

ARMENITE – THULITE – ALBITE VEINS AT RÉMIGNY, QUEBEC: THE SECOND OCCURRENCE OF ARMENITE

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ABSTRACT

At Rémigny, Quebec, fractured, prehnitized and epidotized dioritic rocks are veined and sequentially mineralized with albite, armenite, manganiferous zoisite (thulite) and piedmontite. This occurrence is today the only accessible locality of armenite. The mineral occurs as sheaf-like aggregates of centimetre-long colorless prismatic crystals with hexagonal morphology. The crystals commonly show sector twinning and patch-like microstructure consisting of fine lamellar and cloth-like twinning. Optical properties range from sharply uniaxial to strongly biaxial. Physical properties determined are: H 7–8, density $2.737(12) \text{ g/cm}^3$ (D_{calc} 2.741 g/cm^3), one good prismatic cleavage; strongly biaxial armenite: $2V_x$ $65^\circ (\pm 2^\circ)$, $2V_x$ (calc.) 57.8° , α 1.5505, β 1.5570, γ 1.5590 (± 0.0005); uniaxial armenite: ω 1.556, ϵ 1.550 (± 0.001). All diffraction maxima are compatible with space-group $P6cc$ or $P6/mcc$; cell edges were found to be: a $10.732(7)$, c $13.886(18) \text{ \AA}$. Microprobe and chemical analyses indicate that the structural formula has $T(1) = \text{Si}_9\text{Al}_3$ and $T(2) = \text{Al}_3$, whereas significant variations of interchannel and channel constituents (Na, K, Ba, Sr, Ca, H_2O , CO_2) occur on the B , C and possibly D sites; the average formula is $(\text{Ca}_{1.92}\text{Sr}_{0.07}\text{Na}_{0.03})(\text{Ba}_{0.89}\text{Na}_{0.10}\text{K}_{0.04})(\text{Al}_3.02)(\text{Al}_3\text{Si}_9\text{O}_{30}) \cdot 2[(\text{H}_2\text{O})_{0.91}(\text{CO}_2)_{0.04}]$. The study of hydrothermally-treated armenite suggests that the optical anomalies in the mineral reflect a “short-range-ordered” modulated structure. This microstructure would result from stress arising through ordering of interchannel and channel constituents and, possibly, loss of volatile components. Armenite and associated minerals were deposited from low-temperature ($< 300^\circ\text{C}$) solutions probably related to the surrounding granodiorite.

Keywords: armenite, thulite, manganiferous zoisite, piedmontite, albite, Rémigny, Québec.

SOMMAIRE

À Rémigny (Québec), une diorite, fracturée et altérée avec prehnite et minéraux du groupe de l'épidote, est recoupée de veinules contenant (par ordre paragénetique): albite, armenite, zoisite manganifère (thulite) et piedmontite. Cette minéralisation filonienne est aujourd'hui le seul gîte accessible d'arménite. Le minéral est incolore et se présente en esquilles de cristaux prismatiques à morphologie hexagonale, de dimensions centimétriques. Les cristaux montrent fréquemment un maillage en secteurs ainsi que des plages à fines lamelles maclées en tartan. Le minéral affiche une gamme de propriétés optiques allant de parfaitement uniaxe à fortement biaxe. Les propriétés physiques déterminées sont: dureté 7–8, densité $2.737(12)$

(D_{calc} 2.741), un bon clivage prismatique; pour l'arménite fortement biaxe: $2V_x$ $65^\circ (\pm 2^\circ)$, $2V_x$ (calc.) 57.8° ; α 1.5505, β 1.5570, γ 1.5590 (± 0.0005); pour l'arménite uniaxe: ω 1.556, ϵ 1.550 (± 0.001). Les raies de diffraction sont toutes compatibles avec les groupes spatiaux $P6/mcc$ et $P6cc$ et la maille déterminée a pour côtés a $10.732(7)$, c $13.886(18) \text{ \AA}$. Les résultats de l'analyse chimique et les travaux à la microsonde indiquent que le site $T(1)$ de la formule structurale contient Al_3Si_9 tandis que $T(2)$ est occupé par Al_3 , alors que les éléments situés dans les canaux et entre ceux-ci (Na, K, Ba, Sr, Ca, H_2O , CO_2) montrent des variations significatives entre les sites B , C , et peut-être D . La formule moyenne correspond à $(\text{Ca}_{1.92}\text{Sr}_{0.07}\text{Na}_{0.03})(\text{Ba}_{0.89}\text{Na}_{0.10}\text{K}_{0.04})(\text{Al}_3.02)(\text{Al}_3\text{Si}_9\text{O}_{30}) \cdot 2[(\text{H}_2\text{O})_{0.91}(\text{CO}_2)_{0.04}]$. Le comportement de l'arménite soumise à un traitement hydrothermal fait penser que les anomalies optiques reflètent un arrangement modulé d'unités ordonnées à courte distance. Cet arrangement résulterait de contraintes occasionnées par la mise en ordre des constituants logés dans les canaux et entre ceux-ci, ainsi que, peut-être, par la perte de composants volatils (H_2O , CO_2). L'arménite et ses minéraux associés ont été formés à basse température ($< 300^\circ\text{C}$) à partir de solutions probablement reliées à la granodiorite environnante.

Mots-clés: arménite, thulite, zoisite manganifère, albite, piedmontite, Rémigny, Québec.

INTRODUCTION

Armenite, a rare double-ring silicate of Al, Ca and Ba belonging to the milarite group, was first described by Neumann (1939, 1941) from a vein specimen collected at the Armen mine, a silver-bearing calcite vein-deposit near Kongsberg, Norway. The unique specimen had originally been collected by O.A. Corneliussen in 1877, labeled “Epidote?” and deposited in the collections at the University of Oslo. Until the present finding, the Armen occurrence, no longer accessible, has provided the only known specimen of the mineral. The Rémigny occurrence has yielded fine specimens of coarsely crystalline armenite in addition to spectacular pink zoisite (thulite).

THE RÉMIGNY OCCURRENCE

Rémigny, alongside Lac Rémigny, is located 75 km south of Rouyn-Noranda along routes 101 and 391, in northwestern Quebec (Fig. 1). This new mineral locality consists of a small, 20-m-long road-

