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PGE-BEARING MINERALS IN SILURIAN SEDEX DEPOSITS IN THE POBLET AREA, SOUTHWESTERN CATALONIA, SPAIN

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Abstract

The Lower Llandoverian metasedimentary series of the Prades Mountains, in southwestern Catalonia, Spain, consists of interbedded massive feldspar beds, composed of almost pure anorthite, with chert, phosphate beds, sulfide-rich black shale, massive sulfides and minor calc-silicate beds. The sulfides mainly consist of pyrrhotite with minor chalcopyrite. The metasedimentary rocks are anomalously V- and Cr-rich and contain disseminated minerals bearing precious metals, *e.g.*, sperrylite and palladian löllingite. On the basis of the geological setting of ore formation and the textural relationships among the minerals, a sedex model is proposed for the primary origin of these deposits and occurrences. However, textural patterns and mineral compositions were modified during several episodes. Firstly, Hercynian deformation and associated regional low-grade metamorphism produced cleavage and small-scale veining in the primary associations. Later, contact metamorphism related to Late Hercynian intrusions annealed the mineral associations. A sulfidation stage of mineralization caused replacement of Pd-bearing löllingite by arsenopyrite. During this process, the arsenopyrite structure was unable to accommodate such high Pd contents and, consequently, Pd was precipitated as $PdAs_2$ and scarce small grains of native Pd, disseminated along the löllingite – arsenopyrite contact, in association with argentian gold, and tellurides and selenides of Au, Ag, Bi and Pb.

Keywords: löllingite, palladium, sperrylite, gold, tellurides, selenides, sedex, black shale, metamorphism, Catalonia, Spain.

Sommaire

Les roches métasédimentaires du Llandoverien inférieur des Montagnes de Prades, dans le sud-ouest de la Catalogne, en Espagne, contiennent des alternances de couches à anorthite, de chert, de phosphates, de schiste noir à sulfures (surtout avec de la pyrrhotite et de la chalcopyrite), des sulfures massifs et des calc-silicates. Ces roches sont enrichies en V et Cr, et elles montrent aussi des disséminations de minéraux à métaux précieux, par exemple sperrylite et löllingite palladifère. Le contexte géodynamique et les relations parmi les minéraux suggèrent un modèle primaire de formation du type sedex, mais les compositions minérales et les textures ont été très fortement modifiées par les processus postérieurs. La déformation hercynienne et le métamorphisme régional à faible degré ont produit un clivage et des remobilisations locales en veinules ds minerais. Le métamorphisme de contact lié à la mise en place de roches granitiques tardi-hercyniennes a causé une recristallisation des associations minérales. La löllingite palladifère a été replacée par l'arsénopyrite. Pendant ce processus, le Pd rejeté de la structure de la löllingite precipita sous forme de palladium natif ou de $PdAs_2$ près de l'interface entre les deux minéraux, en association avec l'or argentifère, des séléniures et des tellurures d'or, d'argent, de plomb et de bismuth.

Mots-clés: löllingite, palladium, sperrylite, or, tellurures, séléniures, sedex, schiste noir, métamorphisme, Catalogne, Espagne.

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INTRODUCTION

The Hercynian series of the Catalonian Coastal Ranges, northeastern Spain, contain several sedex-type deposits (Ayora *et al.* 1990). Similar deposits also occur in the Hercynian terranes of the Pyrenees and the Iberian Massif, and in the Montagne Noire district of southern France. Most of the reported occurrences occur in Carboniferous and Cambrian–Ordovician series, but the Silurian series also contains several deposits at its base. In the Prades Mountains, near the Poblet monastery, at the southern part of Catalonian Coastal Ranges (Fig. 1), several sedex deposits hosted by Llandoverian black shale are known. In these deposits, Pd and Pt minerals related to a V–Cr anomaly have been found (Melgarejo 1992, Melgarejo *et al.* 1994). Preliminary analyses of the ore by the lead fire-assay method gave 0.45 ppm Pd, 0.25 ppm Pt, 0.12 ppm Au and 6 ppm Ag.

The occurrence of PGE anomalies in sedimentary rocks has been recently reported in several deposits (Hulbert *et al.* 1992, Coveney *et al.* 1992, Pašava 1993); however, descriptions of the PGE-bearing minerals in these occurrences are sparse. Our aim in this report is to describe the mineral phases that concentrate these elements in the sedex deposits of the Prades Mountains. A description of the accompanying minerals, in particular the V–Cr oxides and V-, Cr-rich silicates, is found in Canet *et al.* (2003).

GEOLOGICAL SETTING

A detailed description of the geology of the area can be found in Canet *et al.* (2003). The Prades Mountains area, located in the southern part of the Catalonian Coastal Ranges (Fig. 1), consists of a Hercynian basement unconformably covered by Mesozoic–Cenozoic series. The Hercynian basement is made up of Lower Paleozoic, Silurian and Devonian metasedimentary rocks, unconformably overlain by Carboniferous series.

In the Prades Mountains, the outcropping Paleozoic series begins with an interbedding of quartzite and black shale (Upper Ordovician – Lower Llandoverian). Above, a Lower Llandoverian ore-bearing unit, up to 30 m thick, comprises a complex interbedding of chert, phosphate beds, anorthite-rich beds, calc-silicates, massive sulfide beds and sulfide-rich shale (Melgarejo 1992). Upper Llandoverian and Wenlockian sedimentary rocks consist of pyrite-rich black shale (Ashauer & Teichmuller 1935).

The Devonian series consists of black shale and quartzite of Eifelian – Famennian age (Melgarejo 1992). The Carboniferous series starts with Tournaisian chert beds ("lidites"). These cherts are followed by a thick sequence, up to 2 km, of a detrital series ranging in age from Visean to Lower Westphalian.

The Hercynian Orogeny deformed all the above-mentioned rocks, and a regional metamorphism was mainly developed under low-grade conditions, in the epizone. The deformation phases produced folds with NW–SE axes and an axial plane dipping toward the northeast. The axial cleavage usually is poorly developed. Thrust structures were produced in the flanks of folds.

