.13	52.16	55.30	52.13
TiO <sub>2</sub>	<0.05	<0.05	<0.05	<0.05	0.08
Al <sub>2</sub> O <sub>3</sub>	0.23	0.74	2.49	2.16	4.31
Cr <sub>2</sub> O <sub>3</sub>	0.13	0.20	<0.05	<0.05	0.13
V <sub>2</sub> O <sub>3</sub>	0.96	1.30	2.80	0.42	3.19
Y <sub>2</sub> O <sub>3</sub>	<0.05	<0.05	<0.05	<0.05	<0.05
FeO*	5.33	5.95	3.97	4.67	4.85
MnO	0.60	0.35	0.14	0.13	0.12
MgO	14.24	13.51	13.67	20.17	18.66
CaO	24.95	24.82	23.97	13.19	12.81
Na <sub>2</sub> O	0.21	0.25	0.52	0.16	0.48
K <sub>2</sub> O	<0.05	<0.05	<0.05	0.21	0.24
F	—	—	—	0.73	0.70
H <sub>2</sub> O**	—	—	—	1.78	1.79
O ≡ F	—	—	—	0.31	0.29
Sum	100.14	100.25	99.87	98.61	99.20
Si	1.983	1.972	1.929	7.792	7.374
Ti	—	—	—	—	0.009
<sup>14</sup> Al	0.017	0.028	0.071	0.208	0.626
<sup>16</sup> Al	—	0.005	0.037	0.151	0.093
Cr	—	0.006	—	—	0.015
V	0.029	0.039	0.083	0.047	0.362
Y	—	—	—	—	—
Fe <sup>3+</sup>	—	—	—	0.010	0.140
Fe <sup>2+</sup>	0.165	0.185	0.122	0.540	0.434
Mn	0.019	0.011	0.004	0.016	0.014
Mg	0.787	0.748	0.753	4.236	3.934
Ca	0.991	0.987	0.950	1.991	1.941
K	—	—	—	0.038	0.043
F	—	—	—	0.325	0.313
OH**	—	—	—	1.675	1.687

Note: Atom proportions based on 6 oxygens for pyroxenes and on 13 cations and 23 oxygens for actinolites.

\* Total Fe as FeO.

\*\* Calculated assuming stoichiometry.

### Other phases

Most other phases such as chlorite replacing clinopyroxene or muscovite contain only traces of V. Sphene is present and contains significant amounts of Al (Al<sub>2</sub>O<sub>3</sub> above 1 wt%) but only traces of rare-earth elements.

### GARNETS IN SKARNS DEVELOPED FROM THE V-BEARING METAPELITES

Skarn minerals have been modified by late stages of hydrothermal alteration, except garnets, which are always birefringent. In type 1 skarn (CAN58), all garnet crystals have a central colored zone identical to the central zone of the metapelite garnets described above. The V<sub>2</sub>O<sub>3</sub> content of the central zone (analysis 8, Table 2) ranges from 0.7 to 19.4 wt%, the lower V contents occurring at the outer rim of this central zone. A large overgrowth of grossular-rich almandine (7 mol%) andradite (10 mol%) garnet (V<sub>2</sub>O<sub>3</sub> < 0.35 wt%) may be interpreted as the result of skarn-stage development of garnet on a pre-existing goldmanite-bearing garnet that served as a nucleus (analysis 10, Table 2). In type 2 skarns (specimen CAN106), most garnets are comparatively homogeneous grossular with V contents in the range of 0.1 to 1.13 wt% V<sub>2</sub>O<sub>3</sub>. Strongly zoned garnets similar to those observed in type

1 skarns are rare, and their colored cores show a maximum of 5.6 wt%  $V_2O_3$ .

These two types of skarns could have originated from the transformation of the two types of metapelites previously described, exemplified by specimens CAN147 and CAN8, respectively.

Access to the host strata by external fluids occurred in two stages as shown by (1) development of the chemical fluctuations observed in the margins of the V-rich garnets and (2) development of large grossular overgrowths at the skarn stage. In the first stage, the fluid was a metamorphic fluid of local origin having little ability for chemical transport and a limited degree of disequilibrium with the host strata. The skarn fluid was of foreign (granitic?) origin, in strong disequilibrium with the host strata, and demonstrated a high efficiency for transporting elements. These differences would explain why the elements introduced in the first growth stage such as Y and Cr are elements showing high concentrations in V-rich black shales (Dabard and Paris, 1986).

### DISCUSSION

There is a considerable compositional similarity between the Coat-an-Noz series and other formations in which goldmanite and other V-bearing phases have been reported (Filippovskaya et al., 1972). In Australia (Morand, 1988), vanadian margarite, andalusite, and muscovite occur in very siliceous Ca-poor Ordovician black slates, which correspond to a more quartz-rich noncalcareous component also known to occur in euxinic series. Ba is high in these siliceous rocks (2000 to 6000 ppm), as it is in the one Ca-poor specimen analyzed for Ba in Coat-an-Noz (CAN58, Ba = 1491 ppm).

In both the Australian and the Brittany locality, the V-bearing silicates are found within the contact aureole of a granite. The presence of garnet appears to be controlled by the CaO content of the rock. The goldmanite content is directly controlled by the V/Al ratio in the bulk rock. In the case of the New South Wales rocks (Morand, 1984), the same V/Al ratio controls the V content of the silicates.

### ACKNOWLEDGMENTS

We thank Professor D. Velde (University P. and M. Curie, Paris) for improvements of the manuscript. We are also indebted to Dr. G.C. Parodi (Musée d'Histoire Naturelle, Paris) for determining the garnet cell dimensions; M. C. Forette and G. Frot (Paris School of Mines, Fontainebleau) for maintaining the electron microprobe and Nicole Vassard (University P. and M. Curie) for major- and trace-element analyses. Dr. V. J. Morand (James Cook University, Townsville, Australia) was kind enough to provide data on the chemical composition of the Australian V-bearing rocks. Journal reviews by Dr. Eric Essene (University of Michigan) and Dr. F. F. Foit, Jr. (Washington State University) are gratefully acknowledged.

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MANUSCRIPT RECEIVED AUGUST 3, 1988

MANUSCRIPT ACCEPTED FEBRUARY 27, 1989