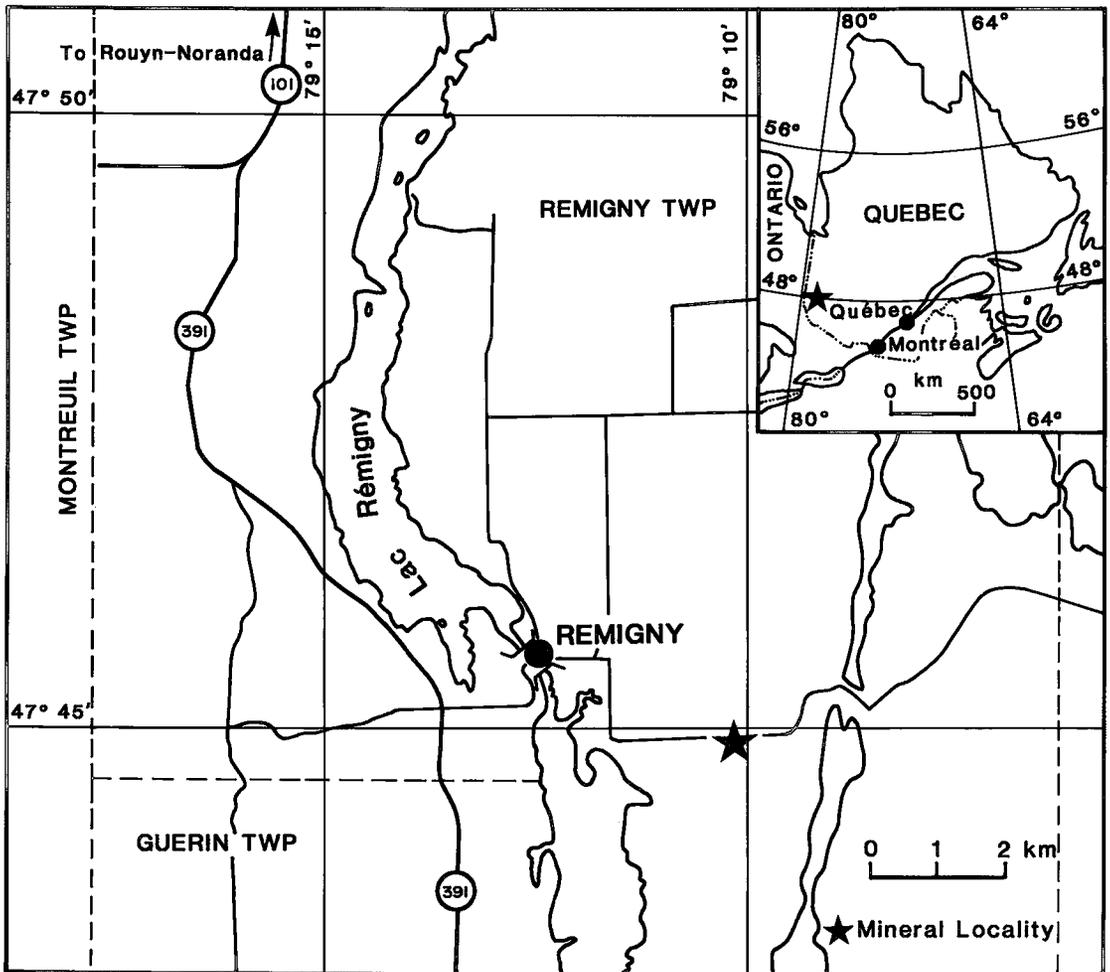


FIG. 1. Index map and location of the Rémigny armenite occurrence.

cut, located 3.9 km from the bridge at Rémigny, along a secondary gravel road that follows in part the boundary between Ranges III and IV of Rémigny Township (Fig. 1).

During mapping of granitoid intrusive bodies in the Pontiac Group, south of Rouyn-Noranda, Larouche (1976) observed, in the rocks exposed in a roadcut east of Rémigny, pink crystals that he tentatively identified as manganiferous tremolite. Subsequent mineral collecting and X-ray-diffraction work led to the identification of the mineral as manganiferous zoisite (thulite). Confirmation of armenite at this locality was made in February 1982 in a study of specimens containing pink zoisite (thulite) collected by two of us (P.T., G.V.) in 1976. A brief description of the mineralogy of this locality has been provided by Poirier (1982).

GEOLOGICAL SETTING

The larger part of Rémigny and adjacent townships is underlain by Archean granitoid batholiths emplaced into the metasedimentary rocks of the Pontiac Group. Chagnon (1968) described the geology of this general area, whereas Larouche (1979) studied the geochemistry and emplacement of the granitoid rocks exposed in a 45-km-long north-south section, extending from Cloutier in the north to Guérin in the south. Larouche (1979) recognized two igneous complexes within the batholith: the older Lac-Frechette complex and the younger Lac-Rémigny complex. The Lac-Frechette complex is centred around the lake of the same name, close to the community of Cloutier, 20 km north of Rémigny. It is made up of quartz-poor alkalic rocks that range prin-

cipally from monzonite to quartz monzonite, but also include small amounts of hornblendite, hornblende pyroxenite, mafic alkali syenite (lusitanite) and quartz diorite. The much larger Lac-Rémigny complex is made up of more siliceous rocks that range from quartz monzodiorite to granodiorite. Pegmatites are common in the area and appear exclusively related to the Lac-Rémigny complex (Larouche 1979). Geochemically, the rocks of the Lac-Frechette complex have higher $\text{Na}_2\text{O} + \text{K}_2\text{O}$ and Sr contents than the rocks at Lac Rémigny. Of particular interest is sample L-206-9 (Larouche 1979, p. 161), a lusitanite from the Lac-Frechette complex containing 1.34% Ba.

LOCAL GEOLOGY

The immediate area surrounding the armenite occurrence offers only limited exposures. The mineral locality lies near the top of a small ridge across the gravel road that leads to the eastern part of the area (Fig. 1). Blasting has created a small 20-m-long rock ledge on the south side of the road, exposing a medium-grained greyish white to greyish pink rock of granitoid aspect. The rock is fractured and locally brecciated; pink minerals (thulite and minor piedmontite) distributed in veins and patches are conspicuous in the rock ledge and in the rock fragments nearby. Locally, lilac to mauve alteration related to "wilsonite", a manganiferous variety of sericite, forms diffuse bands in the rocks. Microscopically, the rock is strongly altered to a mixture of prehnite, epidote, clinozoisite and sericite. Relict plagioclase is present in some specimens, whereas quartz is absent in all samples studied. Locally, the brecciated host-rock contains decimetre-size fragments of white porcelaneous material that consists almost entirely of prehnite. Petrographic examination and chemical analyses (Table 1) indicate that the original rock was plagioclase-rich and corresponds chemically to a feldspathic diorite.

Large outcrops of granodiorite of the Lac-Rémigny complex occur 70 m south of the roadcut exposure. The rock is massive, fresh-looking and contains conspicuous quartz; it is locally veined by small pegmatite and aplite dykes and occasional stringers of quartz. Contrary to the rocks exposed in the roadcut, the granodiorite does not show signs of Mn-metasomatism. From limited field-data, we conclude that the altered dioritic rocks exposed in the roadcut are inclusions within the Lac-Rémigny

granodiorite. Their lack of quartz and high Sr content (Table 1) suggest that they may be related to the earlier alkalic rocks of the Lac-Frechette complex.

MINERALOGY

The altered diorite host-rock is cut by a series of small veins that vary in width from less than 1 mm to 1.5 cm and are irregular in trend, width and attitude. Locally the veins interconnect, giving rise to brecciated host-rock cemented by vein material. Principal minerals identified in the veins are albite, thulite, armenite and piedmontite, whereas small amounts of natrolite, kaolinite, calcite, quartz and hematite are less common. Albite, the most common mineral, imparts a milky white color to the veins. Thulite is second in abundance and is conspicuous owing to the aggregates of pink-colored crystals. Armenite is less abundant and forms colorless to white sheafs of long prismatic crystals. Although some exceptions have been noted, armenite and thulite tend to occur in separate veins. Rare quartz veinlets and stringers also cut the altered dioritic host-rock.

The study is based on the examination of approximately 20 samples originally collected in 1976 and a suite of armenite samples obtained from an additional sampling done in May 1982.

