

## GREENOCKITE AND ASSOCIATED SULFIDE MINERALIZATION FROM THE CALEDONIA GROUP MINES, BLANCA CREEK, LA HUERTA RANGE, SAN JUAN PROVINCE, ARGENTINA

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### ABSTRACT

We document various textural occurrences of greenockite associated with several ore minerals in varying parageneses: pyrite + sphalerite + galena + chalcopyrite ± arsenopyrite ± pyrrhotite ± bornite ± tennantite ± tetrahedrite ± covellite ± chalcocite ± aikinite ± wittichenite ± matildite ± berryite ± miharaite ± geocronite ± hematite ± magnetite from mineralized samples of the Caledonia Group mines, Marayes mining district, La Huerta Range, San Juan province, Argentina, based on reflected light and scanning electron microscope investigations. The mineralization is hosted mainly in metacarbonate outcrops in contact with the granulite basement and associated intermediate to mafic meta-intrusive rocks. We recognize three types of greenockite on the basis of textural and chemical criteria. Type-1 greenockite contains less than 1 mol.% ZnS, but its Fe content varies from 0.2 up to 4.5 mol.% FeS. Type 2 is Zn-rich, with 10–25 mol.% ZnS component and <0.1 to 3 mol.% FeS component, and type 3 has a Zn content of 5–7 mol.% ZnS component and FeS <0.1 mol.%. The presence of complex Ag–Cu–Bi–Pb sulfides point to a late-stage, low-temperature overprint of the primary sulfide parageneses, accompanied by the formation of hypogene greenockite, at least partly at the expense of sphalerite. The near-end-member composition of greenockite and late-stage sphalerite also indicates a low temperature of formation.

*Keywords:* greenockite, textural occurrence, sulfide parageneses, Caledonia Group mines, La Huerta, Argentina.

### SOMMAIRE

Nous documentons des associations texturales variées impliquant la greenockite dans plusieurs paragenèses avec les minéraux de minerais suivants: pyrite + sphalérite + galène + chalcopyrite ± arsénopyrite ± pyrrhotite ± bornite ± tennantite ± tétraédrite ± covellite ± chalcocite ± aikinite ± wittichenite ± matildite ± berryite ± miharaite ± géocronite ± hématite ± magnétite; ces échantillons proviennent des mines Caledonia Group, dans le camp minier de Marayes, chaîne de La Huerta, province de San Juan, en Argentine. Nos observations ont été faite en lumière réfléchie et avec un microscope électronique à balayage. On trouve la minéralisation surtout dans les affleurements de métacarbonate en contact avec le socle granulitique et les roches intrusives intermédiaires à mafiques associées. Nous distinguons trois types de greenockite selon des critères texturaux et compositionnels. La greenockite de type 1 contient moins de 1% de ZnS, et sa teneur en Fe varie de 0.2 jusqu'à 4.5% FeS (sur une base molaire). La greenockite de type 2 est enrichie en Zn, contenant entre 10 et 25% et entre <0.1 et 3% des composants ZnS et FeS, respectivement. La greenockite de type 3 contient entre 5 et 7% de ZnS et moins de 0.1% FeS. La présence de sulfures complexes de Ag–Cu–Bi–Pb témoigne d'une surimposition tardive à faible température de paragenèses de sulfures primaires, accompagnée de la formation de greenockite hypogène, en partie aux dépens de la sphalérite. La pureté compositionnelle de la greenockite et de la sphalérite tardive serait une indication d'une faible température de formation.

(Traduit par la Rédaction)

*Mots-clés:* greenockite, critères texturaux, paragenèses de sulfures, mines Caledonia Group, La Huerta, Argentine.

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INTRODUCTION

The Marayes mining district, located at the southern end of the La Huerta Range, San Juan Province, Argentina (Figs. 1a, b), is mineralized in base and precious metals. The most important mineralization of the Marayes district occurs at the Caledonia Group mines, situated 12 km northeast of the village of Marayes at 31°23'21" S, 67°20'33" W. They were discovered

approximately in 1840 and mined for gold on a minor scale up to 1865. This was followed by gold and zinc mining activities between 1945 and 1958. During this period, production was around 1000 kg gold and 11000 tonnes of zinc concentrate with an average grade of 20 grams gold per tonne and 52 wt% zinc (Lencinas 1993, and references therein).

Even though it is an old mining district, the state of knowledge of the geology of the area is very poor,