Late Hercynian granitic rocks, Permian in age, intruded all the above series, and produced contact-metamorphic aureoles up to 500 m wide (Melgarejo 1992, Serra & Enrique 1989). Several generations of porphyritic dikes cut these intrusions and the metamorphic rocks.

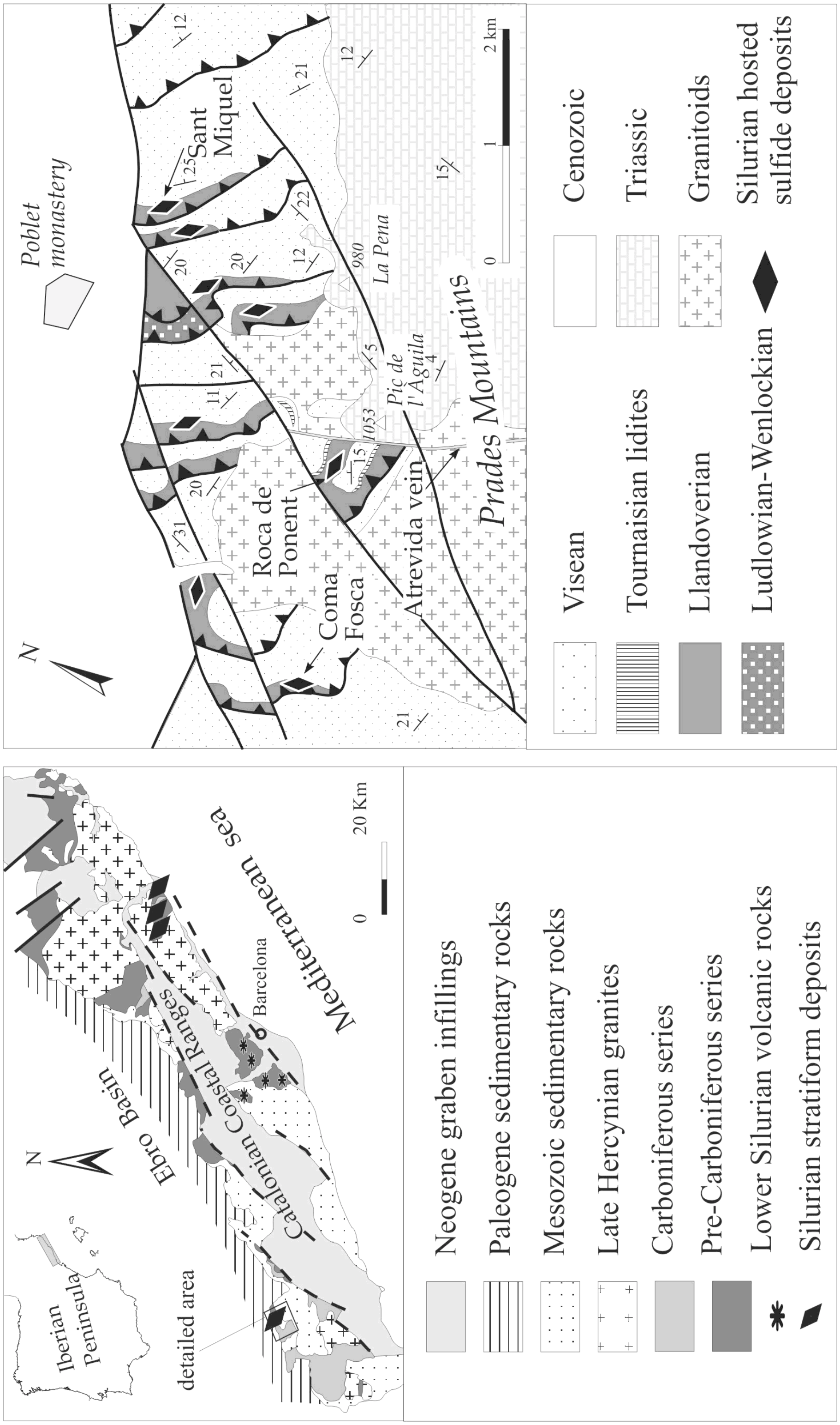
In addition, two types of mineralized quartz veins occur in the vicinity of the leucogranites: a) sulfide-rich quartz veins, with molybdenite, galena, chalcopyrite and sphalerite, accompanied by tellurides of Bi and Ag, and b) quartz veins with scheelite and minor ferberite (Melgarejo & Ayora 1984).

A 200-m-thick Triassic megasequence unconformably overlies the Paleozoic rocks. Alpine faults constitute the boundary between the Prades Mountains Massif and the Cenozoic sediments of the Ebro and Prelitoral basins (Fig. 1). Many of these faults contain Ba–F–Pb–Zn–Cu–Ni–Co–Ag veins. For example, the Atrevida vein is more than 4 km in length, 200 m in depth and up to 8 m in width. The vein filling consists of barite in the uppermost parts and quartz in the deepest levels. The ore minerals consist mainly of galena and sphalerite, although Bi minerals (native bismuth, bismuthinite, Bi tellurides) and Ni–Co arsenides, sulfoarsenides and sulfides (rammelsbergite, skutterudite, gersdorffite, millerite, linnaeite) may locally be dominant. These ores are also accompanied by silver minerals, *e.g.*, acanthite, hessite, pearceite – polybasite, proustite and native silver (Melgarejo & Ayora 1985a, b, Canals *et al.* 1992).

STRUCTURE OF THE SULFIDE-RICH UNITS FROM THE LOWER SILURIAN SERIES

Many ore-bearing Llandoverian showings have been discovered in the Prades Mountains, and most of them acted as loci of detachment along Hercynian thrusts. Therefore, the ore-bearing units crop out as thin belts approximately parallel to the direction of the folds and thrusts of the first tectonic phase, N130°. The most important ore-bearing outcrops in terms of extent, thickness, and mineral contents, are found at Roca de Ponent, Coma Fosca and Sant Miquel (Fig. 1). The outcropping Lower Llandoverian series were affected by thermal metamorphism to various grades.

FIG. 1. Distribution of Silurian stratiform occurrences in the Catalonian Coastal Ranges, and geological map of the northern part of the Prades Mountains. Simplified after Melgarejo (1992).