Albite

Albite occurs in all the veins and was the first mineral deposited. Two generations of albite may be recognized. Early albite deposited against the altered host-rock forms large euhedral and subhedral crystals reaching 1 cm in length. Under the microscope, the crystals are normally twinned, homogeneous and typically clouded by alteration, presumed to be kaolinite. The moderate alteration accounts for the milky white appearance of the albite in hand specimens. The second generation of albite, subordinate to the first, was introduced after the kaolinitization of the first albite. The second albite is clear and vitreous and forms euhedral crystals that vary from 0.3 to 2 mm in length. Locally, clear second-generation albite forms epitactic growths onto first-generation albite (Fig. 2a). Commonly, crystals of the second-generation albite show one or more thin peripheral zones of minute inclusions, suggesting growth from solutions (Fig. 2b). The euhedral tendency of albite and of the succeeding minerals in the paragenetic sequence and the lack of fracturing in the crystals suggest that the fractures remained open throughout the depositional sequence.

Microprobe analyses of several albite crystals of both generations, including peripheral growth-zones and epitactic growths, indicate that the mineral is virtually free of Ca and K. The numerous X-ray spectra recorded with the microprobe EDS system failed

TABLE 1. CHEMICAL COMPOSITION OF HOST-ROCK TO ARMENITE

SiO_2 wt. %	53.58	Na_2O	6.51	LOI (950°C)	2.32
Al_2O_3	25.12	TiO_2	0.45	Total	100.07
MgO	0.84	Fe_2O_3	0.87	MnO	120 (ppm)
CaO	9.21	P_2O_5	0.25	Sr	3330 (ppm)
K_2O	0.84	S	0.08	Ba	477 (ppm)

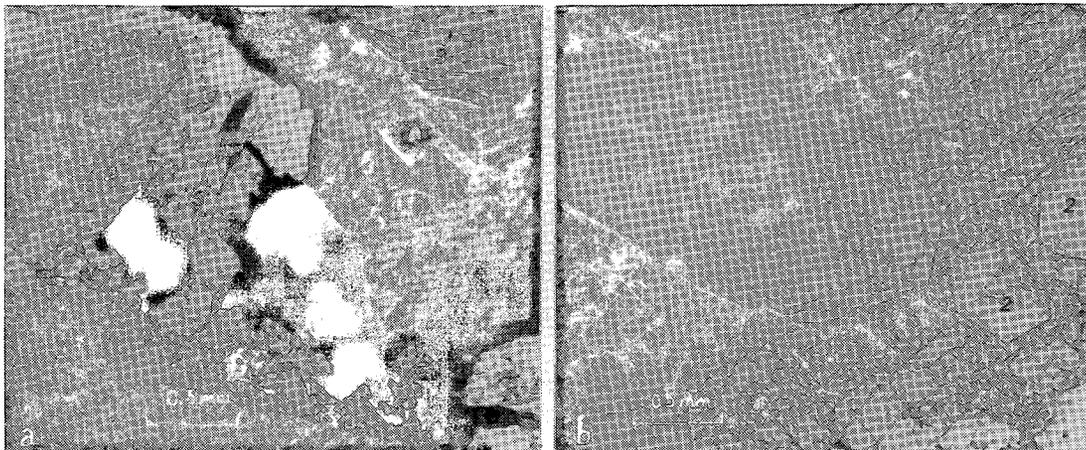


FIG. 2. a) Kaolinitized albite of first generation (1) overgrown by clear albite of second generation (2), and adjoining thulite (3), crossed polars. b) Euhedral albite of second generation, zoned with inclusions (2) and enclosed by thulite (3), crossed polars.

to detect these two elements; their individual concentrations are estimated to be less than 0.15%.

Armenite

Armenite-bearing veins appear fairly commonly at Rémigny; the mineral was observed in four narrow veins in the small rocky ledge as well as in blocks derived from it. Most of the samples studied indicate that the armenite was deposited after the second generation of albite; only one sample contains indications that small amounts of armenite may have

been introduced after kaolinitization of the first albite but before the second albite.

Milarite-group minerals, including species such as osumilite and armenite, show hexagonal morphology and crystallize in space-group $P6/mcc$ (Černý *et al.* 1980, Bakakin *et al.* 1975, Forbes *et al.* 1972). In addition, they commonly show, to varying degrees, anomalous biaxiality, a range of indices of refraction, and complex twinning. In milarite, these anomalies are believed to be related to compositional sector-zoning, particularly with respect to H_2O content (Černý *et al.* 1980).

The Rémigny armenite is similar to the original armenite described by Neumann (1941); the mineral shows hexagonal morphology, exhibits complex twinning and is distinctly biaxial. In addition, microscopic examination of crushed biaxial crystals for oil-immersion work consistently reveals minute fragments or domains (less than 0.05 mm in diameter) of uniaxial character. Some fragments show weak biaxial behavior, suggesting a range of anomalous optical properties. The original specimens discovered at Rémigny consist largely of biaxial armenite, and only one specimen shows small amounts of uniaxial armenite replacing kaolinitized albite of the first generation. Additional material collected shows a range of optical behavior from uniaxial (-) to strongly biaxial (-), with all possible intermediate values. The physical and chemical data presented hereafter aim to characterize the Rémigny armenite.

Physical properties

Typical crystals measure 1 mm by 2.5 cm, although rare crystals exceeding 5 cm in length have been observed (Fig. 3). Physical properties are: hard-

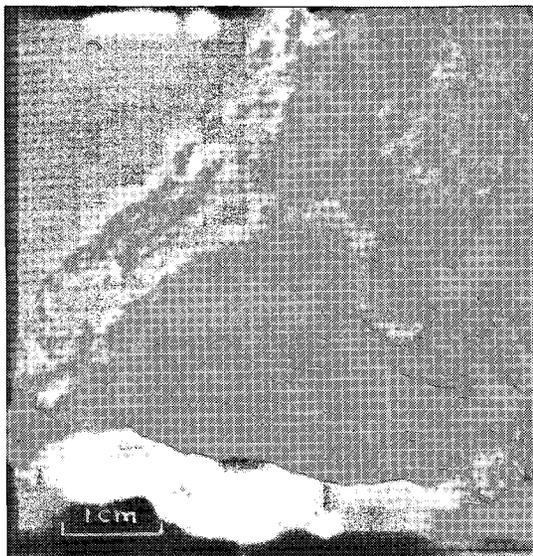


FIG. 3. Armenite crystals from Rémigny.

ness 7–8; density, determined on 26 fragments weighing from 30 to 75 mg using a Berman balance and toluene as medium, is $2.737(12) \text{ g/cm}^3$ ($D_{\text{calc}} 2.741 \text{ g/cm}^3$); one good prismatic cleavage verified by universal-stage work, and probable partings related to the composition planes of the sector twinning. Dehydrated armenite obtained from heating experiments (950°C for 48–96 hrs) is splintery textured and milky white and has a density of $2.68(1) \text{ g/cm}^3$.

Optical properties

Optic axial angles and indicatrix orientation of biaxial armenite were determined on polished thin sections by universal-stage conoscopy. Indices of refraction were measured on crushed material using white light and temperature-controlled immersion oils spaced at 0.002 intervals. All determinations were verified with a refractometer.

