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HELVITE FROM THE FRENCH PYRÉNÉES AS EVIDENCE FOR GRANITE-RELATED HYDROTHERMAL ACTIVITY

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ABSTRACT

The first example of helvite (*s.s.*) to be documented in France has been found in a zone of manganiferous mineralization associated with lower Carboniferous layers of jasper at Loudervielle and Vielle Aure in the Pyrénées. Mineralized areas are localized near granitic cupolas found in rocks regionally folded and metamorphosed at the end of the Variscan orogeny. There are four superimposed associations: 1) a banded sedimentary siliceous and carbonate-rich manganiferous rock with radiolaria, 2) metamorphic Mn-rich silicates, 3) veinlets of Mn-rich minerals cutting across the earlier foliation and stratification, related to hydrothermal circulation around granitic cupolas, and 4) Mn oxides and hydroxides produced by supergene leaching during post-Permian weathering. Rhodochrosite, rhodonite, quartz, tephroite, spessartine, friedelite, braunite, stilpnomelane, chlorite, alleghanyite, sonolite, hübnerite, alabandite, sphalerite, and welinite are associated with the helvite; the crystals of helvite are greenish lemon-yellow, attain 1 cm, and fluoresce red in cathodoluminescence. Electron-microprobe analyses gave SiO_2 32.94, BeO 13.27, MnO 49.32, ZnO 0.37, FeO 0.48, S 5.68, total 99.34 wt.%, close to the end-member composition. The presence of helvite provides evidence for granite-related hydrothermal activity.

Keywords: helvite, Mn-rich silicates, Mn ore deposit, stratiform, metamorphic, hydrothermal, Pyrénées, France.

SOMMAIRE

Le premier exemple de helvite (*s.s.*) a été observé en France dans les minéralisations manganésifères associées à des jaspes de la base du Carbonifère à Loudervielle et Vielle Aure dans les Pyrénées centrales. Les zones minéralisées sont situées à proximité des coupoles granitiques qui recoupent les séries régionales plissées et métamorphisées à la fin de la tectogenèse varisque. Les assemblages riches en manganèse appartiennent à quatre paragenèses superposées: 1) roche siliceuse rubanée et carbonatée (à Mn) avec radiolaires, 2) silicates de manganèse, formés durant le métamorphisme régional varisque, 3) veinules avec minéraux manganésifères, recoupant foliation et stratification, en relation avec des circulations hydrothermales autour des coupoles granitiques, 4) oxydes et hydroxydes de manganèse, résultant de l'altération supergène depuis la fin du Permien. Les associations minérales sont composées de: rhodochrosite, rhodonite, quartz, téphroïte, spessartine, friedelite, braunite, stilpnomélane, chlorite, alleghanyite, sonolite, alabandite, hübnerite, sphalérite, helvite, et welinite. La helvite se présente en grains de 0,1 à 1 cm; sa couleur est jaune-citron légèrement verdâtre. La helvite de Loudervielle et de Vielle Aure montre une fluorescence en rouge à la cathodoluminescence. Les analyses à la microsonde donnent la composition chimique moyenne: SiO_2 32,94, BeO 13,27, MnO 49,32, ZnO 0,37, FeO 0,48, S 5,68, total 99,34% (poids), qui se rapproche du pôle helvite. La présence d'helvite permet de mettre en évidence une activité hydrothermal périgranitique.

Mots-clés: helvite, silicates de Mn, minéralisation en manganèse stratiforme, métamorphique, hydrothermal, Pyrénées, France.

INTRODUCTION

The lower Carboniferous sequence of the central Pyrénées includes a jasper series within which numerous deposits of manganese are found (Fig. 1). The regional geological setting of the mineralization has been described by Bouquet & Stoppel (1975), and Crilat (1983). According to Crilat, the stratigraphic sequence, from base to top, consists of: 1) upper Devonian limestones, a reddish nodular unit with goniatite remains, and shale, grading to a sequence of Tournaisian limestone horizons that individually are 2 m thick, 2) organic-matter-rich jasper, 10 m thick, with phosphate nodules, followed by 15 m of pale jasper that includes pyroclastic layers; four meters below the top of this sequence is an interval of Mn-rich jasper, generally with abundant radiolaria, which is the ore horizon; and 3) Visean limestone with chert, underlying the thick Culm Series, which marks the beginning of the Variscan tectonic episode.

Most early investigators have argued for an origin by metasomatic introduction of manganese into older rocks. Various sources and processes have been mentioned but not proven, and the time of introduction is