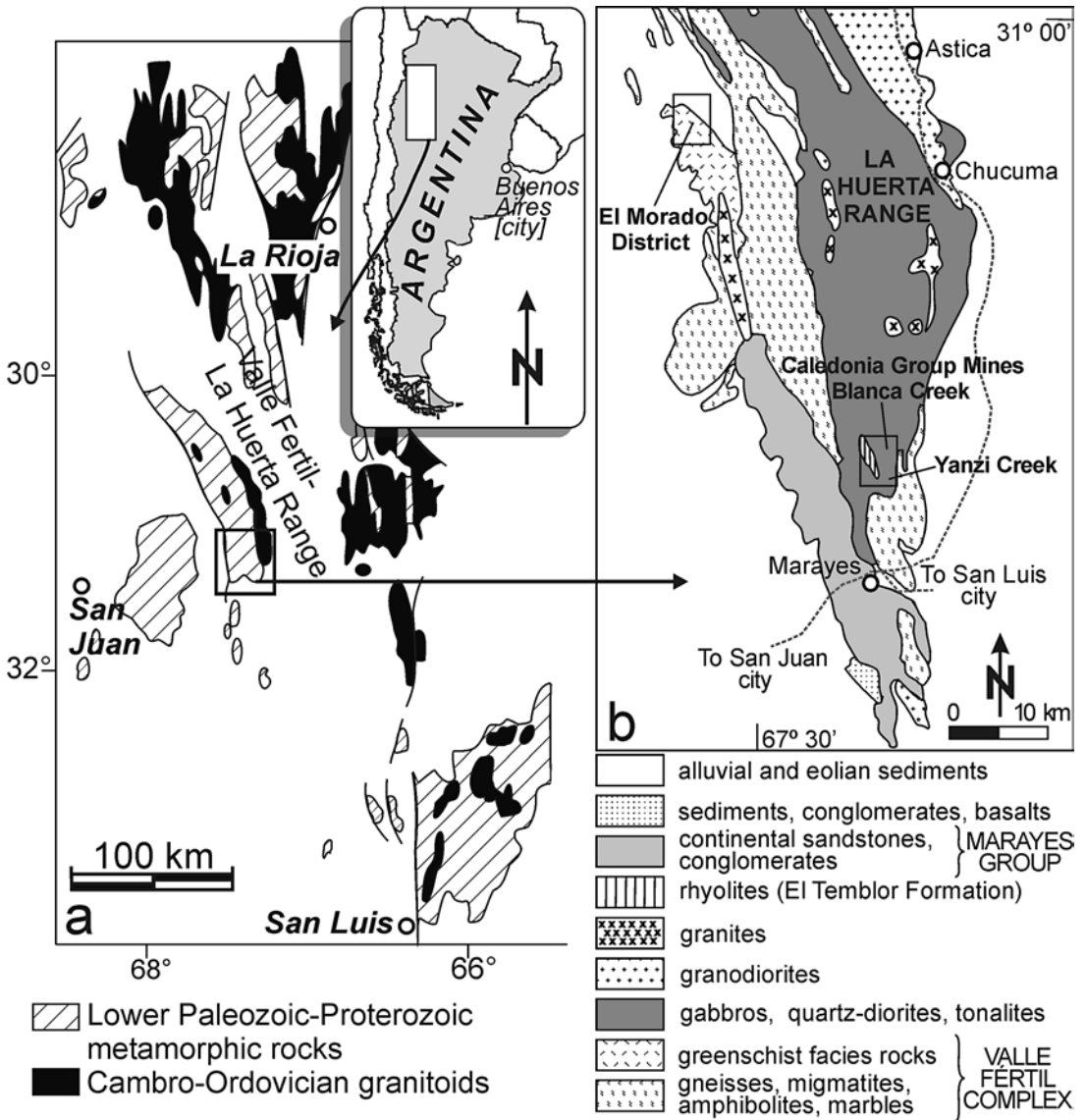


FIG. 1. General geological map of the Sierras Pampeanas showing the position of the study area (box inset) of the Valle Fértil – La Huerta Range (a), and the detailed geological map of La Huerta Range with the locations of the mineralized areas of the Caledonia Group mines, Blanca Creek (b).

and its metallogenesis remains unknown. Among the internal reports and communications is the publication by Stoll (1958), who described the main mines of the Sierra de La Huerta. In fact, no systematic studies concerning the mineralization or the metallogenesis of the area have been carried out.

The presence of greenockite in the mineralized zone of the Caledonia Group mines, which comprises the Caledonia–Albion, Azufre, Blanca and Rajo de la Blenda mine claims, has been reported by Meissl *et al.* (2006) and Mogessie *et al.* (2006). Despite the prevalence of minerals in the ZnS – CdS system and the significance of these minerals, both as a source of economic concentrations of Cd and environmental mineralogy, the literature on them is rather sparse.

Here, we report for the first time a detailed investigation of the different textural occurrences of greenockite there, as well as the presence of sulfide minerals such as aikinite, berryite, geocronite, matildite, miharaite and wittichenite, not previously described from this area. Our data suggest that greenockite formed as a product of hypogene replacement of sphalerite and as a primary mineral associated with various Ag–Cu–Bi–Pb sulfides and Cd-bearing tennantite.

#### BACKGROUND INFORMATION

The cadmium sulfide greenockite, ideally CdS, forms predominantly as a product of weathering of Cd-bearing sphalerite; cadmium usually occurs in sphalerite as a minor element, with a mean content in the range of 0.2–0.7 wt.% (Schwartz 2000). During weathering, the zinc sulfide is commonly transformed to zinc carbonates (*e.g.*, smithsonite), whereas the CdS component crystallizes as the cadmium sulfide greenockite. Greenockite, however, also occurs as a primary mineral in various geological settings, including metamorphosed zinc oxide mineralization (Dunn 1979, Johnson *et al.* 1990), granites (Butler & Thompson 1967), fumaroles (Chaplygin *et al.* 2007), pegmatites (Černý & Harris 1978), hydrothermal ore deposits (Oen *et al.* 1974, Kinnaird 1978, Tarkian & Breskovska 1989, Iizasa *et al.* 1992, Marcoux *et al.* 1993, Tombros *et al.* 2005), and in sediments (Burianova 1960, Davies-Colley *et al.* 1985), shales (Hurlbut 1957) and sediment-hosted lead–zinc deposits (Cornwall 1902, Patterson 1985). In these settings, primary greenockite is commonly associated with sphalerite.

Cadmium sulfide crystallizes in two modifications: a cubic  $\beta$ -form (hawleyite, sphalerite-type structure) and a hexagonal  $\alpha$ -form (greenockite; wurtzite-type structure). The wurtzite–greenockite solid-solution series has been studied by Hurlbut (1957). In the mineralization described here, no wurtzite has been documented. The conditions of formation of greenockite have been investigated in various experimental studies that have shown the existence of complete solid-solution in the system ZnS–CdS at temperatures above 600°C (Skinner

& Bethke 1961, Cherin *et al.* 1970, Tauson & Chernyshev 1977, Osadchii 1986, 1991). According to Tauson & Chernyshev (1977), a narrow miscibility-gap occurs in the ZnS – CdS system between 8 and 9 mol.% CdS at 800°C, 13 and 17 mol.% CdS at 600°C, 21 and 27 mol.% CdS at 400°C, and 23 and 70 mol.% CdS at 250°C. However, in a fumarolic environment, crystals of Cd-rich sulfides in the system ZnS–CdS precipitate mainly at lower temperatures (400°C) than those of Zn (up to 750°C) (Chaplygin *et al.* 2007). The replacement of cadmium by zinc seems a rather complicated process depending on precipitation mechanism, pH,  $f(\text{O}_2)$ ,  $\alpha(\text{H}_2\text{S})$  and possibly  $\text{Cl}^-$  content of the fluid, associated with local mineral–fluid equilibrium (Tauson & Chernyshev 1977, Wright & Gale 2004, Tombros *et al.* 2005).

#### REGIONAL GEOLOGY

The Sierras of La Huerta – Valle Fértil (Figs. 1a, b) are part of the Sierras Pampeanas tectono-stratigraphic province, which include the Upper Proterozoic and Lower Paleozoic metamorphic and igneous rocks of central Argentina. They belong to the Western Sierras Pampeanas (Camino 1979), which are considered the “key” to understanding the connection between the Pampean and Laurentian terranes in the western margin of Gondwana. It is possible to recognize two belts within the basement of the Sierras of La Huerta – Valle Fértil that are parallel to the regional trend of the ranges, each belt with its own petrographic characteristics. The eastern belt mainly contains dioritic and tonalitic meta-intrusive rocks, metagabbros, granodiorites, pegmatites and aplites belonging to the calc-alkaline Famatinian (Early Ordovician) magmatic arc (Pankhurst *et al.* 1998). The western belt is comprised of garnet–sillimanite–cordierite gneisses and pyroxene-bearing amphibolites. Amphibolites are present as large bodies measuring several meters in width as well as thin lenses or xenoliths measuring a few centimeters in width. Gneisses are strongly foliated and characterized by irregular banding. Granulites are present in outcrops that are intercalated with gneisses and amphibolites, showing transitional contacts. Coarse-grained impure dolomitic marble and calc-silicate rocks occur as thick layers (up to 25 m) intercalated concordantly with the foliation of the metamorphic rocks, with gradational contacts. The cadmium-bearing mineralization is found mostly at the contact between the metacarbonates and the high-grade granulite-facies basement rocks. In the area of the Caledonia Group mines, a body of rhyolite with associated intrusive breccias and dykes of Upper Carboniferous – Triassic age ( $246 \pm 8$  Ma, Ramos *et al.* 1988) is documented.