Optical properties of distinctly biaxial armenite found in the Rémigny discovery specimens are as follows: $2V_x 65^\circ (\pm 2^\circ)$ [$2V_x$ (calc) 57.8°], $\alpha 1.5505$, $\beta 1.5570$, $\gamma 1.5590 (\pm 0.0005)$. The crystals commonly show sector-penetration twins forming triplets arranged at 120° (Fig. 4a). Other anomalies typically observed are patches or domains showing fine lamellar twinning, as well as fine cross-hatched and cloth-like or tartan patterns with wavy extinction, reminiscent of twin-related domains in microcline (Fig. 4b). This microstructure is characteristic of biaxial armenite and is pervasively developed in most of the material studied. Compositional zoning of the crystals, if present, is not apparent in ordinary megascopic and microscopic examinations. Universal-stage measurements on sector twins confirm the original

description given by Neumann (1941). The composition planes lie at 120° to one another and are tautozonal, the zone axis being the c axis of the hexagonal crystal. The X optical direction, also $B_x\alpha$, coincides with the zone axis, and the YZ plane lies parallel to the observed cleavage.

Uniaxial armenite has a slightly undulose or diffuse mosaic extinction. It occurs as individual crystals, as a euhedral core within larger twinned crystals (Fig. 4a) and also as small domains or fragments amongst the crushed product of distinctly biaxial armenite. Crystals are uniaxial (–) with $\omega 1.556 \pm 0.001$, close to β index of the biaxial form; ϵ is probably close or equal to 1.550. Its value could not be determined with certainty owing to the difficulty in distinguishing ϵ of the uniaxial phase from α of the biaxial phase in a mixture of the two phases.

Thermal treatments of millimetre-size fragments were carried out to investigate possible changes in optical and structural properties of the mineral. Dry heating at 250°C for 96 hours did not affect the optical properties nor induce measurable weight-loss. Likewise, hydrothermal treatment at 300°C and 0.7 kbar $\text{P}(\text{H}_2\text{O})$ for 235 hours left the material unchanged; fine lamellar and cloth-like patterns as well as biaxial optics were still present. Hydrothermal treatment for a period of 30 days at 475° and 1 kbar $\text{P}(\text{H}_2\text{O})$ produced a mixture of clear unaltered fragments and white, saccharoidal, altered armenite. X-ray-diffraction examination of the altered fragments revealed a mixture of celsian and armenite. Petrographic examination of the unaltered armenite from this experiment showed that all crystals decreased in index of refraction to less than 1.557 and, although some crystals retained slightly biaxial optics, most

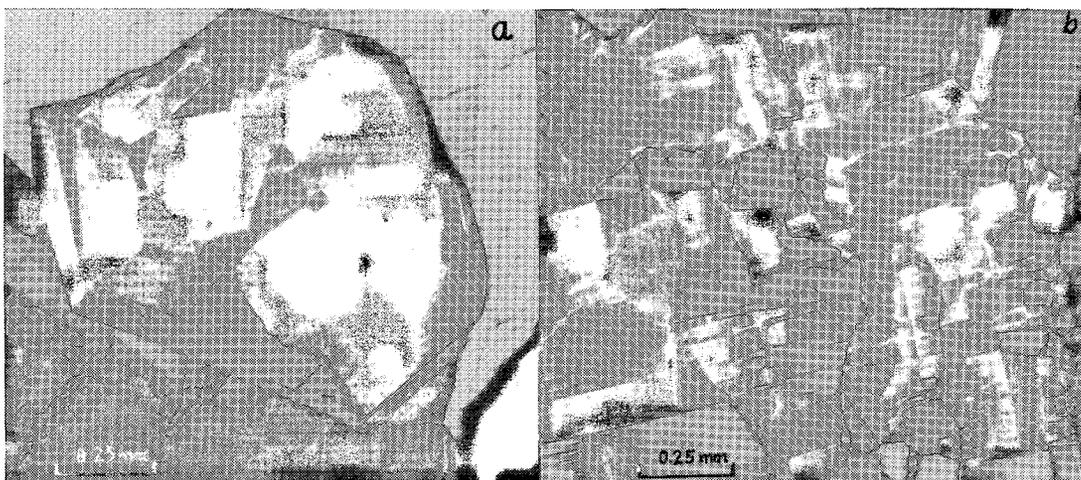


FIG. 4. a) Euhedral uniaxial armenite crystal (at extinction) overgrown by complexly twinned biaxial armenite, crossed polars. b) Details of cloth-like and cross-hatched patterns in twinned armenite, crossed polars.

crystals are uniaxial (-) with ϵ 1.550 and ω 1.555 (± 0.001). Most hydrothermally treated fragments appear optically homogeneous, and only rare grains show distinct twin-lamellae; cross-hatched and tartan patterns were not observed. Subsequent X-ray-diffraction and infrared absorption work (see next section) failed to document significant structural differences between hydrothermally treated armenite and its natural counterpart.

Dehydrated armenite obtained by dry heating at 950°C for 96 hours is uniaxial (-), with ω 1.552 and ϵ 1.550 (± 0.001), emphasizing the marked influence of the volatile components (H₂O and CO₂) on the indices of refraction of the mineral. Under the microscope, dehydrated armenite shows no evidence of fusion, and fragments have a fibrous texture due to subparallel flame-like fractures. Cross-hatched and tartan patterns of twinning are not visible in the dehydrated material.

Chemistry

Chemical data obtained by various methods on specimens of Rémigny armenite are given in Table 2. These, in general, agree well with the chemical composition determined on the original material by Neumann (1941). X-ray-fluorescence analysis of pressed armenite powders indicates that Fe, Ti, Mg and Mn are absent, whereas neutron-activation analysis shows that the mineral is free of rare-earth elements.

The armenite structure (Bakakin *et al.* 1975), like that of milarite (Černý *et al.* 1980), consists of hexagonal doubled tetrahedral $T(1)_{12}O_{30}$ rings stacked along the *c* axis. The $T(1)_{12}O_{30}$ units are linked at

their base to the top of the underlying ring-unit by tetrahedrally co-ordinated $T(2)$ cations and joined laterally by octahedrally co-ordinated *A* cations. The *B* sites are located between neighboring *A* octahedra, whereas the *C* and *D* sites alternate along the tunnels, the *C* sites lying between stacked $T(1)_{12}O_{30}$ units and the *D* sites occupying the centre of the ring units. The resulting structural formula is ${}^{\nu}A_2 {}^{\text{ix}}B_2 {}^{\text{xii}}C {}^{\text{xviii}}D {}^{\text{iv}}T(2)_3 {}^{\text{iv}}T(1)_{12}O_{30}$ (Forbes *et al.* 1972). The data from Table 2 indicate that for the Rémigny armenite, the twelve $T(1)$ sites are populated by 3Al + 9Si, and the $T(2)$ sites are occupied by 3Al. Slight excesses or deficiencies in SiO₂ and Al₂O₃ shown in the analytical data (Table 2) are believed to result principally from inaccuracies in the microprobe results. The analyses obtained by an energy-dispersion system (EDS) tend to yield slightly high SiO₂ and Al₂O₃ contents because of an interference of the Sr spectrum with the Si peak. The coefficients of variation (C.V.) for Al₂O₃ and SiO₂ of the numerous analyses by EDS methods are small (C.V. SiO₂ 0.88%; C.V. Al₂O₃ 0.67%), suggesting that Al and Si are present in the correct proportions required by the structural formula. Larger variations are encountered for the interchannel and channel constituents, namely Ca (C.V. 5.5%), Ba (C.V. 2.5%) and water (C.V. 8.9%) and, to some extent, for the minor constituents Sr, Na and K. The Ba content is consistently too low to occupy the *B* sites completely, whereas the Ca content may show slight deficiencies or excesses relative to the *A* sites. The lack of obvious correlation between excess Ca and Ba content indicates that the minor constituents Sr, K, Na, H₂O and excess calcium, if required, interact to complete the occupancy of the *A*, *B* and *C* sites. Based on the structural data of Bakakin *et al.* (1975) and Černý *et al.* (1980), the site occupancy in armenite may be as follows: $T(1)$ Si₉Al₃; $T(2)$ Al₃; *A* Ca (Sr); *B* Ba, Na, K, H₂O, (Ca?); *C* K, Na, Ba; *D* H₂O(?), CO₂(?). Normalized to an anhydrous basis of 30 oxygen atoms, the average armenite (Table 2, no. 6) yields the following tentative formula: $(Ca_{1.92}Sr_{0.07}Na_{0.03})_{\Sigma 2.02}(Ba_{0.89}Na_{0.10}K_{0.04})_{\Sigma 1.03}(Al_{3.02}(Al_3Si_9O_{30})_2 \cdot 2[(H_2O)_{0.91}(CO_2)_{0.04}]$. Although the *A* and *B* sites are assumed to be filled with minor amounts of Sr, Na and K, it is uncertain whether this distribution is correct; these minor constituents may be lodged in the unoccupied *C* site and water may be partitioned between the *B* and *D* sites.