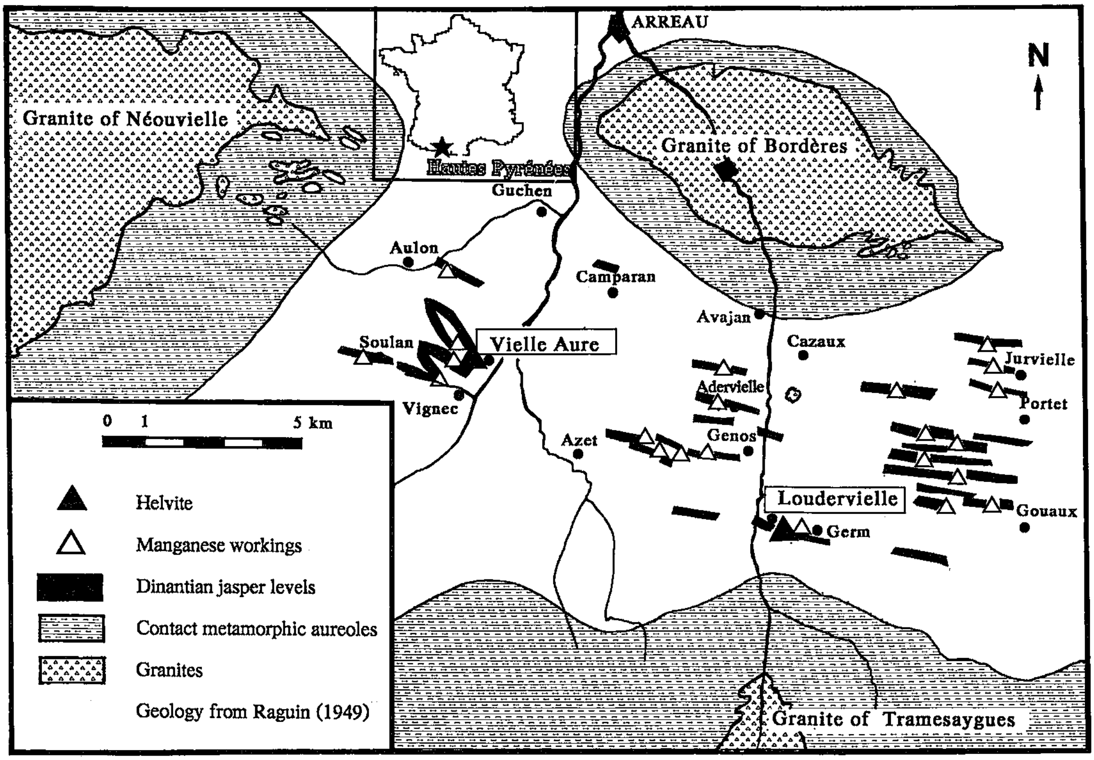

FIG. 1. Locality map of Mn deposits in the Hautes Pyrénées, France.

only inferred. These hypotheses have been challenged by Pélissonnier (1956) and Crilat (1983), who emphasized the stratabound character of the manganese-bearing assemblages, especially in volcanogenic units, and their consanguinity with the jasper horizons. Many other well-known examples (Roy 1981, Dasgupta *et al.* 1990) support the synchronous deposition of Mn-bearing minerals with jasper, chert and tuffs.

It seems likely, however, that Mn-silicates in the jasper-rich interval could not originate under synsedimentary environments or early diagenetic conditions; such minerals are formed only under metamorphic conditions. Crilat (1983) presented evidence for at least two stages of metamorphism in this area: 1) a regional, syntectonic, low-grade metamorphism (chlorite, muscovite, biotite, albite), and 2) a later, static contact metamorphism (sillimanite, andalusite, biotite, chlorite) associated with the emplacement of granite plutons. The conditions of the regional dynamic metamorphism and the structural occurrence of rhodonite, spessartine, tephroite, braunite (Table 1) are consistent with their formation during metamorphism. On one hand, it is likely that these silicates crystallized isochemically along stratigraphic (sedimentary) layers of favorable composition. On the other hand, other Mn-bearing silicates like friedelite, manganiferous humite-group minerals (alleghanyite and sonolite), helvite, stilpnomelane and welinite

TABLE 1. SEQUENCE OF CRYSTALLIZATION OF THE MINERALS

	Diagenesis	Dynamic metamorphism	Contact metamorphism	Hydrothermal
Alabandite				—
Braunite		—		
Friedelite			—	—
Helvite				—
Hübnerite				—
Humite*				—
Hyalophane		—	—	
Quartz	—	—	—	—
Rhodochrosite	—	—	—	—
Rhodonite		—	—	—
Sphalerite				—
Spessartine		—	—	—
Stilpnomelane			—	—
Tephroite		—	—	
Welinite				—

(*) Manganiferous humite-group minerals.

[$Mn_6WSi_2(O,OH)_{14}$)], as well as nonsilicates (hübnerite and alabandite) and sulfides (sphalerite, chalcopyrite, galene, cobaltite), cannot have crystallized during the low-grade regional metamorphism, in view of their occurrence as late veinlets or in vugs. The minerals require compositions of a fluid phase and fugacities of volatile constituents achieved only in hydrothermal systems near intrusive bodies. Watanabe & Kato (1970) stated that alabandite is found exclusively in deposits metamorphosed by granitic intrusions. Kayupova (1960) showed that friedelite may result from peribatholithic hydrothermal activity. Hübnerite is found exclusively in hydrothermal ores. Kato (1970) explained its formation by the reaction of a fluid containing tungsten with rhodochrosite.

THE LOUDERVIELLE AND VIELLE AURE DEPOSITS

The Mn-mineralized zone at Loudervielle occurs within jasper as a lens 80 m long, 50 m across and 3 m thick, that strikes N60°E. The jasper horizons are commonly banded. The general tectonic pattern and microtectonic fractures indicate that the orebodies owe their lenticular shape to boudinage.

The Vielle Aure manganese deposit was the more important in terms of production. A 50-m-long adit was exploited from 1850 to 1902 in the upper mineralized layer of jasper, which forms the core of a strongly folded synform. The general trend of this structure is nearly east–west. The mineralized layer is about 60 cm thick where not thickened by folding, at the portal of the adit. The thickening of the Mn-layer is well developed deeper in the adit, where the layer is repeated by intense isoclinal folding and boudinage.