#### MINERALIZATION

Based on the early literature (Stoll 1958), the ore deposits in the La Huerta Range are classified into three

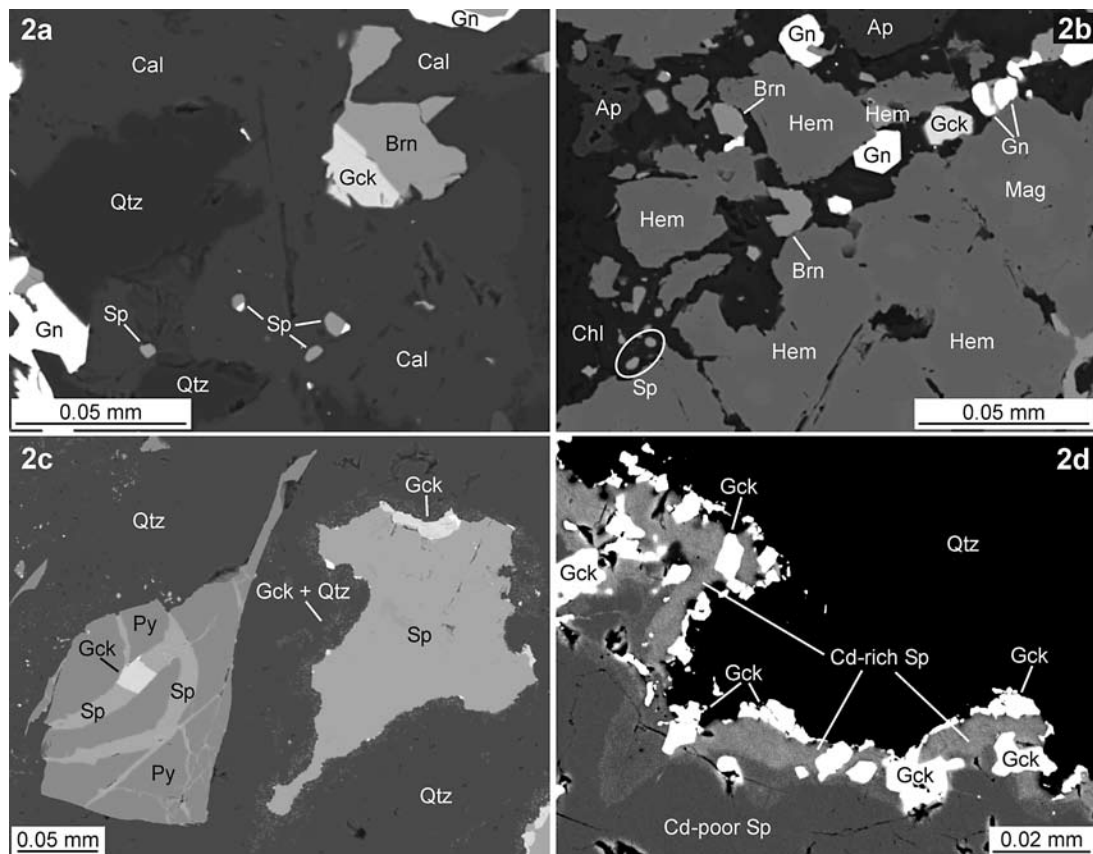
groups: 1) sulfide deposits along shear zones in non-calcareous metamorphic rocks, including auriferous pyrite deposits (*e.g.*, Caledonia–Albion mines in Blanca Creek) and galena–sphalerite deposits with carbonate gangue (*e.g.*, Bella Blenda and Cristal Blenda mines in Yanzi Creek), 2) lenticular deposits of auriferous quartz (*e.g.*, El Morado mining district), and 3) fissure veins with argentiferous galena (*e.g.*, Santo Domingo Creek mines). The deposits are believed to be pre-Tertiary and related to the Upper Carboniferous – Triassic magmatic – metallogenic cycle, according to Ramos *et al.* (1988), Lencinas (1993) and Castro de Machuca *et al.* (2005, 2007, and references therein). The Caledonia Group mines represent a pyrite–gold deposit, apparently formed at considerable depth and at moderate to high temperatures. The greater part of the commercial-grade ore was in the gossan outcrops, formed by supergene enrichment in the zone of cementation, the primary ore being poor in gold.

We sampled the mineralized areas of the Caledonia Group mines (Caledonia–Albion, Azufre, Blanca and Rajo de la Blenda veins) in Blanca Creek. Field observations confirm that the mineralized zones are mostly associated with replacement along fault zones within

the high-grade basement and the occurrence of meta-carbonate outcrops. In some areas, massive rhyolite and rhyolite breccias of Upper Permian age intruded the granulitic basement and may have played a role in the mineralization process (Ramos *et al.* 1988, Lencinas 1993, Castro de Machuca *et al.* 2005, 2007). In this paper, we deal with cadmium-bearing sulfide and associated mineralization at the Caledonia Group mines.

#### *Greenockite and associated minerals*

Representative samples collected from the mineralized zone of the Caledonia Group mines and some samples from the Institute of Geology of the University of San Juan have been investigated using transmitted and reflected light microscopy for primary identification of ore and gangue minerals and observation of textural features. These microscopic investigations and SEM–EDX analyses of representative mineralized samples reveal the presence of several ore minerals in varying parageneses: greenockite + pyrite + sphalerite + galena + chalcopyrite ± arsenopyrite ± pyrrhotite ± bornite ± tennantite ± tetrahedrite ± covellite ± chalcocite ± aikinite ± wittichenite ± matildite ± berrylite ±



miharaite ± geocronite ± hematite ± magnetite (Table 1). The main gangue mineral is quartz. Three different textural types of greenockite can be distinguished.

Type-1 greenockite occurs as small, individual crystals associated with bornite, galena, chalcopyrite, pyrite, hematite, magnetite and tiny grains of sphalerite within late-stage, narrow veinlets and cracks filled with calcite, chlorite, apatite, quartz and K-feldspar (sample BMC-1, Figs. 2a, b) in a strongly altered gneissic rock in contact with metacarbonates. The major ore minerals within this rock are pyrite and magnetite. Hematite typically replaces magnetite at the rim of grains.

In samples BM3-2, BM3-3 and BM4-2, type-1 greenockite occurs as a product of the hypogene

replacement of sphalerite. It forms a narrow, discontinuous rim with Cd-rich sphalerite around corroded, primary Cd-poor sphalerite (Figs. 2c, d, e, f) and generally accompanied by wittichenite or rarely enclosing berryite (Figs. 2e, f). These sphalerite–greenockite intergrowths are rimmed by a corona of tiny (<1 μm) grains of greenockite enclosed in quartz (Fig. 2e). Replacement textures involving Cd-rich sphalerite, greenockite, galena and hematite can also be observed within cracks of primary, Cd-poor sphalerite (Fig. 2g). Cracks filled with Cd-rich sphalerite and greenockite within pyrite may indicate simultaneous growth of these phases (Fig. 2c). Hematite typically accompanies this type of greenockite (Figs. 2f, 1g).