Poblet monastery
Sant Miquel
Roca de Ponent
Coma Fosca
Atrevida vein
Pic de l'Àguila
La Pena
Prades Mountains
2 km
Visean
Tournaisian lidites
Llandoverian
Ludlowian-Wenlockian
Cenozoic
Triassic
Granitoids
Silurian hosted sulfide deposits
Iberian Peninsula
detailed area
Ebro Basin
Catalonian Coastal Ranges
Barcelona
Mediterranean sea
20 Km
Neogene graben infillings
Paleogene sedimentary rocks
Mesozoic sedimentary rocks
Late Hercynian granites
Carboniferous series
Pre-Carboniferous series
Lower Silurian volcanic rocks
Silurian stratiform deposits

The stratigraphy of the ore-bearing interval can be described as an interstratification of roughly monomineralic beds, from millimeters to several decimeters in individual thickness. These are anorthite-rich beds, phosphate beds, sulfide-rich shales, massive sulfide beds, and scarce calc-silicate layers. A detailed description of all these units is found in Canet *et al.* (2003).

Ore minerals mainly occur disseminated within the above-mentioned metasedimentary units. In all cases, pyrrhotite is the most common ore mineral, whereas chalcopyrite is less abundant. In addition, many other ore minerals occur in minor amounts, including minerals containing precious elements. V–Cr oxides, rutile and ilmenite are common as disseminations in the sulfide-rich shales, whereas V- and Cr-bearing silicates occur mainly in the anorthite-rich beds (Canet *et al.* 2003). Uraninite is common as minuscule grains in all the beds.

Although most sulfides occur disseminated within the above-described rocks, they can form massive beds and lenses up to 20 cm thick. Pyrrhotite, sphalerite and chalcopyrite are the main components of these lenses. Galena is very rare, and minor amounts of scheelite are present. The massive sulfides are especially abundant in Sant Miquel and Coma Fosca.

Small pyrrhotite – chalcopyrite veins cross-cut the sulfide-rich metasedimentary rocks. These first-generation veins are irregular in shape and distribution. They have limited continuity and a thickness of less than 3 mm. They are restricted to the sulfide-bearing units, thus suggesting that they were remobilized during regional metamorphism.

All the assemblages mentioned exhibit textures indicating that they were affected by the Hercynian deformation and the Late Hercynian thermal metamorphism.

Finally, some undeformed late veins of pyrite crosscut all the above assemblages. In addition, late, undeformed and unmetamorphosed of pyrite replaces pyrrhotite, and gives rise to a bird's-eye texture.

Conditions of Analysis

The mineral associations have been studied in thin and polished sections. Images obtained with a scanning electron microscope (SEM) and qualitative analyses were produced using a JEOL and a Cambridge Stereoscan 120 electron microscopes at the Serveis Científico-Tècnics de la Universitat de Barcelona (Spain). The samples were carefully examined in backscattered electron (BSE) mode, in order to determine the distribution of heavy elements in mineral grains. The minerals were quantitatively analyzed with a JEOL electron microprobe (energy-dispersion mode) at Carleton University, Ottawa, Canada, and in wavelength-dispersion mode using a CAMECA SX–50 at the Serveis Científico-Tècnics of the University of Barcelona, and a CAMEBAX at the Musée d'Histoire Naturelle, Paris. Conditions of analysis of the ore minerals were: 25 kV, 20 nA, beam diameter of 1 μm, and a counting time of 10 s. We used the following standards: nickel oxide (Ni*K*α), galena (Pb*L*α), ZnS (Zn S*K*α), Ag_2Te (Te*L*α), silver metal (Ag*L*α), gold metal (Au*L*α), guanajuatite (Se*L*α), palladium metal (Pd*L*α), platinum metal (Pt*L*α), cobalt metal (Co*K*α), gallium arsenide (As*L*α), bismuth metal (Bi*L*α), indium antimonide (Sb*L*α), and hematite (Fe*K*α).

Minerals of the Platinum Group and Ag–Au: Modes of Occurrence

All the platinum-group minerals (PGM) appear in the sulfide-rich shale beds, and are linked to As; Pt is found as sperrylite ($PtAs_2$), and Pd mainly occurs in the löllingite structure, or as a Pd arsenide. Other palladium minerals (native palladium, stibiopalladinite), argentian gold, and Ag–Au–Pb tellurides and selenides (hessite, petzite, clausthalite, altaite) typically occur related to the contact between palladian löllingite and arsenopyrite. An idealized distribution of the precious-metal-bearing minerals in these rocks is shown in Figure 2.

Sperrylite

Sperrylite, $PtAs_2$, is the only Pt mineral found in these deposits, and only in the Sant Miquel occurrence. It is uncommon, and occurs disseminated in the sulfide-rich shale horizons as small, round crystals (up to 10 μm in diameter). Sperrylite formed before the contact metamorphism, as is indicated by the development of triple-point annealing contacts with pyrrhotite grains (Fig. 3). The grains of sperrylite are surrounded by later veins of pyrite, but in contrast to löllingite, they do not display a reaction rim of S-rich PGM. The mineral composition approaches that of the ideal formula (Table 1).

Palladian löllingite

Palladian löllingite is the most common Pd-bearing mineral in the Sant Miquel occurrence. It occurs as small grains (up to 100 μm in size) that, in all cases, are partly replaced by Pd-free arsenopyrite (Fig. 4). This replacement is due to late sulfidation processes, and it takes place at the same time as the replacement of pyrrhotite by pyrite. X-ray mapping demonstrates that the palladium is concentrated in the löllingite crystals (Fig. 5). The palladium contents are very variable from grain to grain, as well as within each grain. The amount of Pd ranges between 0 (the most common value) up to 3 wt.% (Table 1). Although there is no documentation related to PGE contents in löllingite, Gervilla *et al.* (1991) have experimentally demonstrated that other arsenides (for example, Ni–Co arsenides reported in the Betic–Rifean ultrabasic rocks in Spain and Morocco) may contain