STRUCTURE AND MINERALOGY OF THE Mn-BEARING LAYERS

Although primary sedimentary structures are generally well preserved in most of the layers of jasper, the mineralized horizons, on the other hand, display various metamorphic textures. These textures become more poorly preserved as the Mn content increases. The initial synsedimentary structures, where present,

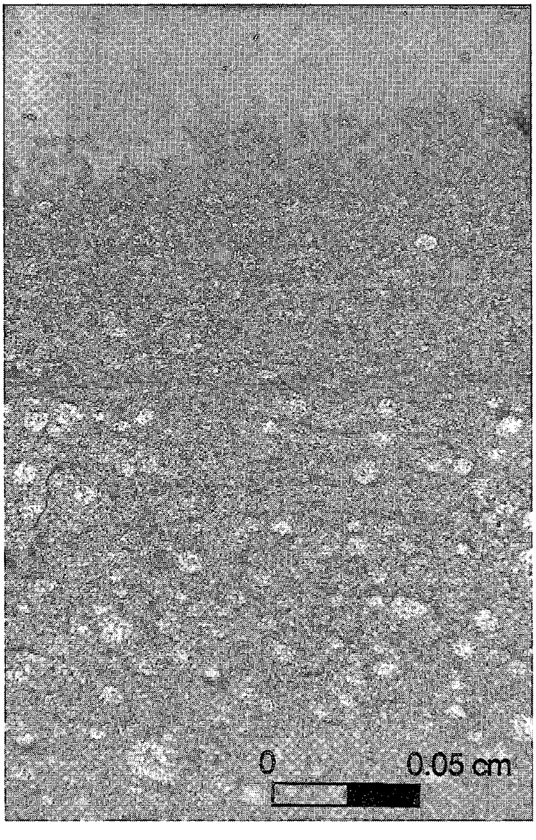

FIG. 2. Bedded manganiferous cherts (dark) and radiolarites (light).

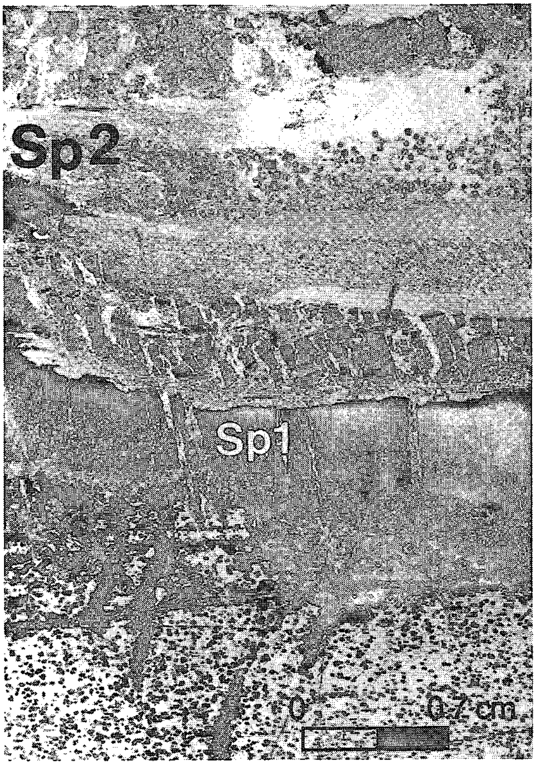

FIG. 3. Layered metamorphic spessartine [Sp1] (in black), with later fractures filled by friedelite [Fr] and euhedral spessartine [Sp2], well exhibited in the upper part.

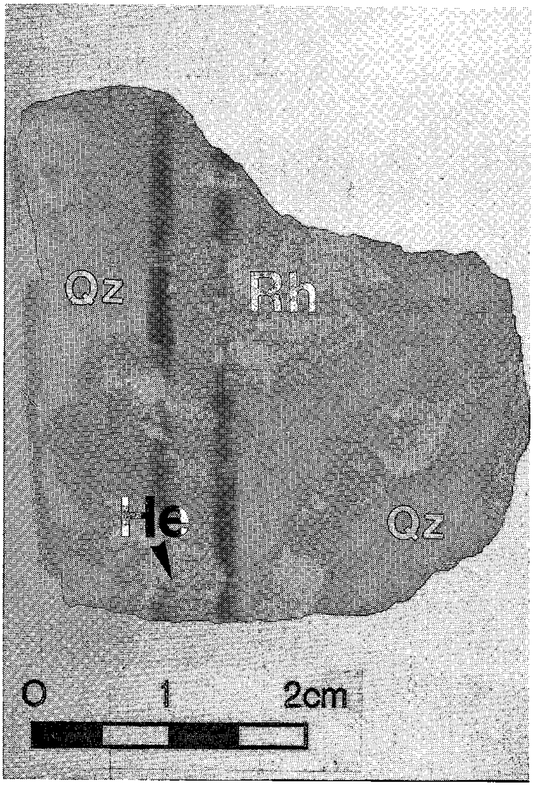

FIG. 4. Helvite (He) with rhodochrosite (Rh) and quartz (Qz) in brecciated Mn-rich jasper from Loudervielle.

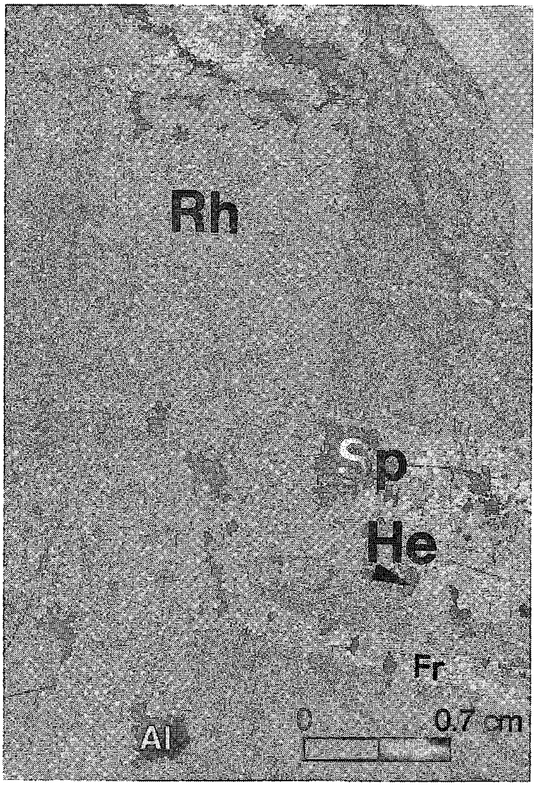

FIG. 5. Fractures with rhodochrosite (Rh), friedelite (Fr), alabandite (Al), sphalerite (Sp) and helvite (He) from Vielle Aure.