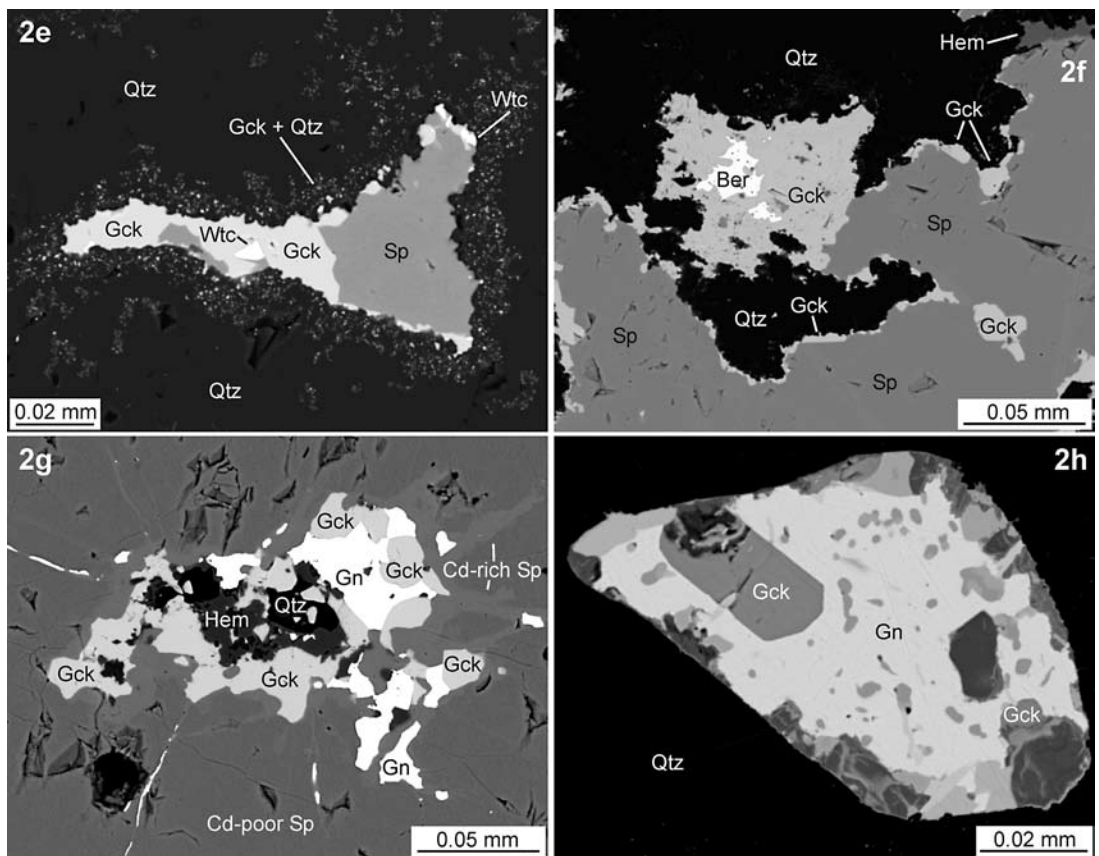


FIG. 2. Back-scattered electron (BSE) images of greenockite. (a) Greenockite of type 1 (Gck) with sphalerite (Sp), galena (Gn) and bornite (Brn) within calcite (Cal) and quartz (Qtz). Sample BMC-1. (b) Greenockite of type 1, sphalerite, galena (white) and bornite within a crack of largely "hematitized" (Hem) magnetite (Mag) with chlorite (Chl). Sample BMC-1. (c) Greenockite of type 2 with sphalerite in crack of pyrite (Py) (left), as replacement of corroded sphalerite (right), and as tiny grains intergrown with quartz around corroded sphalerite (right). Sample BM3-2. (d) Greenockite of type 2 and Cd-rich sphalerite replacing Cd-poor sphalerite. Sample BM3-2. (e) Tiny grains of greenockite within quartz and greenockite of type 2, with wittichenite (Wtc) replacing Cd-poor sphalerite. Sample BM3-2. (f) Greenockite of type 2 with inclusion of berryite (Ber) and replacing sphalerite. Sample BM3-3. (g) Greenockite of type 2 with galena and hematite within Cd-rich and Cd-poor sphalerite. Sample BM3-3. (h) Euhedral greenockite of type 3 with various Ag-Cu-Bi-Pb sulfides (medium grey shades) within galena. Sample BM3-2.

TABLE 1. ASSEMBLAGES OF SULFIDE MINERALS IN GREENOCKITE-BEARING SAMPLES

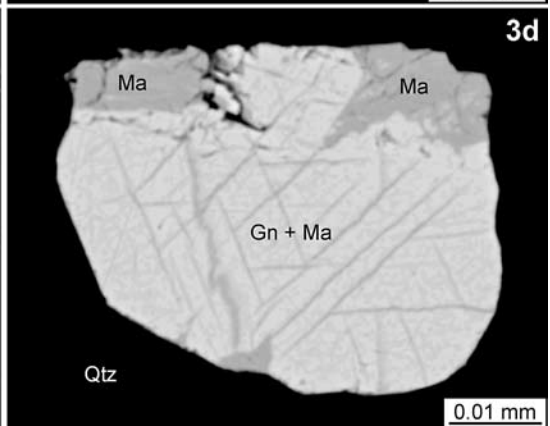
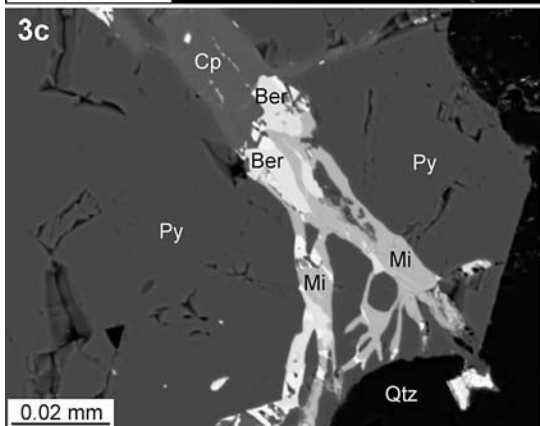
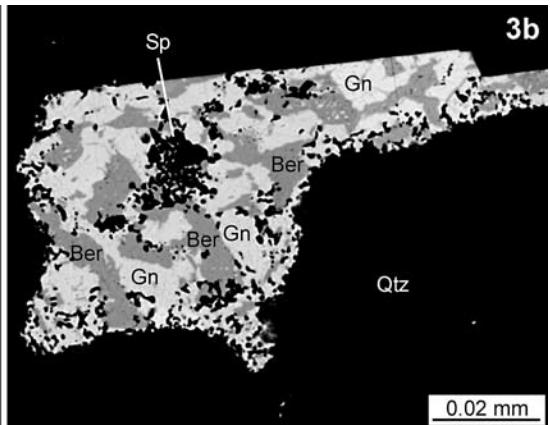
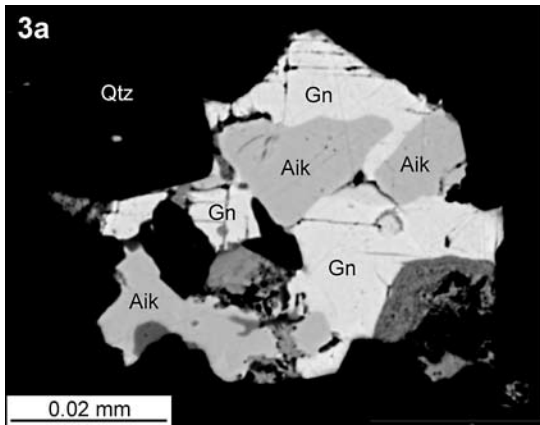
	BMC-1	BM3-2	BM3-3	BM4-2
Pyrite	++	++	+	+
Pyrrhotite			+	+
Sphalerite	+	+	++	+
Greenockite	+	+	+	+
Galena	+	+	+	+
Chalcopyrite	+	+	+	+
Bornite	+			
Arsenopyrite		+	+	+
Copper sulfide minerals (covellite, chalcocite)		+	+	
Tennantite	+	+	+	
Tetrahedrite	+			
Aikinite	PbCuBiS <sub>3</sub>	+		
Wittichenite	Cu <sub>3</sub> BiS <sub>3</sub>	+		+
Matildite	AgBiS <sub>2</sub>	+		+
Berryite	Cu <sub>2</sub> Ag <sub>2</sub> Pb <sub>2</sub> Bi <sub>2</sub> S <sub>18</sub>	+	+	
Miharaite	PbCu <sub>4</sub> FeBiS <sub>8</sub>	+	+	
Geocronite	Pb <sub>14</sub> (Sb,As) <sub>6</sub> S <sub>23</sub>	+		