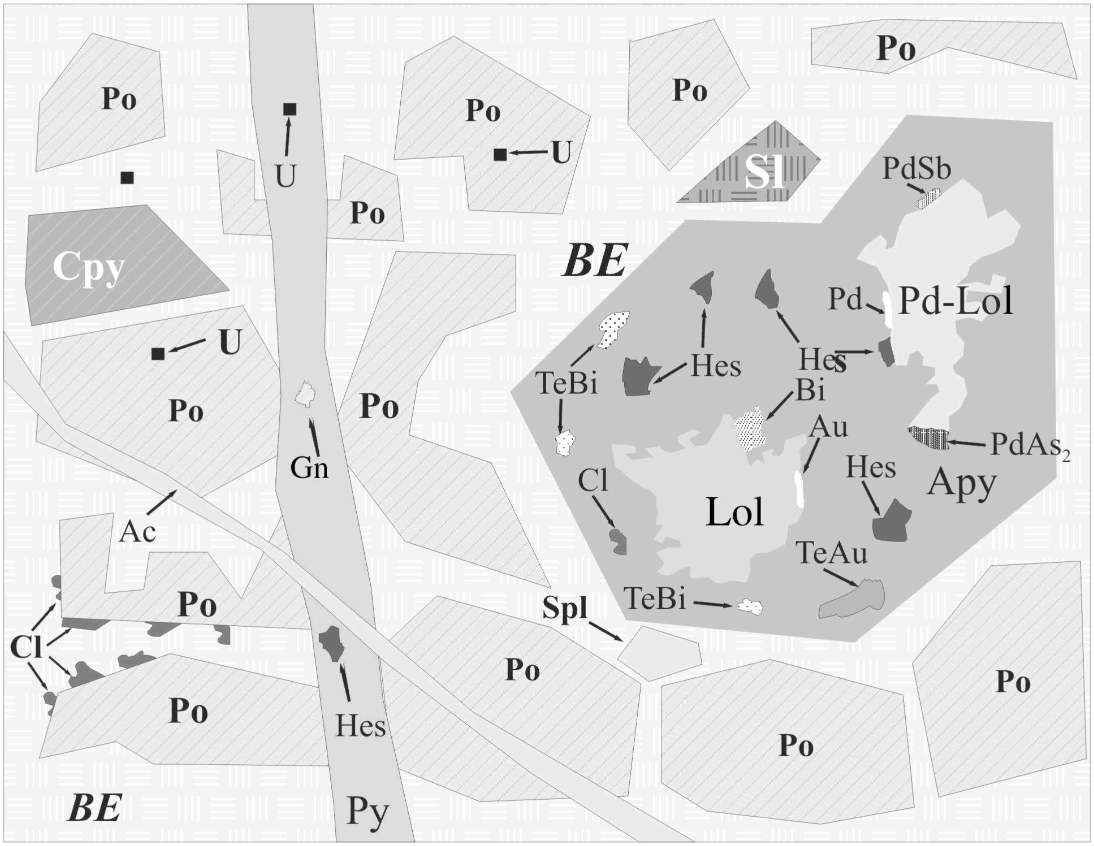


FIG. 2. Idealized sketch showing the distribution of precious metals and some associated mineral phases in the Prades Mountains deposits. Po, pyrrhotite; BE, late generation of pyrite replacing pyrrhotite, with bird's-eye texture. Symbols: Spl: sphalerite, Cpy: chalcopyrite, Cl: clausthalite, Hes: hessite, Apy: arsenopyrite, $PdAs_2$: palladium arsenide, Au: argentian gold, Pd: native palladium, PdSb: stibiopalladinite, TeAu: petzite, TeBi: bismuth tellurides, Lol: löllingite, Pd–Lol: palladian löllingite, Gn: galena, Ac: acanthite, U: uraninite.

important amounts of Pd (up to 8.8 wt.%). Cabri *et al.* (2002) also reported the occurrence of traces of Pd in löllingite crystals.

Other Pd minerals

Native palladium and stibiopalladinite were found only in one sample as small platelets less than 2 μm in diameter, rimming the contact between palladian löllingite and arsenopyrite. The size of these grains did not allow quantitative chemical analyses. Moreover, a Pd–As mineral phase less than 3 μm in diameter occurs as small grains at this contact. Electron-microprobe analyses suggest a composition close to $PdAs_2$ (Table 1), which could correspond to an unnamed Pd arsenide.

Argentian gold

Argentian gold appears in the Sant Miquel and Roca de Ponent occurrences, at the replacive contact between löllingite and arsenopyrite, or as small inclusions into the arsenopyrite crystals (Fig. 6). It forms small irregular grains, up to 30 μm in size, with an average composition of $Au_{65}Ag_{35}$ (Table 1). A similar relationship between gold grains and the löllingite – arsenopyrite contact has already been reported in Archean lode-gold deposits (Neumayr *et al.* 1993).

Mercurian silver

Mercurian silver was found only in one case, at the löllingite – arsenopyrite replacive contact in the Sant

TABLE 1. CHEMICAL COMPOSITION AND STRUCTURAL FORMULA OF PRECIOUS-METAL-BEARING MINERALS, SILURIAN SEDEX DEPOSITS IN THE POBLET AREA, SOUTHWESTERN CATALONIA, SPAIN