show finely laminated jasper with silica-rich laminae alternating with laminae rich in phyllitic or epiclastic material. The silica-rich laminae commonly contain numerous radiolarian remains. Where present, rhodochrosite appears as more or less coalescent, disseminated polycrystalline spots. Jasper microstructures contain microcrystalline to cryptocrystalline silica and carbonates, the synsedimentary or at least early diagenetic origin of which is proved by the presence of synsedimentary breccia and compaction fractures. The spots of rhodochrosite have an amoeboid cross-section, and are generally fine grained, and locally colloform or radially crystallized. The presence of euhedral recrystallized rhodochrosite may be related to these low-grade early metamorphic conditions or to diagenetic processes. Radiolaria become elongate in the limbs of microfolds, whereas some jasper layers thicken in the core of folds (Fig. 2).

The secondary structures in the layers of jasper are attributed to three events: 1) Variscan regional metamorphism, synchronous with the folding, 2) static contact metamorphism, which develops early around cupolas of granite, and 3) later hydrothermal processes occurring after polystage fracturing of the host rocks.

Only oriented grains of minerals, including Mn-bearing silicates (rhodonite, tephroite, braunite), quartz, and rhodochrosite, elongate parallel to axial planar foliation, unequivocally represent Variscan growth. Some minerals without preferred orientation may be related to the Variscan event, for example, fine-grained, disseminated to coalescent garnet (spessartine 1), located only within specific laminae (Fig. 3), and later brecciated and cemented by a second or third episode of crystallization. Also belonging to this group of possible Variscan minerals are rhodonite, braunite, tephroite, stilpnomelane and chlorite.

The peribatholithic metamorphic transformations are easily recognized. Minerals formed during this static event have a random orientation that overprints former structures. Crushing has produced hydrothermally cemented breccia. Quartz exhibits triple-junction boundaries, and rhodochrosite forms large euhedral crystals invading the rocks. The silicates of

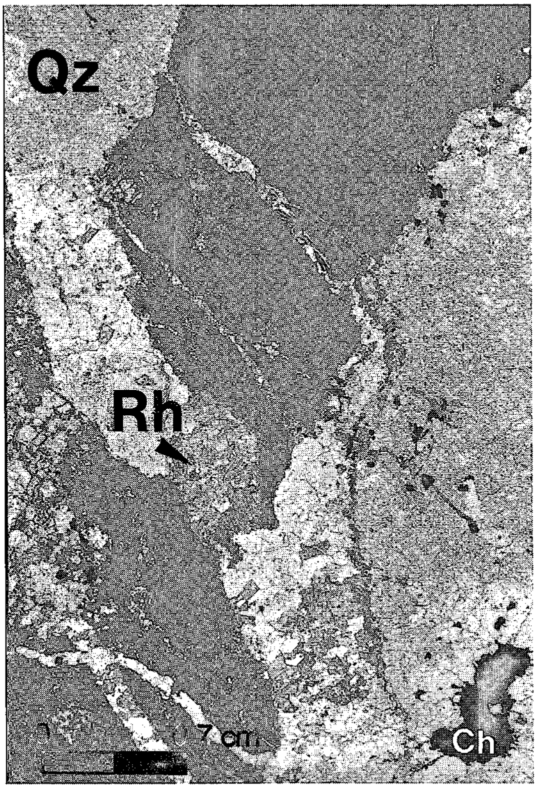

FIG. 6. Fractures with quartz (Qz), rhodochrosite (Rh), chalcopyrite (Ch) from Vielle Aure.

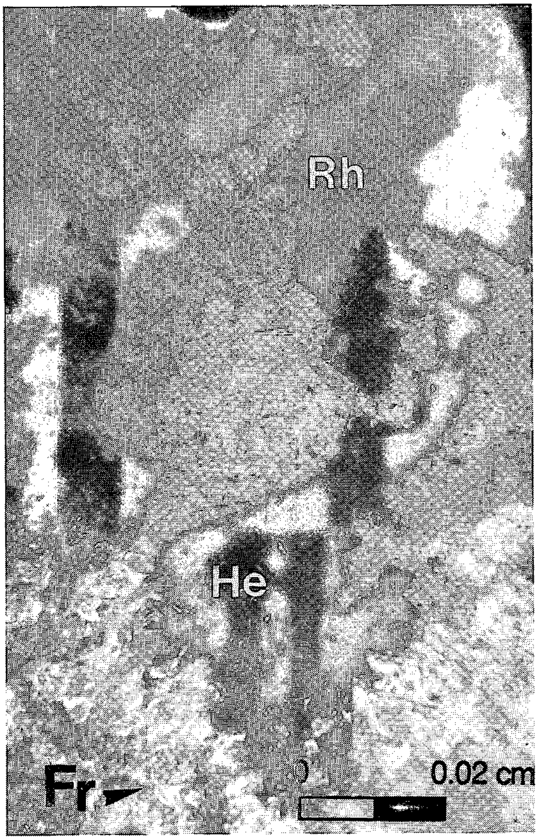

FIG. 7. Fracture filing with rhodochrosite (Rh), friedelite (Fr) and helvite (He) from Vielle Aure.

Mn, among which rhodonite is dominant, either crystallized directly by reaction between quartz and carbonates, or recrystallized from regional synmetamorphic minerals. Tephroite, braunite, stilpnomelane, and some of the friedelite likely have the same origin. Spessartine 2 is somewhat later, as indicated by inclusions of previously formed minerals (friedelite, rhodochrosite).