TABLE 2. CHEMICAL DATA ON REMIGNY ARMENITE

	1	2	3	4	5	6
SiO ₂ wt. %	47.02	47.96	47.62	48.01(.42)	na	47.6(18.04)
Al ₂ O ₃	25.78	24.66	26.90	28.04(.19)	na	27.0(6.05)
CaO	9.51	9.71	9.53	9.40(.52)	8.90-10.15	9.50(3.86)
Na ₂ O	na	na	na	0.27(.09)	0.16- 0.46	0.36(0.13)
K ₂ O	na	na	na	0.20(.08)	0.10- 0.16	0.15(0.04)
BaO	11.90	12.41	11.68	10.96(.28)	11.80-12.92	12.05(1.79)
SrO	0.32	0.32	0.65	na	0.55- 0.74	0.62(0.14)
H ₂ O	-	-	-	-	2.6 - 3.28	2.90(3.66)
CO ₂	-	-	-	-	0.08- 0.96	0.31(0.16)
LOI(950°C)	-	-	-	3.20	-	-
TOTAL	94.53	95.06	96.38	100.08		100.49

1,2. Microprobe analyses by wavelength-dispersive methods. Analyst: D.C. Harris, Geological Survey of Canada. Operating conditions: 20 KV, 0.02µA; standards: barite, gehlenite, kaersutite, synthetic strontianite plagioclase. 3. Average of two analyses by microprobe wavelength-dispersive methods. Analyst: P. Samson. Operating conditions: 15KV, .02µA; standards: albite, sanidine, diopside, anorthite glass, barian glass. 4. Average of 38 analyses by microprobe energy-dispersive methods on six samples. Standard deviations are given in parenthesis. Loss on ignition is the average value determined for four of the six samples; analyst: P. Samson. 5. Range of values determined on six samples. H₂O and CO₂ by chromatography; alkalis and alkali earths by atomic absorption. Analysts: C. Dallaire and J.L. Bastien, Ecole Polytechnique. 6. Estimated average composition of Rémigny armenite. Unit-cell content based on cell edges determined is given in parenthesis.

Crystallography

Armenite yields good X-ray-diffractometer patterns (Table 3, Fig. 5a), and all diffraction maxima may be indexed in space group $P6/mcc$. They are also consistent with space group $P6cc$. Cell edges of the Rémigny armenite [a 10.732(7), c 13.886(18) Å] are only very slightly different from those of the Nor-

TABLE 3. X-RAY POWDER-DIFFRACTION DATA ON ARMENITE

$d_{\text{meas.}}^1$	I	hkl	$d_{\text{calc.}}$	d^2	I
9.29 ⁹	35	100	9.294	9.31	55
6.94 ⁸	47	002	6.943	6.94	80
5.56 ³	6	102	5.562	5.56	6
5.37 ³	8	110	5.366	5.36	6
-	-	-	-	4.92	2
-	-	-	-	4.66	2
4.24 ⁸	73	112	4.246	4.25	65
3.86 ⁰	98	202	3.862	3.86	100
3.50 ⁹	5	210	3.513	3.50	6
3.40 ⁴	100	211	3.406	3.41	90
3.24 ⁸	3	104	3.252	3.25	4
3.09 ⁶	48	300	3.098	3.10	40
2.91 ³	74	114	2.915	2.91	90
2.78 ⁰	71	204	2.781	2.78	80
2.68 ⁴	41	220	2.683	2.68	40
2.57 ⁷	24	310	2.575	2.58	20
-	-	303	2.578	-	-
2.53 ³	21	311	2.534	2.53	12
2.50 ¹	27	222	2.503	2.50	12
2.468	12	214	2.469	2.47	10
2.415	6	312	2.417	2.42	4
2.311	8	006	2.314	2.31	8
-	-	304	2.311	-	-
2.249	12	313	2.252	2.25	8
-	-	106	2.246	-	-
2.202	14	402	2.203	2.20	10
2.122	28	224	2.123	2.12	25
-	-	116	2.125	-	-
2.068	9	206	2.072	2.07	10
-	-	314	2.070	-	-
-	-	305	2.068	-	-
2.029	37	410	2.028	2.03	35
1.946	34	107	1.940	1.944	24
1.888	18	315	1.889	1.887	18
1.854	16	306	1.854	1.853	14
1.751	45	226	1.752	1.757	45
-	-	414	1.751	-	-
1.734	8	008	1.736	1.733	16
-	-	332	1.732	-	-
1.704	6	-	-	1.703	6
1.640	13	-	-	1.637	12
1.590	7	-	-	1.588	10
1.586	6	-	-	-	-
1.567	9	-	-	1.567	6
1.512	12	-	-	1.510	16

1. Armenite from Rémigny. Data from internal-standard-controlled (Silicon, NBS no. 640) diffractometer measurements using monochromatized $\text{Cu}\alpha$ radiation. Intensity given is from peak area on diffractograms. Preferential orientation was eliminated by using a rotating specimen-holder and mounting the powder as described by Foscal-Mella (1976). Indexing was carried out using a large-size Bunn chart for hexagonal crystals; cell edges were calculated using a computer program written by one of us (G.P.). Calculated parameters are: a 10.732(7), c 13.886(18) Å. 2. Armenite from Armen, Norway (PDF 20112, British Museum (Natural History), No. BM 1947, 290).

wegian armenite (a 10.690, c 13.898 Å: PDF 20-112). Tennyson (1960) also determined cell edges for the Norwegian mineral (a 10.69, c 13.90 Å). Intensities given in Table 3 are average intensities from three specimens and have a relative accuracy of approximately $\pm 10\%$. Differences in intensities of some reflections between the Armen and the Rémigny samples are probably not significant and may result from the different method used (microdensitometer) for measuring the Armen mineral (*cf.* PDF 20-112) The cell content of the average Rémigny armenite, based on the cell edges and density determined, is given in Table 2.