++: Major sulfide minerals; +: minor and accessory sulfide minerals.

Very rarely, type-3 greenockite occurs as euhedral crystals within galena, accompanied by various Ag–Cu–Bi–Pb sulfides (BM3–2, Fig. 2h).

Apart from greenockite, several Ag–Cu–Bi–Pb–(As–Sb) sulfides are identified for the first time from a number of mineralized samples of the Caledonia Group mines using reflected-light microscopy and electron-microprobe analyses. Aikinite (PbCuBiS<sub>3</sub>) is typically intergrown with galena (Fig. 3a). Berryite [Cu<sub>3</sub>Ag<sub>2</sub>Pb<sub>3</sub>Bi<sub>7</sub>S<sub>16</sub>] occurs intergrown with galena and sphalerite (Fig. 3b), with miharaite and chalcopyrite in cracks of pyrite (Fig. 3c), or as an inclusion in greenockite (Fig. 2f). Matildite (AgBiS<sub>2</sub>) typically forms exsolution lamellae in galena or, rarely, small grains adjacent to galena (Fig. 3d). Tennantite [(Cu,Ag,Fe,Zn)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>] occurs as individual grains with Cd-poor sphalerite, chalcopyrite and hematite (Fig. 3d) or with hematite around galena (Fig. 3f). Wittichenite (Cu<sub>3</sub>BiS<sub>3</sub>) occurs widespread but in small amounts with greenockite of type 2 (Fig. 2e) and as inclusions or adjacent to galena (Fig. 3g).

Less common sulfide minerals, only encountered rarely are: geocronite [Pb<sub>14</sub>(Sb,As)<sub>6</sub>S<sub>23</sub>] as one mono-



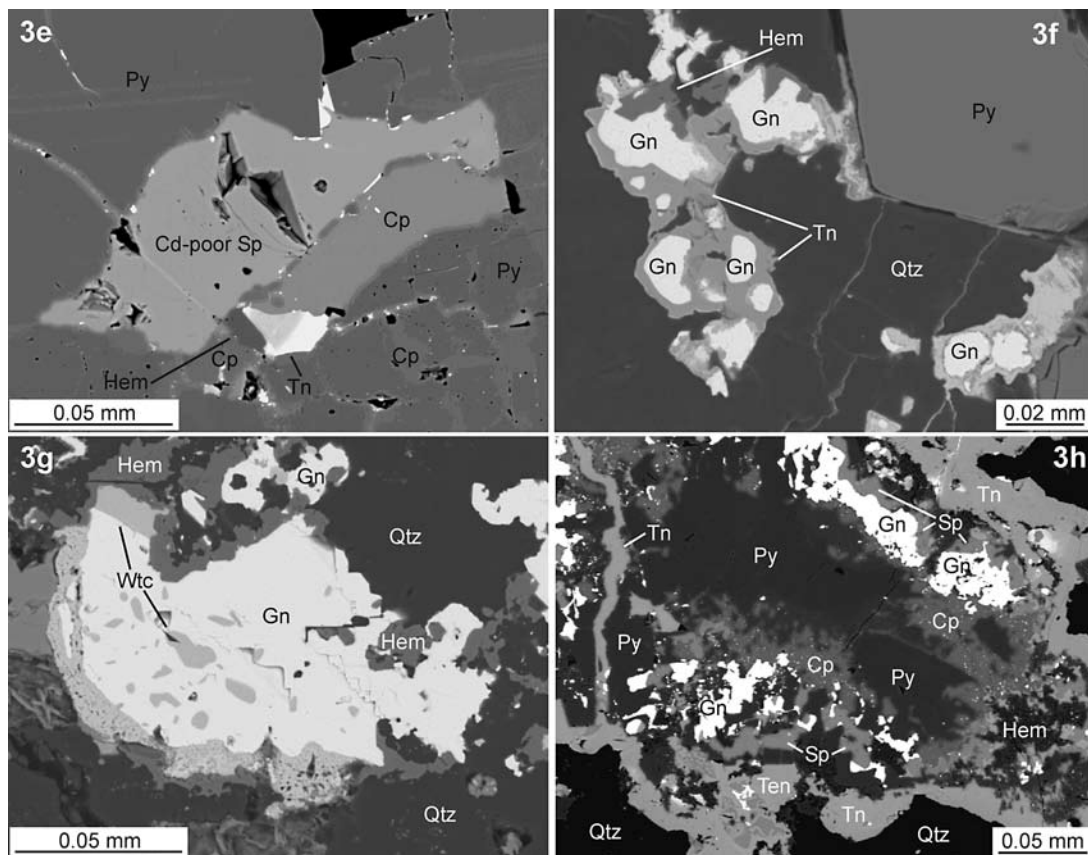


FIG. 3. Back-scattered electron (BSE) images of various sulfides. (a) Aikinite (Aik) intergrown with galena (Gn). Sample BM3-2. (b) Berryite (Ber) intergrown with galena and sphalerite (Sp). Sample BM3-2. (c) Miharaite (Mi), berryite and chalcocopyrite (Cp) within crack of pyrite (Py). Sample BM3-3. (d) Exsolution blebs of matildite (Ma) in galena; at the rim of the galena, possibly primary matildite. Sample BM3-2. (e) Cd-bearing tennantite (Tn) with varying Bi content with Cd-poor sphalerite, chalcocopyrite, hematite (Hem) within pyrite. Sample BM3-2. (f) Cd-bearing tennantite with hematite rimming galena. Sample BM4-2. (g) Wittichenite (Wtc) mostly within galena with hematite. Sample BM4-2. (h) Zoned aggregate of sulfides with pyrite, chalcocopyrite, galena, sphalerite, tennantite and hematite. Sample BMC-2.

phase inclusion in pyrite, miharaite ( $\text{PbCu}_4\text{FeBiS}_6$ ) with berryite and chalcocopyrite in cracks of pyrite (Fig. 3c), and tetrahedrite  $[(\text{Cu}, \text{Fe}, \text{Ag}, \text{Zn})_{12}\text{Sb}_4\text{S}_{13}]$  adjacent to galena.