The above-mentioned mineral assemblages do not imply any introduction of elements during metamorphism, and therefore may have originated from isochemical reactions. This is not the case for the next event, during which minerals filled polystage fractures developed in the contact-metamorphosed rocks, following the emplacement of the granite plutons. This system of fractures can be related to fluid overpressure or to batholith shrinkage due to cooling. Fracture fillings are composed mainly of quartz and rhodochrosite, associated with helvite, friedelite, stilpnomelane, chlorite, alabandite, alleghanyite, sonolite, sphalerite, hüebnerite, and welinite (Figs. 4, 5, 6). The formation of these minerals in fractures requires the presence of such components as S, Be, B, Zn, W, Cl, F and H_2O. Manganese, Si, and CO_2 in these fractures are almost certainly leached from the surrounding wallrocks, which contain these elements. However, S, Be, B, Zn, W, Cl, F and H_2O require metasomatic introduction *via* the presence of fluids that either evolved from granitic magmas or were leached from granitic rocks.

DETERMINATION OF HELVITE

Within the late-stage veinlets, helvite appears in a quartz–rhodochrosite gangue with stilpnomelane and chlorite (Fig. 7) in association with welinite and scarce, small, bright red lamellae of hübnerite. The helvite is a greenish lemon-yellow, garnet-like in appearance, isotropic, with high relief and triangular sections (Figs. 8, 9). Scanning electron microscopy reveals the tetrahedral habit of the mineral and a distinct (111) cleavage (Fig.10). Infrared absorption spectroscopy confirms the determination of helvite, as do powder X-ray-diffraction data [cubic, *a* 8.24(7) Å].

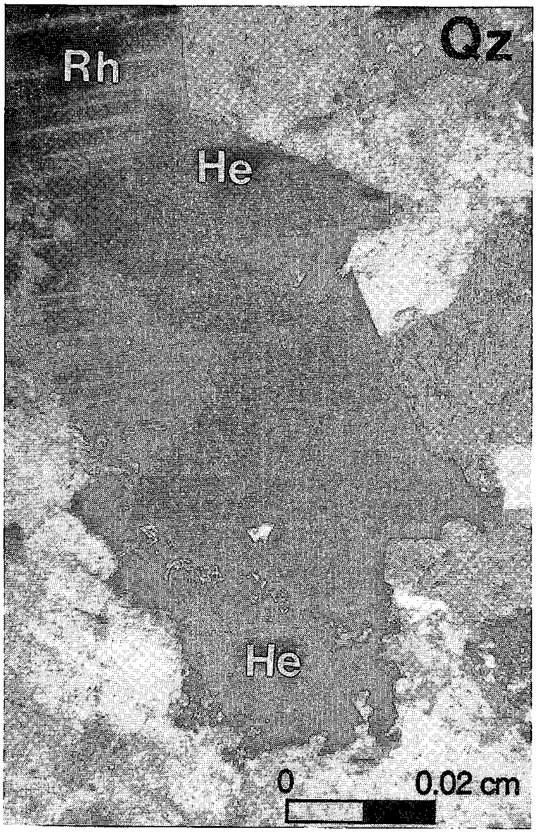

FIG. 8. Triangular sections of helvite (He) in rhodochrosite (Rh) and quartz (Qz) from Loudervielle.

FIG. 9. Triangular sections of helvite from Vielle Aure (electron microscopy).

The helvite from Loudervielle and Vielle Aure exhibits a red fluorescence, observed using a Technosym spectrophotometer operated at 12–14 kV and 530–580 µA, as does helvite *sensu stricto* from syenite pegmatites of Saga and Sandoy in the Oslo region (Larsen 1988).

The chemical composition of the helvite-group minerals can be expressed stoichiometrically as $C_8(Be_6Si_6O_{24})S_2$, where C represents Mn^{2+} (helvite), Fe^{2+} (danalite) or Zn^{2+} (genthelvite). Dunn (1976, 1977) has shown that there is a complete solid-solution between helvite and danalite, and between danalite and genthelvite. Intermediate compositions between genthelvite and helvite are lacking.

Helvite was analyzed with an automated CAMEBAX electron microprobe at the Camparis Center, Université Pierre et Marie Curie, Paris. The analytical conditions were 15 kV, 30 nA, counting time between 10 and 20 s depending on the elements. Synthetic oxides and natural silicates were used as standards. Electron-microprobe data reveal that two helvite grains from Vielle Aure and one from Loudervielle

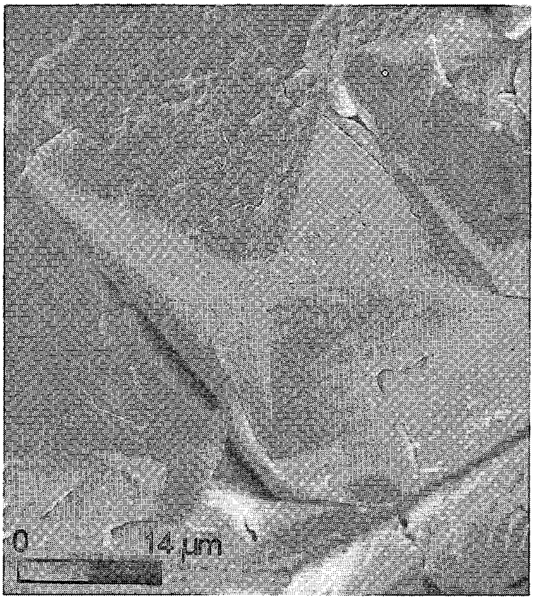

FIG. 10. Tetrahedral habit of helvite (electron microscopy).