Dehydration of armenite, as with milarite (Černý *et al.* 1980), alters significantly the cell parameters

and the intensity of some reflections, particularly (112) and (202) (Fig. 5c). Dehydrated armenite, after dry heating at 950°C for 96 hours, is hexagonal and has a 10.607 (6) and c 14.020 (15) Å. The decreased in a and increase in c upon dehydration parallels the behavior of milarite and underlines the role of H_2O in preventing the collapse of the framework structures into the (001) plane (Černý *et al.* 1980).

Prolonged hydrothermal treatment of armenite (475°C, 1 kbar $\text{P}(\text{H}_2\text{O})$, 30 days) was carried out in an attempt to induce possible Si-Al disorder between $T(1)$ and $T(2)$ tetrahedra. Except for a very slight, possibly insignificant change in cell dimensions [a 10.704(10), c 13.900(16) Å], armenite thus treated yielded X-ray-diffraction patterns and infrared-absorption spectra virtually identical to those of natural armenite (Figs. 5a, b; 6a, b). The identity of the two absorption spectra in the $T(1)$ -O and $T(2)$ -O band regions (1200 - 300 cm^{-1} ; Povarennykh 1978) is taken as evidence that no Si-Al interchange between $T(1)$ and $T(2)$ sites occurred as a result of the hydrothermal treatment. Also, the close similarity in cell dimensions between natural and hydrothermally treated armenite indicates that the H_2O content of the mineral has not been significantly modified during hydrothermal treatment.

Anomalous biaxiality and microstructures found in armenite are an exact replica of those described for milarite by Černý *et al.* (1980). These investigators attributed the cause of these anomalies in milarite to stresses arising through compositional sector-zoning, mainly related to interchannel B -site occupancy and involving H_2O in particular. Though the chemical data for armenite presented in this work do outline distinct compositional variations, no obvious correlation between optic axial angles and composition could be found. Similar cases of anomalous biaxiality and microstructures have been documented by Foord & Cunningham (1978) and, in most cases, have been attributed to stresses resulting from compositional zoning. In some instances, uniaxiality may be restored by heat treatment or cooling (Foord & Mills 1978). Uniaxial-biaxial properties in other ring-structured silicates such as osumilite and cordierite-indialite minerals have been tentatively correlated with channel constituents, particularly Na, H_2O , CO_2 and Fe (Goldman *et al.* 1977, Goldman & Rossman 1978, Selkregg & Bloss 1981, Armbruster & Bloss 1981). More recently, the transition of hexagonal indialite to orthorhombic cordierite has been identified as a first-order reaction involving Si-Al ordering (Putnis & Bish 1983). Under nonequilibrium conditions, below 1450°C, the transformation takes place *via* a continuous sequence of metastable "short-range-ordered" modulated structures (Putnis 1980a, b); with annealing, the modulated structure coarsens to form domains that meet at twin boundaries.

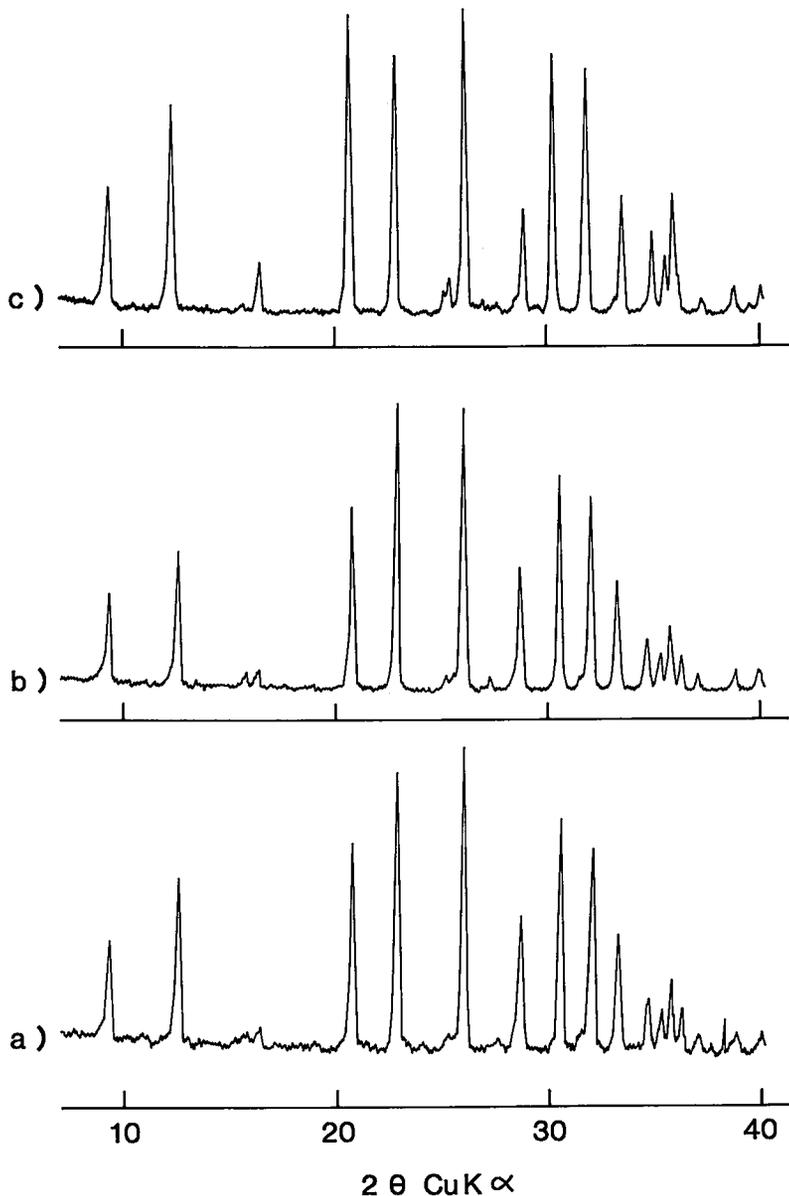


FIG. 5. Diffractograms of natural armenite (a), hydrothermally treated armenite (b) and dehydrated armenite (c).

The microstructures found in armenite are strongly suggestive of a stress-induced modulated structure similar to that described in transformed cordierite by Putnis (1980a, b). The microstructured armenite may well be orthorhombic or of lesser symmetry on a short-range-order basis (biaxial optics) and yet be hexagonal on a long-range or average basis (X-ray-diffraction pattern). The Rémigny armenite crystal-

lized from relatively low-temperature solutions (< 300°C). The high activation-energy associated with Si-Al ordering precludes consideration of a low-temperature Si-Al ordering scheme of an initially Si-Al disordered armenite. The results of infrared-absorption spectroscopy and the behavior of armenite under prolonged hydrothermal treatment also militate against Si-Al ordering as a cause for the op-

tical anomalies in the mineral. The fact that hydrothermal treatment was effective in restoring uniaxial optics and removing the microstructure in the majority of the crystals, while not significantly affecting the H₂O content, strongly suggests that the anomalies in armenite are related to the distribution of interchannel and possible channel constituents. We suggest that during crystallization, positional disorder of Ba, Sr, K, Na, H₂O and CO₂ amongst interchannel *B* sites and, possibly, channel *C* and *D* sites, favors the development of hexagonal symmetry; ordering of these constituents, coupled or not with loss of volatile components (H₂O, CO₂), induces stresses from which a modulated structure develops.