	Js-β	*Au*	*Hes* (1)	*Hes* (2)	*PdAs₂* (1)	*PdAs₂* (2)	*Spy* (1)	*Spy* (2)	*Spy* (3)	*Ptz* (1)	*Apy* (1)	*Lol* (1)	*Lol* (2)	*Lol* (3)	*Lol* (4)	*Lol* (5)	*Lol* (6)	*Lol* (7)	*Lol* (8)
Ag wt.%	-	65.00	63.50	62.15	-	-	-	-	-	38.40	-	-	-	-	-	-	-	-	-
Au	-	21.90	-	-	-	-	-	-	-	22.40	-	-	-	-	-	-	-	-	-
Pd	-	-	-	-	39.40	38.10	-	-	0.12	-	0.09	1.80	2.70	1.50	0.30	0.17	0.13	0.62	2.39
Pt	-	-	-	0.26	-	-	53.39	53.10	52.59	-	0.01	-	-	-	-	0.11	-	0.00	0.35
Te	21.20	0.20	36.20	37.15	0.50	0.60	-	-	-	30.30	-	0.30	0.30	0.30	0.30	-	-	-	-
Fe	0.10	6.00	-	0.12	2.30	3.30	2.63	2.56	2.89	4.10	32.92	21.40	21.70	22.10	23.90	23.37	23.92	21.65	20.82
Bi	76.26	2.10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ni	-	-	-	-	1.00	1.20	0.10	0.05	-	-	0.14	4.10	3.70	3.70	3.30	3.38	3.22	3.89	3.51
Co	-	-	-	-	0.30	0.40	0.02	0.08	0.03	-	0.92	1.80	1.20	1.80	1.40	1.32	1.11	1.48	1.98
S	2.69	2.30	-	0.07	0.20	0.10	0.19	0.12	0.24	1.10	19.39	0.40	0.40	0.80	1.60	1.28	1.43	1.81	0.55
As	-	4.00	-	-	54.20	55.80	42.62	42.76	42.56	2.50	46.38	69.90	70.30	69.30	69.20	70.04	69.88	70.80	71.12
Sb	-	-	-	-	0.90	1.20	-	-	-	-	-	0.30	0.30	0.30	0.30	-	-	-	-
Total	100.55	101.50	99.70	99.75	98.80	100.70	98.94	98.67	98.43	98.80	99.84	100.00	100.60	99.80	100.30	99.67	99.69	100.25	100.72
Ag *apfu*	-	0.629	2.075	1.964	-	-	-	-	-	2.998	-	-	-	-	-	-	-	-	-
Au	-	0.116	-	-	-	-	-	-	-	0.958	-	-	-	-	-	-	-	-	-
Pd	-	-	-	-	1.000	0.939	0.000	0.000	0.004	-	0.001	0.019	0.029	0.016	0.003	0.002	0.001	0.006	0.025
Pt	-	-	-	0.005	-	-	0.952	0.948	0.937	-	0.000	-	-	-	-	0.002	-	-	0.007
Te	1.800	0.002	1.000	0.993	0.011	0.012	-	-	-	2.000	-	0.005	0.005	0.005	0.005	-	-	-	-
Fe	0.020	0.112	-	0.007	0.111	0.155	0.164	0.160	0.180	0.618	0.952	0.808	0.815	0.831	0.877	0.859	0.876	0.774	0.771
Bi	3.960	0.010	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	0.020	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ni	-	-	-	-	0.046	0.054	0.006	0.003	0.000	0.000	0.004	0.147	0.132	0.132	0.115	0.118	0.112	0.132	0.124
Co	-	-	-	-	0.014	0.018	0.001	0.005	0.002	0.000	0.025	0.064	0.043	0.064	0.049	0.046	0.039	0.050	0.070
S	0.910	0.075	-	0.007	0.017	0.008	0.020	0.013	0.026	0.289	0.977	0.026	0.026	0.052	0.102	0.082	0.091	0.112	0.035
As	-	0.056	-	-	1.953	1.954	1.980	1.987	1.974	0.281	1.000	1.968	1.969	1.942	1.893	1.918	1.909	1.888	1.965
Sb	-	-	-	-	0.020	0.026	-	-	-	-	-	0.005	0.005	0.005	0.005	-	-	-	-

Symbols: *Js-β*: joséite-β, *Au*: argentian gold, *Hes*: hessite, *PdAs₂*: arsenic–palladium mineral, *Spy*: sperrylite, *Ptz*: petzite, *Apy*: arsenopyrite, *Lol*: löllingite. The electron-microprobe data are expressed in wt.% and converted to atoms per formula unit (*apfu*).

Miquel occurrence. It occurs as fine platelets less than 1 μm in diameter. This size prevents quantitative chemical analyses.

Ag and Au tellurides

Petzite, Ag_3AuTe_2, and hessite, Ag_2Te, occur in association with clausthalite (PbSe) and altaite (PbTe). With the exception of hessite, which grains can reach 50 μm in size, the size of the above minerals is always smaller than 10 μm (Fig. 6). Chemical data are given in Table 1. Precious metal tellurides occur in two positions: forming individual grains sparsely distributed within the silicate matrix, and related to the late sulfur-rich minerals (Fig. 6). They are randomly distributed as irregular grains inside arsenopyrite, but they can also occur as irregular grains at the border of pyrrhotite grains, as well as into sulfidation-induced veins composed of pyrite.

Acanthite

Acanthite, Ag_2S, occurs as scarce, small irregular grains (up to 20 μm in diameter) disseminated in the sulfide-rich shale horizons; it can also occurs at the contact between pyrrhotite grains or in the pyrite veinlets. In the Roca de Ponent deposit, acanthite has also been found as a product of infilling of late veinlets that cut the last replacement of pyrite; thus, it is probably epigenetic and related to the mineralization that gave the Atrevida Ba–F–Pb–Ni–Co–Ag–As Alpine vein.

Other Metallic Minerals

Pyrrhotite

Pyrrhotite is the most common ore mineral in all the deposits and occurrences studied. Beds of more than 50% pyrrhotite, up to 1 cm thick, are very common. The shape and size of pyrrhotite grains depend on the grade of contact metamorphism. In deposits affected by lower grades, pyrrhotite is fine grained, and grains are flattened according to the regional schistosity; euhedral hexagonal platelets are common. In those deposits affected by a higher grade of metamorphism, pyrrhotite is usually coarse-grained and anhedral, and displays a granoblastic texture with the associated silicates.