TABLE 2 . COMPOSITION OF HELVITE FROM LOUDERVIELLE AND VIELLE AURE Mn DEPOSITS

Analysis	1	2	3	4 #	5 #	6 #	7	8	9
MnO (wt.%)	48.63	46.10	47.11	49.66	49.77	50.65	49.06	51.75	49.70
FeO	0.80	1.01	0.53	0.86	0.86	0.20	0.17	0.18	0.14
ZnO	0.56	0.95	0.76	0.45	0.39	0.14	0.28	0.11	0.07
CaO	0.07	0.03	0.04	0.07	0.07	– –	– –	– –	– –
BeO*Cal	13.23	12.70	12.78	13.11	13.19	13.49	13.46	13.51	13.20
SiO2	33.58	33.16	33.55	32.39	32.33	33.47	32.38	32.76	33.44
Al2O3	0.12	0.08	– –	0.08	0.09	0.03	– –	– –	0.02
S	5.50	5.62	5.62	5.70	5.69	5.55	5.68	5.80	5.63
MgO	0.02	0.04	– –	0.01	0.03	– –	– –	– –	0.01
WO3	0.20	– –	– –	– –	– –	0.47	– –	0.19	– –
F-	– –	0.52	0.48	– –	– –	– –	– –	– –	– –
Cl-	– –	0.06	0.03	– –	– –	– –	0.05	– –	– –
Total°	**99.46**	**97.44**	**98.08**	**99.32**	**99.38**	**99.88**	**99.85**	**99.90**	**99.42**
Numbers of ions on the base of Al + Be + Si = 12 following Dunn (1976)									
Mn	7.55	7.35	7.45	7.82	7.99	7.78	7.77	7.80	7.75
Fe	0.12	0.16	0.08	0.03	0.03	0.13	0.13	0.13	0.02
Zn	0.08	0.13	0.10	0.02	0.02	0.06	0.05	0.05	0.01
Ca	0.01	0.01	0.01	– –	– –	0.01	0.01	0.01	– –
Σ	**7.76**	**7.65**	**7.64**	**7.87**	**8.04**	**7.98**	**7.97**	**8.00**	**7.78**
Be	5.82	5.74	5.73	5.90	6.03	5.99	5.97	6.00	5.84
Si	6.15	6.24	6.27	6.10	5.97	5.99	6.00	5.98	6.16
Al	0.03	0.02	– –	– –	– –	0.02	0.02	0.02	– –
Σ=12	**12.00**	**12.00**	**12.00**	**12.00**	**12.00**	**12.00**	**12.00**	**12.00**	**12.00**
S	1.88	1.98	1.97	1.90	1.99	1.97	1.98	1.97	1.94

***BeO is calculated following Dunn (1976), (Zn + Mn + Fe) / Be = 4 / 3 ; ° All totals less O = S; wt.% is weight percent ; analysis 1 to 3 from the helvite of Loudervielle; 4 # to 6 # from Vielle Aure and studied by X-ray diffraction ; and 7 to 9 from Vielle Aure.**

(Table 2) show very limited compositional variation. The concentration of Be cannot be measured by this method; it was estimated following Dunn (1976) and Hassan & Grundy (1985), according to the theoretical formula: [Mn + Fe^{2+}+ Zn + Ca + Mg]:Be = 4/3.

These values were used to calculate the number of ions on the basis of 12 (Al+Be+Si) per unit cell (Hassan & Grundy 1985). The number of Al atoms is insignificant. The Be atoms total from 5.73 to 6.03, and Si atoms, from 5.97 to 6.24. These trends in the helvite from Loudervielle and Vielle Aure are due to the vaporization of Be during the electron-microprobe analyses. The analytical data show that the sum of the interframework cations do not exceed the maximum value of 8. The number of S atoms reported seems reasonable, with the value close to the maximum of 2. The average compositions found are as follows: $(Mn_{7.47}Fe_{0.11}Zn_{0.09})_{\Sigma 7.67}(Be_{5.77}Si_{6.21}O_{23.92})S_{1.94}$ (Loudervielle) and $(Mn_{7.81}Fe_{0.06}Zn_{0.04})_{\Sigma 7.91}(Be_{5.94}Si_{6.05}O_{23.97})S_{1.98}$ (Vielle Aure). The Mn content (Fig. 11) corresponds to that of helvite *sensu stricto*.

CONDITIONS OF CRYSTALLIZATION OF THE HELVITE

In the case of the hydrothermal veins of the Chvaletice in Bohemia, Čech & Povondra (1969) noted that all chemical species necessary for the formation of helvite, except Be, can be abstracted from the surrounding rocks, enriched as they are in Mn, Fe, S, and Si. The composition of helvite-group minerals depends on both $f(S_2)$ and $f(O_2)$ (Bilal & Fonteilles 1988). Genthelvite and helvite were synthesized by Fursenko & Klyakhin (1982) and Fursenko (1982); no other experimental study seems to have been published.

The composition of helvite is equivalent to a mixture of phenakite, tephroite and alabandite, according to the relation [*cf.* Burt 1988 for the genthelvite relation]:

$$2\ Mn_4(BeSiO_4)_3S = 2\ MnS + 3\ Be_2SiO_4 + 3\ Mn_2SiO_4 \qquad (1)$$

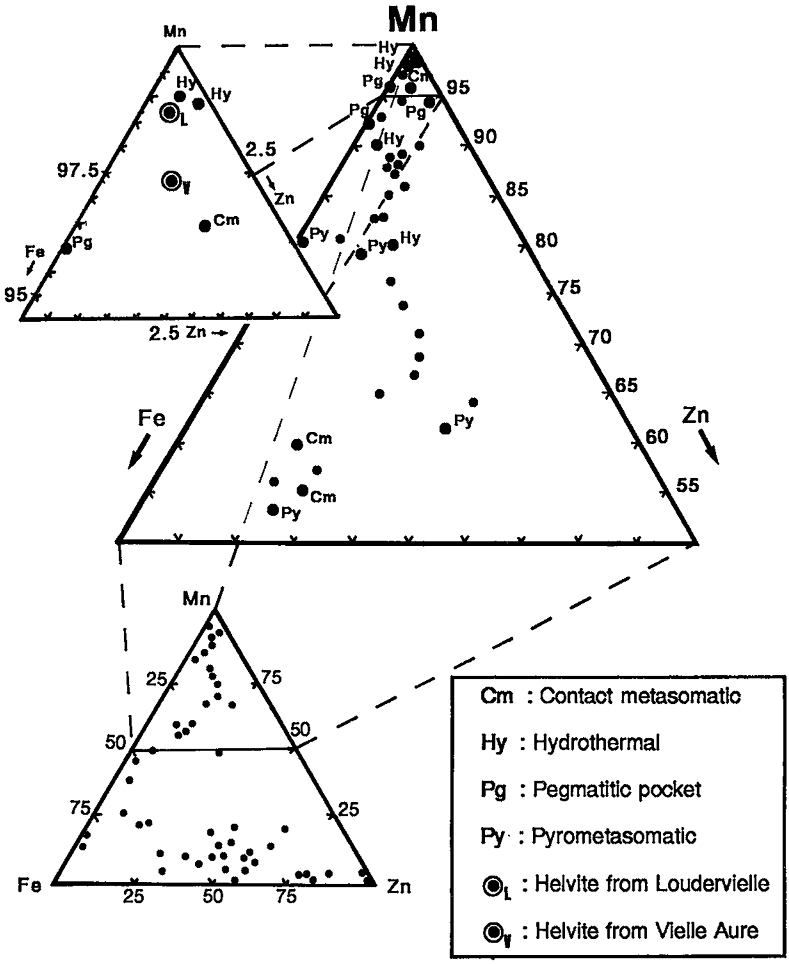

FIG. 11. Plots of compositions of helvite-group minerals (from Dunn 1976), together with averaged composition of helvite from Loudervielle and Vielle Aure (this study).

The following reaction was proposed by Bilal & Fonteilles (1988) for the case of helvite in the Sucuri granite, in Brazil:

$$8\,MnSiO_3 + 3\,Be_2SiO_4 + S_2 = Mn_8Be_6Si_6O_{24}S_2 + 5\,SiO_2 + O_2 \quad (2)$$

Beus (1965) emphasized that the main mass of Be in metasomatic deposits is introduced, together with fluorine, during the end stage of formation of the skarns; fluorite may be present, and Be may have been transported as fluorine complexes. The beryllium–fluorine association is not essential in hydrothermal deposits. Be also can migrate as carbonate and fluorocarbonate complexes (Samchuck & Mitskevich 1980):

$$Be(OH)_2 + CO_3^{2-} = Be(OH)CO_3^- + OH^- \quad (3)$$

or

$$Be(OH)_2 + 2\,F^- = Be(OH)F_2^- + OH^- \quad (4)$$

The activity of alumina plays an essential role in the stability of beryllium minerals; phenakite or helvite (or both) are stable where it is low, and beryl or chrysoberyl are stable where it is high (Bilal & Fonteilles 1991). For the helvite-bearing veinlets of Loudervielle and Vielle Aure, I propose the following reaction with rhodochrosite (or rhodonite), alabandite, in the absence of phenakite:

$$6\,MnCO_3 + 6\,Be(OH)CO_3^- + 6\,SiO_2 + 2\,MnS = Mn_8Be_6Si_6O_{24}S_2 + 12\,CO_2 + 6\,OH^- \qquad (5)$$

or

$$6\,MnSiO_3 + 6\,Be(OH)CO_3^- + 2\,MnS = Mn_8Be_6Si_6O_{24}S_2 + 6\,CO_2 + 6\,OH^- \qquad (6)$$

Fluid-inclusion data were obtained using a Linkam TH 600 heating and cooling stage attached to a Leitz miscrocope. Fluids inclusions are relatively abundant in the veins described above, in quartz, rhodochrosite and helvite. They are primary fluid inclusions, that formed during the growth of these hydrothermal phases. The inclusions range up to 15 µm in size, with an average of 5 µm. Our data thus far support the following conclusions: 1) Melting temperatures of ice in the range −15 to −20°C indicate high-salinity aqueous solutions, 19–20 equivalent wt% NaCl. 2) Pressure- and salt-corrected filling temperatures range from 300 to 350°C during the hydrothermal stage. In the opinion of Perez *et al.* (1990), the fluid inclusions in genthelvite from the alkaline ring of Taghouaji complex (Aïr Mountains, Niger) reveal that it precipitated from a low-salinity aqueous fluid at temperatures higher than 375°C and pressures greater than 220 bars. Casadevall & Ohmoto (1977) determined temperatures up to 250°C at 0.2 kbar for the formation of helvite at the Sunnyside mine, Colorado, in hydrothermal veins; these veins are linked to late volcanotectonic collapses (formation of calderas).

As a whole, the Loudervielle and Vielle Aure Mn deposits exhibit a late paragenesis of Mn phases that may be related to the percolation type of skarn. In the Costabonne tungsten deposit in the French Pyrénées (Guitard & Laffite 1958), helvite occurs with garnet, actinolite and calcite. This is a point of comparison with the Costabonne occurrence. The convective movements of fluids and, perhaps, their source may be related to late Variscan granitic activity (Bordères, Néouvielle, Tramesaygues: Fig. 1). On the basis of the proximity of these granitic bodies, a cupola may well be present under the mineralized areas.

CONCLUSIONS

Structural relationships in the Loudervielle and Vielle Aure deposits in the French Pyrénées clearly show that the veinlets containing helvite postdated the Variscan metamorphic phase (or phases). Moreover, helvite is associated with mineralogical phases containing elements not generally associated with synsedimentary or regional metamorphic environments (Be, W, As). On the contrary, these elements are characteristic of hydrothermal activity, especially that associated with granitic intrusive bodies.