Hematite is a typical constituent of the late-stage mineralization associated with greenockite, Cd-rich sphalerite and complex sulfides (Figs. 2b, f, g, 3e, f, g).

#### COMPOSITIONS OF THE MINERALS

Back-scattered electron imaging of selected areas and qualitative and quantitative mineral analyses were done on carbon-coated polished thin sections with a SEM JEOL JSM 6310 equipped with an Oxford Link ISIS EDX system and a Microspec WDX system (for

S and Cd) at the Institute of Earth Sciences, University of Graz, Austria. Analytical conditions were: 20 kV accelerating voltage, 6 nA probe current, and 100 s counting time for EDX spectra. Standards used were  $\text{CuFeS}_2$  (S, Fe, Cu), metallic Mn, ZnS (Zn),  $\text{Pd}_3\text{As}$  (As), CuSe (Se), metallic Ag, metallic Cd, NiSb (Sb),  $\text{PbTe}$  (Te, Pb), and  $\text{Bi}_2\text{Te}_3$  (Bi). The detection limits for the EDX are 0.1 wt.% for Ag, Cu, Fe, Mn, Zn; 0.2 wt.% for Sb, Te; 0.3 wt.% for Se; 0.5 wt.% for As; 0.9 wt.% for Bi; 1.5 wt.% for Pb. Sphalerite was also checked for its Ga, Ge and In content. These were invariably found to be less than 0.2 wt.%. The detection limit for Cd was established at 0.1 wt.%. Overlap of  $\text{AgL}\beta$  line on  $\text{CdL}\alpha$  was estimated to be 0.3 wt.% Cd per 100 wt.% Ag and corrected accordingly.

*Greenockite and sphalerite*

Type-1 greenockite has a Zn content of less than 1 mol.% ZnS, but a variable Fe content, from 0.2 to 4.5 mol.% FeS. The composition of sphalerite varies between 0.4 and 1.3 mol.% CdS component and 0.5 to 8 mol.% FeS component (Table 2, anal. 1–4). Systematic zoning could not be observed, which may be due to the very small grain-size of these minerals. Type-2 greenockite is Zn-rich, with 10–25 mol.% of the ZnS component and <0.1 to 3 mol.% of the FeS component (Table 3, anal. 1–4). Individual grains may show a patchy distribution of Zn and Fe. The tiny grains of

TABLE 2. REPRESENTATIVE COMPOSITIONS OF GREENOCKITE AND SPHALERITE GRAINS

	1 Gck	2 Gck	3 Sp	4 Sp	5 Gck	6 Gck
Zn wt. %	0.30	0.48	61.09	59.65	2.84	2.52
Fe	< 0.1	0.22	0.24	4.59	< 0.1	< 0.1
Cd	78.33	76.23	1.29	1.07	74.76	74.15
S	22.16	22.30	30.41	33.26	22.45	21.98
Total	100.84	99.23	*93.03	*98.57	100.05	98.65
Zn	0.007	0.010	0.984	0.894	0.062	0.056
Fe	--	0.005	0.005	0.081	--	--
Cd	1.000	0.980	0.012	0.009	0.944	0.953
S	0.993	1.005	0.999	1.016	0.994	0.991
Cd/(Cd + Zn)	0.993	0.990	0.012	0.010	0.938	0.944

Results of electron-microprobe analyses. Columns 1 and 2 show the compositions of individual grains of greenockite, and columns 3 and 4 show the composition of individual grains of sphalerite from sample BMC-1, representing textural type 1. Columns 5 and 6 show the composition of grains of greenockite in galena from sample BM3-2, representing textural type 3. \*: low total due to very small grain-size. The amounts of Ag, Bi, As, Cu, Mn, Pb, Sb, Se and Te are below detection limit (see text).

TABLE 3. REPRESENTATIVE COMPOSITIONS OF GREENOCKITE AND SPHALERITE REPRESENTING TEXTURAL TYPE 2

sample	1 Gck BM3-2	2 Gck BM3-2	3 Gck BM3-3	4 Gck BM3-3	5 Sp BM3-2	6 Sp BM3-2	7 Sp BM3-3	8 Sp BM3-3	9 Sp BM3-3	10 Sp BM3-2
Zn wt. %	8.28	5.06	9.90	8.85	63.56	57.13	53.06	61.74	62.55	61.74
Fe	< 0.1	< 0.1	0.33	1.17	3.25	8.64	12.11	0.44	1.11	1.28
Cd	68.66	71.43	65.76	65.76	0.43	0.34	0.30	4.50	3.92	4.89
S	23.23	22.46	23.65	23.21	33.14	34.06	33.63	32.25	33.21	31.93
Total	100.22	98.95	99.64	98.99	100.38	100.17	99.10	98.93	100.79	99.84
Zn <i>apfu</i>	0.173	0.110	0.205	0.185	0.940	0.835	0.780	0.945	0.935	0.941
Fe	--	--	0.008	0.029	0.056	0.148	0.208	0.008	0.019	0.023
Cd	0.835	0.899	0.791	0.798	0.004	0.003	0.003	0.040	0.034	0.043
S	0.992	0.991	0.996	0.988	1.000	1.015	1.009	1.007	1.012	0.993
Cd/(Cd + Zn)	0.845	0.891	0.794	0.812	0.004	0.004	0.004	0.041	0.035	0.044

Results of electron-microprobe analyses. Columns 1–4 show compositions of greenockite replacing sphalerite. Columns 5–7 show compositions of sphalerite replaced by greenockite. Columns 8–10 show compositions of late-stage, Cd-rich sphalerite. The amounts of Ag, Bi, As, Cu, Mn, Pb, Sb, Se and Te are below the detection limit (see text).

greenockite within quartz appear to have a similar composition, but owing to their very small grain-size, the analytical totals are very low. Partial analyses give 0.056 at.% Zn, 0.950 at.% Cd and 0.994 at.% S in the formula. Primary sphalerite is Cd-poor, with *ca.* 0.3 mol.% of the CdS component, but variable Fe content ranging from <1 to 21 mol.% FeS (Table 3, anal. 5–7). The distribution of Fe is patchy, with a tendency for Fe to be enriched in the core of individual grains of sphalerite. Late-stage, Cd-enriched sphalerite has up to 4.5 mol.% CdS, but is invariably poor in Fe (<3 mol.% of the FeS component) (Table 3, anal. 8–10). Type-3 greenockite contains 5–7 mol.% ZnS and <0.1 mol.% FeS (Table 2, anal. 5, 6). The chemical composition of the three different textural types of greenockite is plotted in Figure 4 in comparison with data from the literature. The compositions show distinctions among the three types.

Although sphalerite occurs in all samples and shows extreme variation in the concentration of Fe substituting for Zn, no sphalerite was found in the paragenesis with pyrrhotite and pyrite so as to be used as a geobarometer.

*Associated sulfides and oxides*

Tennantite is usually zoned and variably enriched in cadmium (1.44–4.08 wt.%), bismuth (4.34–17.84%) and silver (<0.16–1.16%). Zinc is more abundant than iron. The single grain of tetrahedrite encountered has a Cd content of <0.1 wt.% (Table 4).