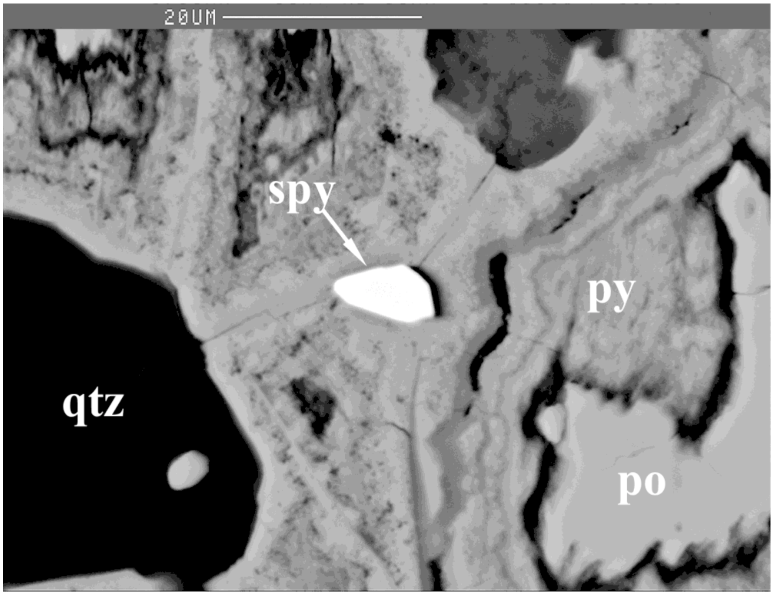


FIG. 3. Sperrylite grain (spy) in sulfide-rich shale, associated with pyrrhotite (Po) and late-generation pyrite (py). Note the quartz grains (qtz) as a component of the metapelites. SEM, BSE image. Scale bar: 20 μm.

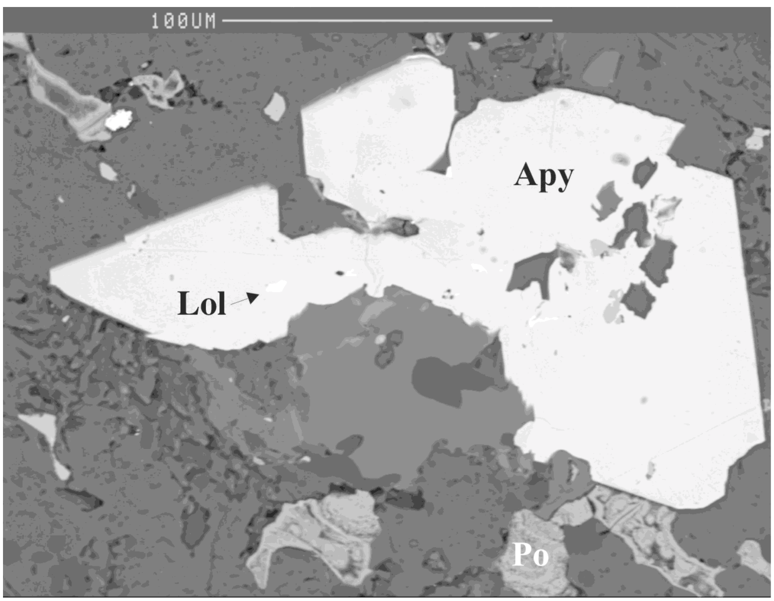


FIG. 4. Palladian löllingite (Lol) replaced by arsenopyrite (Apy) in sulfide-rich shale. Pyrrhotite (Po) has been almost completely replaced by late pyrite. SEM, BSE image. Scale bar: 100 μm.