At Loudervielle and Vielle Aure, isochemical recrystallization during Variscan regional metamorphism was overprinted by the effect of hydrothermal activity. Many elements, especially Be, W, As, Cu, Pb, and Zn were introduced by the hydrothermal activity, which also mobilized Mn from the surrounding rocks.

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REFERENCES

BEUS, A.A. (1965): *Geochemistry of Beryllium and Genetic Types of Be Deposits.* W.H. Freeman and Co., San Francisco, California.

BILAL, E. & FONTEILLES, M. (1988): Conditions d'apparition respectives de l'helvite, de la phénacite et du béryl dans l'environnement granitique: exemple du massif de Sucuri (Brésil). *C.R. Acad. Sci. Paris* **307**(11), 273-276.

_____ & _____ (1991): Chemical properties of helvite group minerals in different types of occurences. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). Balkema, Rotterdam, The Netherlands (733-736).

BOUQUET, C. & STOPPEL, D. (1975): Contribution à l'étude du Paléozoïque des Pyrénées centrales (Hautes vallées de la Garonne et de l'Aure). *Bull. BRGM, 2ème sér., sect.* **1**, 7-61.

BURT, D.M. (1977): Chalcophile–lithophile tendencies in the helvite group: genthelvite stability in the system $ZnO–BeO–Al_2O_3–SiO_2–SO_{-1}–F_2O_{-1}$. *Trans. Am. Geophys. Union* **58**, 1242 (abstr.).

_____ (1988): Stability of genthelvite, $Zn_4(BeSiO_4)_3S$: an exercise in chalcophilicity using exchange operators. *Am. Mineral.* **73**, 1384-1394.

CASADEVALL, T. & OHMOTO, H. (1977): Sunnyside mine, Eureka mining district, San Juan County, Colorado: geochemistry of gold and base metal ore deposition in a volcanic environment. *Econ. Geol.* **72**, 1285-1320.

ČECH, F. & POVONDRA, P. (1969): Helvite from hydrothermal veins at Chvaletice, Bohemia. *Acta Univ. Carolinae, Geol.* **1**, 1-11.

CRILAT, S. (1983): Le Dévonien supérieur et le Carbonifère inférieur des Pyrénées et de la Montagne Noire (Frasnien, Famennien, Tournaisien). *Bull. du Projet Int. de Corrélations Géologiques (IUGS-UNESCO) Newslett.* **5**, 1285-1320.

DASGUPTA, H.C., BANERJEE, H., FUKUOKA, M., BHATTACHARYA, P.K. & ROY, S. (1990): Petrogenesis of metamorphosed manganese deposits and the nature of precursor sediments. *Ore Geol. Rev.* **5**, 359-384.

DUNN, P.J. (1976): Genthelvite and the helvite group. *Mineral. Mag.* **40**, 627-636.

——— (1977): The helvite group. *Mineral. Rec.* **8**, 92-93.

FURSENKO, D.A. (1982): Dependence of the composition of helvite on the acidity–basicity of mineralizing solutions. *In* Fiz.-khim. issled. mineralo-brazuyuhch. Sistemakh (A.A. Godovikov, ed.). Akademia Nauk SSSR, Sib. Otb., Inst. Geol. Geofiz., Novosibirk, USSR (in Russ., not seen; *Chem. Abstr.* **98**, 219084n).

——— & KLYAKHIN, K.A. (1982): Synthesis of minerals of the helvite group. *In* Vses. Sovesch. po eksperim. i tekh. mineral. i petrogr. [Mater] **10**, 119-126 (1978) (Yu. P. Melnik, ed.). Naukova Dumka, Kiev, Ukrainian SSR, USSR (in Russ., not seen; *Chem. Abstr.* **98**, 201508u).

GUITARD, G. & LAFITTE, P. (1958): Les calcaires métamorphiques et les skarns du Pic de Costabonne. *Mém. Sci. de la Terre, Nancy* **VI**(1-2), 57-137.

HASSAN, I. & GRUNDY, H.D. (1985): The crystal structures of helvite group minerals, $(Mn,Fe,Zn)_8(Be_6Si_6O_{24})S_2$. *Am. Mineral.* **70**, 186-192.

KATO, A. (1970): Hübnerite from Kaso mine, Tochigi Prefecture, Japan. *J. Mineral. Soc. Japan 3*, 432-433 (in Japanese).

KAYUPOVA, M.M. (1960): Friedelite from the iron–manganese deposits of Dzhumart and Kamys in central Kazakhstan. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.* **135**, 1290-1292.

LARSEN, A.O. (1988): Helvite group minerals from syenite pegmatites in the Oslo Region, Norway. Contribution to the mineralogy of Norway, No. 68. *Norsk Geol. Tidsskr.* **68**(2), 119-124.

PÉLISSONNIER, H. (1956): Caractère syngénétique du manganèse des Hautes Pyrénées. *XXème Congrès Géol. International* **V**, 174-195.

PEREZ, J.-B., DUSAUSOY, Y., BABKINE, J. & PAGEL, M. (1990): Mn zonation and fluid inclusions in genthelvite from the Taghouaji complex (Aïr Mountains, Niger). *Am. Mineral.* **75**, 909-914.

RAGUIN, E. (1949): *Géologie des gîtes minéraux.* Masson et Cie, éditeurs, Paris, France.

ROY, S. (1981): *Manganese Deposits.* Academic Press, London, U.K.

SAMCHUCK, A.I. & MITSKEVICH, B.F. (1980): Complexing of beryllium in carbonate solutions. *Geochem. Int.* **9**, 1371-1376.

WATANABE, T., YUI, S. & KATO, A. (1970): Metamorphosed bedded manganese deposits of the Noda – Tamagawa mine. *In* Volcanism and Ore Genesis (T. Tatsumi, ed.). Univ. Tokyo Press, Tokyo, Japan (143-152).

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