The suggestion that a modulated structure may occur at low temperatures in armenite offers an interesting perspective in the study of the structural evolution of milarite-group minerals. Kinetic studies combining TEM, optical and X-ray methods are needed in order to clarify the mechanism that results in a continuous variation of optical properties of armenite from sharply uniaxial to strongly biaxial.

EPIDOTE MINERALS

The principal epidote mineral in the vein mineralization at Rémigny is manganese zoisite or thulite. Locally and rarely, thulite contains a small core or inclusions of iron-rich zoisite. Also locally, small quantities of piemontite replace the thulite. Like armenite, the thulite was deposited after the second generation of albite. The thulite–armenite relationship is difficult to assess with certainty, for the two minerals seldom occur in the same specimen. Two observations of thulite and armenite in contact with each other suggest that thulite is interstitial to armenite and therefore paragenetically later than armenite.

Thulite

Thulite-bearing veins and patches are widespread in the rocks exposed along the ledge and in blocks derived from it. The conspicuous pink mineral in these rocks originally attracted our interest in the locality. Thulite generally occurs as radial and sheaf-like aggregates of pale to medium pink prismatic crystals measuring 1 to 8 mm in length. Rare samples may contain thulite crystals reaching up to 3 cm in length (Fig. 7a). X-ray diffractograms of eight samples selected at random, using the method of Seki (1959) for distinguishing orthorhombic and monoclinic zoisite, indicate that the mineral is orthorhombic. Petrographic examination shows it to be β -zoisite (Deer *et al.* 1962). The following optical properties were observed: $2V_z$ 60–70°; optic axial plane normal to the {100} cleavage; pleochroism and dispersion are not noticeable.

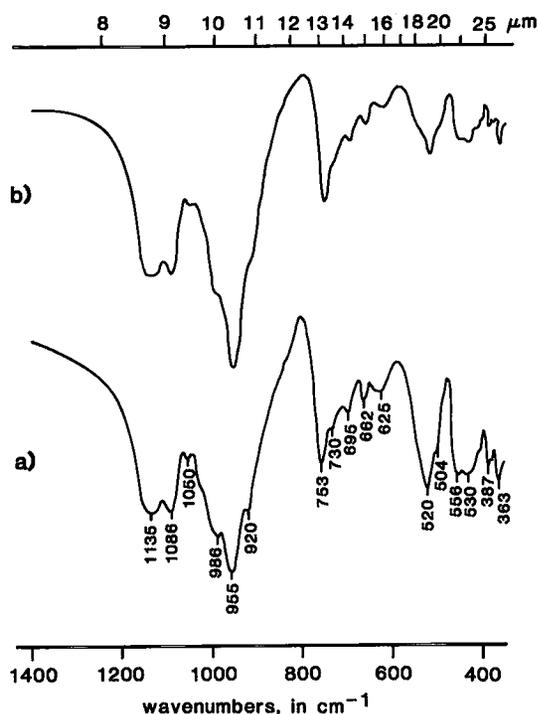


FIG. 6. Infrared absorption spectra of armenite: a) armenite (0.8% in KBr), b) hydrothermally treated armenite (0.5% in KBr).

The name *thulite* has been used for Mn-bearing varieties of zoisite (Deer *et al.* 1962). However, Mn-bearing monoclinic zoisite appears more frequently than suspected, and Abrecht (1981) has suggested a distinction be made between Mn-bearing orthorhombic and monoclinic zoisite. The Rémigny thulite may accordingly be referred to as orthorhombic thulite. Chemical data on thulite obtained by microprobe EDS methods are given in Table 4. Most crystals generally have a low content of Mn (in the range 0.05 – 0.20%); the iron content is also quite low, generally less or barely above the detection limit of the EDS system (approximately 0.05%). The highest Mn content determined, 0.74%, was recorded from crystals with the darker shades of pink.

Iron-rich zoisite

A few samples of thulite-rich material contain sparse euhedral crystals of distinctly more birefringent, iron-rich, probably monoclinic zoisite (hence, clinozoisite) (Fig. 7b). The crystals range in size from 0.05 to 0.5 mm and may occur as a core or inclusions with the thulite, or as individual prisms within sheaf-like aggregates of thulite crystals. Their high content of iron (Table 4, no. 2) is accompanied

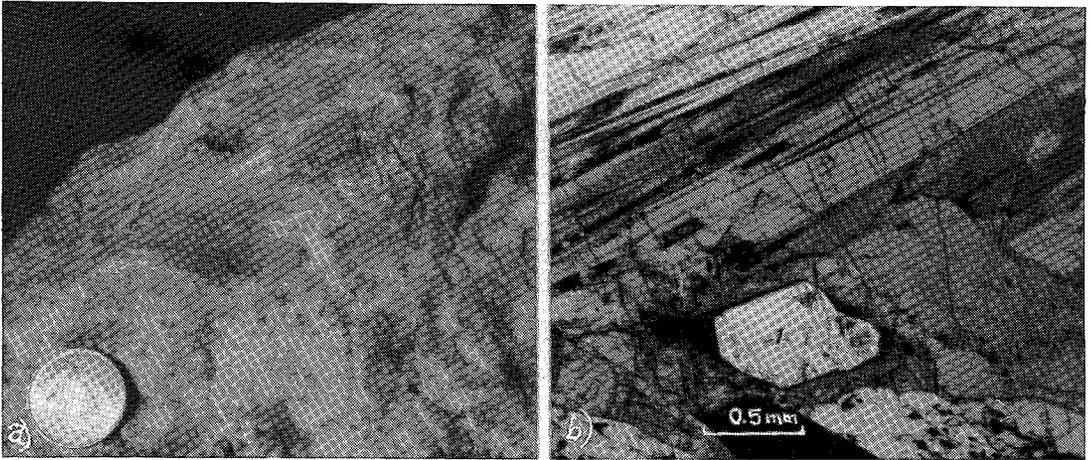


FIG. 7. a) Thulite crystals on altered host rock. b) Euhedral core of iron-rich zoisite (1) within thulite, crossed polars.

TABLE 4. MICROPROBE DATA ON EPIDOTE MINERALS

		1	2	3
SiO ₂	wt. %	39.45	38.48	40.69
Al ₂ O ₃		33.15	26.69 _b	30.97
Fe ₂ O ₃		.05	9.66 _b	0.49
Cr ₂ O ₃		-	.05	-
Mn ₂ O ₃		-	-	3.38 ^c
CaO		23.88	23.79	24.71
MnO		0.41 ^a	0.10	-
TOTAL		96.94	98.77	100.24

Ⓢ

a Range of MnO concentrations in thulite is between 0.05% and 0.74%.

b Range of Fe₂O₃ observed is 4.40% to 11.6%.

c Range of Mn₂O₃ observed is 3.1% to 10.1%.

1. Thulite, average of 21 analyses by microprobe energy-dispersive methods. P. Samson analyst.

2. Iron-rich zoisite as a core or inclusions within thulite.

3. Piedmontite overgrowths on thulite.

by a decrease in Al compared to iron-free zoisite, suggesting that most of the iron is present in the ferric state. The iron-rich zoisite has no noticeable pleochroism and may show outer zones with anomalous blue interference colors terminating sharply against thulite. The mineral is thought to have formed locally, in the early stage of the zoisite mineralization, from small amounts of iron present in the mineralizing solutions. Their crystallization rapidly depleted the solutions in iron, leading to the deposition of nearly iron-free manganeseiferous zoisite.