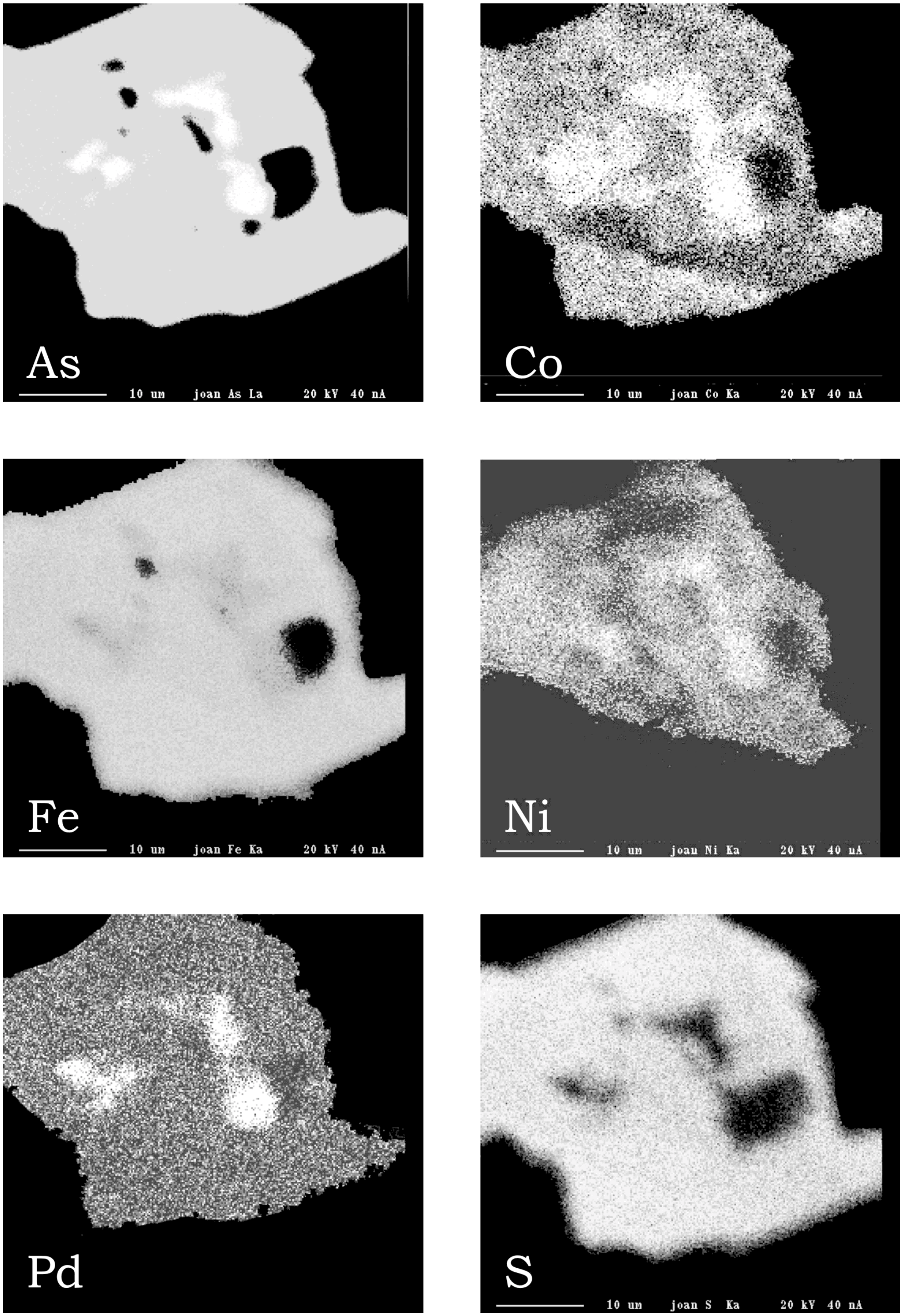


FIG. 5. X-ray mapping of arsenopyrite – palladian löllingite grains, showing a good correlation of Pd, Co and As. Brighter areas in the first figure are löllingite. Electron-microprobe data; scale bar: 10 μm.

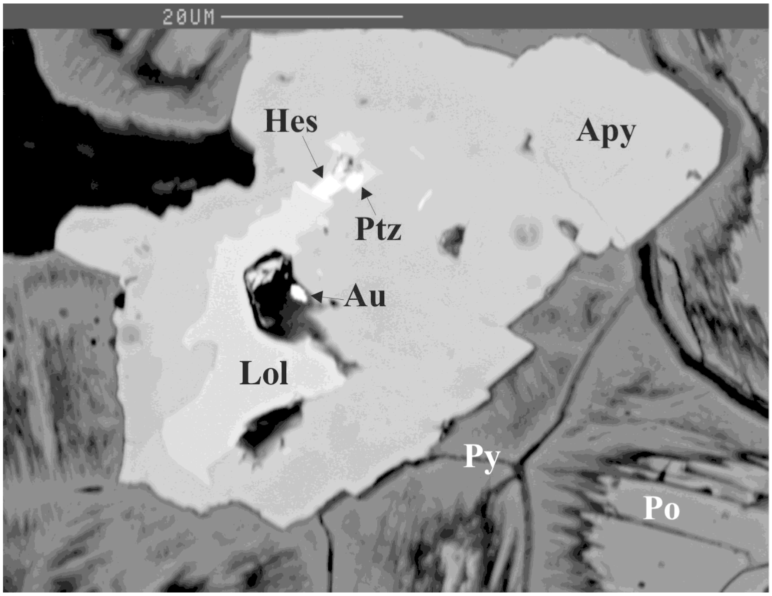


FIG. 6. Distribution of some precious metals in relation to the arsenopyrite – löllingite contact: Argentian gold (Au) close to the contact between löllingite (Lol) and arsenopyrite (Apy) and hessite (Hes) and petzite (Ptz) enclosed in arsenopyrite. The association is surrounded by pyrrhotite (Po), almost completely replaced by late pyrite (Py). SEM, BSE image. Scale bar: 20 μm.

In addition to disseminated grains and massive beds, pyrrhotite usually is the dominant mineral infilling the first-generation veinlets. These veins are irregular in shape, and consist only of sulfides. These veins are older than the thermal metamorphism, as indicated by annealing textures of its sulfide grains. Most grains of pyrrhotite are affected by late sulfidation, leading to its replacement by pyrite, typically with a bird's-eye texture.

Arsenopyrite

Arsenopyrite grains are relatively common in the pelitic matrix. They form diamond-shaped subhedral to euhedral crystals, usually smaller than 2 mm across, produced by the replacement of löllingite. In most cases, the löllingite crystals have been almost completely replaced, and only some irregular relics remain. Arsenopyrite crystals are very rich in inclusions of precious-metal-bearing minerals.

Chalcopyrite

Chalcopyrite is the third ore mineral in abundance (after pyrrhotite and late pyrite), and occurs in all deposits as anhedral grains up to 100 μm in diameter. It is usually found in the massive pyrrhotite beds, or in the first-generation veinlets. Chalcopyrite crystals have been affected by all episodes of deformation and metamorphism.

Pyrite (*and marcasite*)

Sulfur-rich sulfides are rare in these deposits. At least three types of pyrite, all of them post-deformation, can be observed in these deposits. The first was produced by the replacement of pyrrhotite, and consists of poikiloblastic subhedral or anhedral crystals, up to 300 μm in size. The second type of pyrite occurs in veinlets, up to 2 cm wide, along with galena, sphalerite and chalcopyrite. The third type of pyrite formed as a late replacement of pyrrhotite, which leads to the development of the bird's-eye texture. Pyrite is accompanied by barite and acanthite, and therefore it could be related to the Alpine hydrothermal processes that led to vein-type barite mineralization in the area.

Sphalerite

Anhedral grains of sphalerite up to 50 μm in size are scattered among the silicate matrix, and in the first-generation veinlets. Sphalerite grains display textural evidence of equilibrium with pyrrhotite and, in general, they do not contain chalcopyrite blebs. The sphalerite is

Fe-rich (up to 11 wt.% Fe), as expected by its association with pyrrhotite, and has low contents of Mn (1.6 wt.%) and Cd (0.4 wt.%).

Pb selenides and tellurides

Clausthalite, PbSe, is common in sulfide-rich shale from all the deposits, and it is the main Pb mineral in all these outcrops, whereas altaite (PbTe) and galena are very rare. Like hessite, these minerals occur at the border of pyrrhotite grains, as irregular inclusions (up to 20 μm) in arsenopyrite, in association with argentian gold and with pyrite in late veinlets, thus suggesting a connection with late sulfidation in the area.

Bi minerals

Bismuth tellurides, mainly joséite-β (Bi_4Te_2S) and native bismuth, are very abundant as inclusions in arsenopyrite from the Roca de Ponent occurrence, associated with argentian gold (Fig. 7). In this outcrop, the arsenopyrite crystals can be seen with the naked eye and are concentrated in discrete millimeter-thick beds.