All other major and minor sulfides have cadmium contents below the detection limit of the WDX analytical system used (<0.1 wt.%). Typical compositions



of the rare sulfide minerals are given in Table 5. The limited data point to complex parageneses of minerals documented for the first time in the Caledonia Group mines.

## DISCUSSION AND CONCLUSIONS

Stoll (1958) suggested that most of the auriferous quartz-sulfide veins in the Caledonia Group mines are due to replacement along N-S-striking shear zones in propylitized gneissic and meta-igneous host-rocks. The veins strike north-south and dip steeply to the east. The country rock is predominantly marble and related basement rocks, showing minor oxidized patches of sulfides and geochemical base-metal anomalies. The mineralization process seems to be mainly sulfide replacement of the carbonate, with minor filling along discordant steeply dipping shear-zones in the basement rocks. Known down-dip extension is more than 150 meters in the Caledonia and Azufre veins, and they range from 40 to over 150 meters long and 1 to 2.5 meters thick.

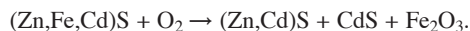
As given in the foregoing sections, greenockite occurs in three different textural types mainly associated with sphalerite and locally with galena. This occurrence is similar to what has been reported by Tarkian & Breskovska (1989) from the Madjarovo Pb-Zn ore district, eastern Rhodope, Bulgaria. In their case, as the Cd concentration in sphalerite did not exceed 0.33 wt.% and the galena is Cd-free, they suggested that the source of the cadmium cannot be sphalerite because of the very low content and the textural relationships. They concluded that the greenockite is of hypogene origin, and crystallized from late-stage hydrothermal

solutions, which were characterized by low Zn and high Cd values.

In the case of the greenockite from the Caledonia Group mines, we have shown three different textural occurrences that indicate a primary origin, as well as evidence of hypogene alteration of Cd-bearing sphalerite. The alteration of sphalerite and the formation of greenockite of type 2 may have taken place involving the following processes:

1. Formation of primary, Cd-bearing sphalerite with the usual range of Cd content (*ca.* 0.3 mol.% CdS) and highly variable Fe content (<1 to 21 mol.% FeS).

2. Partial dissolution of primary sphalerite and replacement by quartz + tiny grains of greenockite (Fig. 2e), together with the formation of Zn-rich greenockite coexisting with Cd-rich and Fe-poor sphalerite and Cu-Bi-Pb-Ag sulfides, *e.g.*, wittichenite (Figs. 2c-f). At the same time, deposition of Zn-rich greenockite and Cd-rich sphalerite within cracks in pyrite has also taken place (Fig. 2c). Whether there is only redistribution of Cd formerly contained within primary sphalerite or addition of Cd together with Cu, Bi, Ag, Pb during greenockite formation is not clear. The presence of hematite together with greenockite (Fig. 2g) also points to the involvement of oxidation reactions like:



Zn-poor greenockite and slightly Cd-enriched sphalerite in sample BMC-1 have formed as separate grains in late-stage cracks not involving replacement processes, except for the partial oxidation of magnetite to hematite adjacent to the cracks (Fig. 2b). Very rare greenockite of type 3 (Fig. 2h), with an intermediate Zn content

TABLE 4. REPRESENTATIVE COMPOSITIONS OF TENNANTITE AND TETRAHEDRITE

sample	Tn BM3-2	Tn BM3-2	Tn BM3-2	Tn BM4-2	Tn-Td BM4-2	Td BM3-2
Cu wt. %	35.19	36.73	41.92	40.88	37.75	35.47
Ag	1.16	0.31	0.16	0.16	0.68	2.65
Fe	1.02	1.89	2.73	0.25	< 0.1	6.57
Zn	4.68	6.54	7.34	7.54	7.45	< 0.1
Cd	4.08	1.62	1.44	1.22	0.25	< 0.1
As	8.41	10.11	14.98	15.24	6.76	< 0.5
Sb	5.16	< 0.2	< 0.2	3.49	11.01	29.07
Bi	14.65	17.84	4.34	4.09	10.77	< 0.9
S	24.54	24.22	27.58	27.26	25.14	24.29
Total	98.89	99.26	100.49	100.13	99.81	98.05
Cu <i>apfu</i>	9.56	9.84	9.98	9.95	9.94	9.54
Ag	0.19	0.05	0.02	0.02	0.04	0.42
Fe	0.32	0.57	0.74	0.07	--	2.01
Zn	1.24	1.70	1.70	1.78	1.91	--
Cd	0.63	0.24	0.19	0.17	0.04	--
As	1.93	2.29	3.03	3.14	1.51	--
Sb	0.73	--	--	0.44	1.51	4.08
Bi	1.21	1.45	0.31	0.30	0.86	--
S	13.19	12.86	13.03	13.13	13.12	12.95
Total	29.00	29.00	29.00	29.00	29.00	29.00

Results of electron-microprobe analyses. Tn: tennantite, Td: tetrahedrite.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF RARE SULFIDES

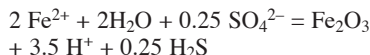
sample	Aikinite BM3-2	Wittichenite BM3-2	Berryite BM3-3	Matildite BM3-2	Miharaite BM3-3	Geocronite BM3-2
Cu wt. %	10.83	38.16	6.31	< 0.1	26.70	< 0.1
Ag	< 0.1	< 0.1	7.14	28.64	< 0.1	< 0.1
Fe	0.55	< 0.1	< 0.1	< 0.1	7.22	< 0.1
As	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	3.51
Sb	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	12.37
Pb	36.08	< 1.5	20.18	< 1.6	21.72	67.08
Bi	35.54	41.93	49.23	53.81	22.97	< 0.9
S	16.32	19.32	16.91	16.43	20.06	16.82
Total	99.32	99.41	99.77	98.88	98.67	99.78
Cu <i>apfu</i>	0.99	3.00	3.04	--	3.92	--
Ag	--	--	2.03	1.03	--	--
Fe	0.06	--	--	--	1.21	--
As	--	--	--	--	--	2.02
Sb	--	--	--	--	--	4.39
Pb	1.01	--	2.98	--	0.98	13.97
Bi	0.99	1.00	7.21	0.99	1.02	--
S	2.95	3.00	15.74	1.98	5.87	22.62
Total	6.00	7.00	31.00	4.00	13.00	43.00

Results of electron-microprobe analyses. The amount of Cd is below the detection limit of 0.1 wt. %.

and without any accompanying sphalerite, point to a Zn-poor fluid during its formation.

Greenockite associated with sphalerite having varying concentrations of ZnS and CdS in greenockite and sphalerite, respectively, has been reported (Table 6) from epithermal deposits (Marcoux *et al.* 1993, Tombros *et al.* 2005), hydrothermal (Oen *et al.* 1974, Tarkian & Breskovska 1989), stratiform Pb–Zn–Ag deposits (Patterson 1985), fumaroles (Chaplygin *et al.* 2007) and from the present study. Based on the textural data and the ZnS concentration in greenockite (<1 mol.% for type-1, 10–25 mol.% for type-2, and 5–7 mol.% for type-3 greenockite) and comparison with the literature data, it seems that the greenockite from Caledonia Group mines is of hydrothermal origin. Further evidence for the hydrothermal origin is indicated by the associated various sulfide and oxide parageneses.