Piedmontite

Small amounts of piedmontite are present in some thulite specimens as small, deep red to purplish specks and anhedral grains. The mineral is easily identified in thin section by its characteristic yellow

to deep red pleochroism. Piedmontite formed last in the sequence of epidote minerals; it typically replaces thulite in irregular patches and along grain boundaries. The mineral has variable contents of Mn (Table 4, no. 3). Calculations indicate that most of the Mn is present in the trivalent state. In contrast with most occurrences of piedmontite (Deer *et al.* 1962), the Rémigny mineral has a surprisingly low iron content (Fe₂O₃ in the range of 0.20 – 0.50%). Abrecht (1981) has shown that divalent Mn replaces Ca in thulite, and is responsible for the pink color of the mineral. This would indicate that Mn behaves as a divalent cation during most of the deposition of the epidote minerals at Rémigny; the appearance of piedmontite at the end of the sequence probably reflects a change in the oxidation state of the system rather than a change in the elemental composition of the solutions.

ACCESSORY MINERALS

Small or trace quantities of natrolite, kaolinite, calcite, quartz and specular hematite have been identified in the specimens studied. These are present only locally, and no attempt is made here to give detailed descriptions; their positions within the paragenetic sequence are imperfectly known.

Natrolite forms delicate milky white rosettes in vugs and amongst thulite-piedmontite aggregates, suggesting that it is late in the paragenetic sequence. Likewise, powdery, cream to beige kaolinite locally covers armenite and thulite, suggesting that it also is a late mineral. Small crystals of clear calcite were observed in two samples; the position of calcite in the paragenetic sequence is unknown. Small crystals of quartz and specks of specular hematite were observed in one and two specimens, respectively; their

position in the mineral sequence is also undetermined.

CONCLUSIONS

The armenite-thulite-albite mineralization at Rémigny occurs as veins within fractured, prehnitized and epidotized dioritic rocks. The mineralized host-rock has limited extent and probably represents an inclusion of a former feldspathic diorite within the younger Lac-Rémigny granodiorite. The abundance of prehnite in the host rock and the general mineralogy of the vein material, dominated by pure albite and iron-poor manganiferous zoisite, are indicative of a low temperature of formation compatible with low-temperature metamorphism. Preliminary examination of fluid inclusions in armenite indicates the presence of minute two-phase inclusions (liquid and gas), with temperatures of homogenization in the range 215–226°C. Though these temperatures must be regarded as minimal values, it is unlikely that temperature during vein mineralization exceeded 275 to 300°C.

A petrographic and chemical investigation of the vein material reveals a succession of well-delineated mineralizing episodes of marked chemical contrast. These are perhaps best seen as a series of events rather than a continuous process. The first such event probably involved the pervasive hydration of the dioritic host-rock, producing a mixture of prehnite and epidote minerals. The limited amount of field information presently available permits only a speculation on the origin of these fluids and of the chemical constituents deposited in the veins. We suggest that hydrous fluids related to the terminal stages of evolution of the Lac-Rémigny complex (Larouche 1979) were responsible for the alteration of the dioritic host-rocks. The prolonged action of these fluids was accompanied by the successive deposition in fractures of constituents leached elsewhere, resulting in albite, armenite, thulite, piedmontite and small quantities of accessory minerals.

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REFERENCES

- ABRECHT, J. (1981): Pink zoisite from the Aar Massif, Switzerland. *Mineral. Mag.* **44**, 45-49.
- ARMBRUSTER, T. & BLOSS, F.D. (1981): Mg-cordierite: Si/Al ordering, optical properties and distortion. *Contr. Mineral. Petrology* **77**, 332-336.
- BAKAKIN, V.V., BALKO, V.P. & SOLOV'YEVA, L.P. (1975): Crystal structure of milarite, armenite, and sogdianite. *Sov. Phys. Cryst.* **19**, 460-462.
- ČERNÝ, P., HAWTHORNE, F.C. & JAROSEWICH, E. (1980): Crystal chemistry of milarite. *Can. Mineral.* **18**, 41-57.
- CHAGNON, J.-Y. (1968): Région des Lacs des Quinze et Barrière, comté de Témiscamingue. *Ministère Rich. Nat. Qué., Rapp. géol.* **134**.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals: 1. Ortho- and Ring Silicates*. Longmans, London.
- FOORD, E.E. & CUNNINGHAM, C.G. (1978): Thermal transformation of anomalously biaxial dimetric crystals. *Amer. Mineral.* **63**, 747-749.
- & MILLS, B.A. (1978): Biaxiality in 'isometric' and 'dimetric' crystals. *Amer. Mineral.* **63**, 316-325.
- FORBES, W.C., BAUR, W.H. & KHAN, A.A. (1972): Crystal chemistry of milarite-type minerals. *Amer. Mineral.* **57**, 463-472.
- FOSCAL-MELLA, G. (1976): *Analyse Minéralogique des Argiles Glaciaires*. Mém. de thèse M.Sc.A., Dép. Génie minéral, École Polytechnique, Montréal, Qué.
- GOLDMAN, D.S. & ROSSMAN, G.R. (1978): The site distribution of iron and anomalous biaxiality in osu-milite. *Amer. Mineral.* **63**, 490-498.
- , ——— & DOLLASE, W.A. (1977): Channel constituents in cordierite. *Amer. Mineral.* **62**, 1144-1157.
- LAROUCHE, C. (1976): Sequence of granitic intrusions in the Pontiac Group, intrusive tectonics and associated mineralizations. *Ministère Rich. Nat. Qué., Field Work in 1976*, **4**, 90-91.
- (1979): *Archean Granitoid Intrusions into the Pontiac Group, Lac Rémigny Area, Northwestern Quebec*. M.Sc. thesis, Carleton Univ., Ottawa, Ont.

- NEUMANN, H. (1939): Armenite, a new mineral: preliminary note. *Norsk Geol. Tidsskr.* **19**, 312-313.
- _____. (1941): Armenite, a water-bearing barium-calcium-alumosilicate. *Norsk Geol. Tidsskr.* **21**, 19-24.
- POIRIER, M. (1982): Étude de la minéralisation de thulite-armenite-albite dans un type de diorite de Lac Rémigny, Québec. Projet de fin d'études, École Polytechnique, avril 1982.
- POVARENNYKH, A.S. (1978): The use of infrared spectra for the determination of minerals. *Amer. Mineral.* **63**, 956-959.
- PUTNIS, A. (1980a): Order-modulated structures and the thermodynamics of cordierite reactions. *Nature* **287**, 128-131.
- _____. (1980b): The distortion index in anhydrous Mg-cordierite. *Contr. Mineral. Petrology* **74**, 135-141.
- _____. & BISH, D.L. (1983): The mechanism and kinetics of Al, Si ordering in Mg-cordierite. *Amer. Mineral.* **68**, 60-65.
- SEKI, Y. (1959): Relation between chemical composition and lattice constants of epidote. *Amer. Mineral.* **44**, 720-730.
- SELKREGG, K.R. & BLOSS, F.D. (1980): Cordierites: compositional controls of Δ , cell parameters, and optical properties. *Amer. Mineral.* **65**, 522-533.
- TENNYSON, C. (1960): Berylliummineralien und ihre pegmatitische Paragenesis in den Graniten von Tittling/Bayerischer Wald. *Neues Jahrb. Mineral. Abh.* **94**, 1253-1265.

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