In most of the mineralized samples, hematite is the major Fe-oxide. Precipitation of hematite may have been caused by mixing of reduced ferrous-iron-bearing fluid with another fluid carrying sulfate or oxygen, yielding hydrogen ion plus hematite according to the following reaction (Barnes 1997):



The sulfate reduction in this reaction may well be the source for the sulfide precipitated in chalcopyrite, bornite and chalcocite, as documented in the mineralized samples of the Caledonia Group mines. Reactions such as this are considered to play a role in many hematite-bearing deposits in connection with hematitic alteration.

Patterson (1985) reported that cadmium is found in traces in sphalerite coexisting with greenockite and is not detected at all in galena in the Lady Loretta mineralization in northwestern Queensland. He suggested that there has been significant decoupling

of the geochemical coherence of cadmium and zinc during the formation of the mineralization, which may reflect the changes in physical or chemical conditions during sulfide deposition. These may be related to local oxidizing conditions, as hematite and barite are common accessory minerals in the mineralization. Note that efficient separation of cadmium and zinc can occur in relatively oxidizing environments, as shown by the typical occurrence of cadmium sulfides as supergene minerals (Oen *et al.* 1974).

The presence of Ag–Cu–Bi–Pb sulfides may point to a late-stage, low-temperature overprint of the primary sulfide parageneses, accompanied by the formation of hypogene greenockite, at least partly at the expense of sphalerite. However, on the basis of exsolution textures, one may also conclude that these phases have crystal-

TABLE 6. COMPARISON OF MOL.% ZnS IN GREENOCKITE AND MOL.% CdS IN SPHALERITE FROM VARIOUS OCCURRENCES AND IN THE PRESENT STUDY

	mol.% ZnS in greenockite	mol.% CdS in sphalerite
<b>Epithermal</b>		
Tombros <i>et al.</i> (2005)	< 1; 32-33	<< (wurtzite!)
Marcoux <i>et al.</i> (1993)	5-14	< 0.1-1
<b>“Hydrothermal”</b>		
Oen <i>et al.</i> (1974)	1-5	0.2
Tarkian & Breskovska (1989)	6-11	< 0.3
Hurlbut (1957)	42-59	--
Present study	<1	0.4-1.3 (type 1)
Present study	10-25	0.3; 3-4.5 (type 2)
Present study	5-7	-- (type 3)
<b>Stratiform Pb-Zn-Ag</b>		
Patterson (1985)	8-18	0.1-0.5 (3)
<b>Fumaroles</b>		
Chaplygin <i>et al.</i> (2007)	5-68	0-8

--: sphalerite is not present

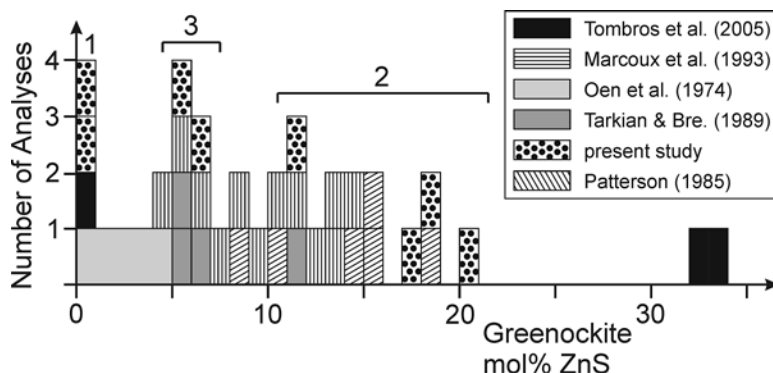


FIG. 4. Histogram showing the variation in mol.% ZnS of our greenockite in comparison with data on greenockite from the literature.

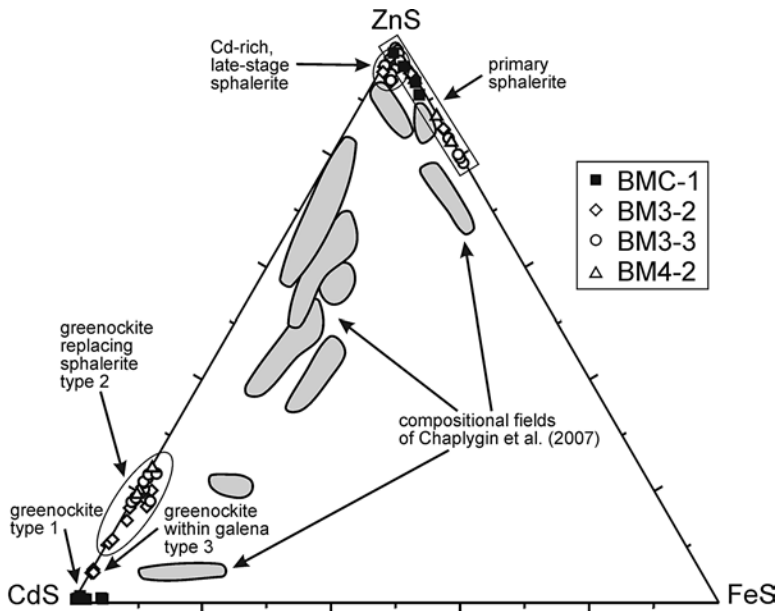


FIG. 5. Composition of greenockite and sphalerite from the Caledonia Mines mineralization in comparison with greenockite, wurtzite and sphalerite from active fumaroles (modified from Chaplygin *et al.* 2007).

lized during cooling rather than by overprinting. The almost end-member composition of greenockite (Fig. 5) and late-stage sphalerite (this study) also point to a low-temperature formation. This is in accordance with the findings of Tauson & Chernychev (1977), who reported a miscibility gap in the ZnS – CdS system between 23 and 70 mol.% CdS at 250°C. In contrast, greenockite and sphalerite from active fumaroles crystallize at temperatures from 400 to 725°C, showing a wide range of solid solutions (Chaplygin *et al.* 2007).

In some parageneses, mineral zonation from a pyrite core to a tennantite rim is observed (Fig. 3h). This is similar to syngenetic hydrothermal mineral zonation related to stratiform sulfide enrichment of volcanic origin. In such mineral deposits, the general sequence of crystallization involved metals in the sequence Fe – Cu – Zn – Pb – Ag – Ba, similar to what we have documented in the mineralized samples of the Caledonia Group mines. It is important to note that the emplacement and genesis of the ore deposits from the Sierra de La Huerta are attributed to the Upper Carboniferous – Triassic tectonomagmatic activity by Ramos *et al.* (1988) and Castro de Machuca *et al.* (2005, 2007, and references therein). Lencinas (1993) noticed that the subvolcanic rhyolitic rocks normally show minor Au and Ag anomalies and are spatially coincident with the occurrences of ore, suggesting a possible genetic rela-

tionship. The formation of greenockite in the Caledonia Group mines could be attributed to low-temperature hydrothermal fluids rich in Cd and poor in Zn or the alteration of Cd-bearing sphalerite, or both.

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