Molybdenite and tungstenite

Molybdenite platelets (about 2 × 50 μm) are sparsely distributed throughout all the sulfide-rich shale horizons. Molybdenite occurs both in association with pyrrhotite in the pelitic matrix, or within the late veins of pyrite. In the first case, molybdenite grains are arranged according the regionally developed slaty cleavage; in the second one, it forms radial aggregates or single crystals randomly oriented. Tungstenite develops a thin syntactic rim on molybdenite (Fig. 8).

PARAGENETIC SEQUENCE

The sequence of crystallization of the sulfide ores in the Silurian deposits from the Prades Mountains was reported by Alfonso *et al.* (2002); Canet *et al.* (2003) describe the sequence defined by the accompanying minerals. A synthesis of all these data is shown in Figure 9.

The textural patterns of the main disseminated sulfides (pyrrhotite, chalcopyrite and sphalerite) suggest a syngenetic origin with the host Llandoverian metasedimentary rocks. This assemblage of minerals was clearly formed before deformation and thus is premetamorphic, as indicated by the development of cleavage in the deposits located in the outermost part of the contact-metamorphic aureole, and by the development of annealing textures in those located in the innermost part of the contact aureole. Textures typical of ore deposits formed in submarine environments, such as framboids and botryoids (Large 1983, Pesquera & Velasco 1993, Valdés-Nodarse *et al.* 1993, Pérez & Melgarejo 1998), are not preserved.

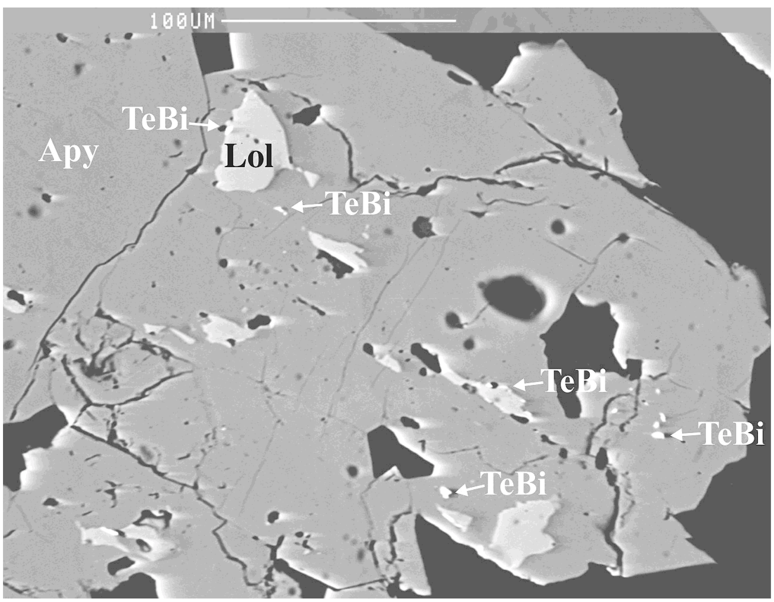


FIG. 7. Replacement contact between Pd-free löllingite (Lol) and arsenopyrite (Apy), enriched in bismuth tellurides (TeBi). SEM, BSE image. Scale bar: 100 μm.

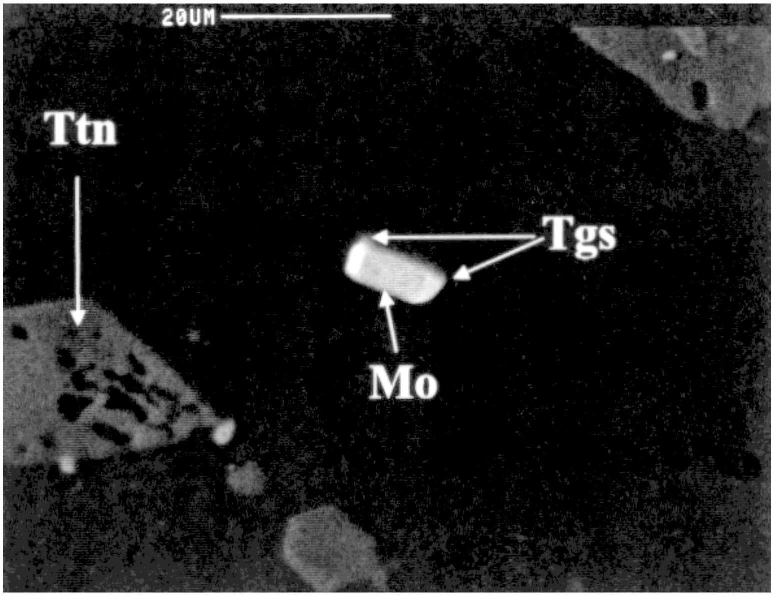


FIG. 8. Molybdenite platelet (Mo) rimmed by tungstenite (Tgs), accompanied by titanite (Ttn). SEM, BSE image. Scale bar: 20 μm.

On the other hand, in the case of several fine-grained ore minerals, it is difficult to establish the timing of formation. Molybdenite, for example, is euhedral and fine-grained, and in no case seems to replace other minerals. Therefore, it can also be considered as syngenetic. Either molybdenite or jordisite (amorphous Mo-sulfide) occurs in many black-shale-hosted sedimentary-exhalative deposits (Fan 1983, Coveney & Cheng 1991). In addition, Pašava *et al.* (1996) reported the presence of disseminations of molybdenite in the black shale units of the Bohemian Massif, in association with framboidal pyrite. These authors consider that the Mo was derived from submarine hydrothermal-volcanogenic activity.

Sperrylite displays the same textural patterns (annealing triple points, rounded grain borders) as the associated sulfide minerals (chalcopyrite, pyrrhotite). Therefore, we conclude that the Pt was present in the sediment before the contact metamorphism. Furthermore, the syngenetic formation of pyrrhotite indicates a low activity of sulfur in the hydrothermal solutions, and in those conditions, löllingite formed instead of arsenopyrite (Scott 1983). This fact also suggests that the PGE were present in the sedimentary unit before metamorphism took place.

Other minerals (galena, löllingite, scheelite) are included in poikiloblastic minerals and could have formed early. In addition, the anoxic environment of the sedimentary basin could favor the formation of tungstenite ($W^{4+}S_2$), although small amounts of scheelite could also be formed at this stage.

The general occurrence of cordierite and "chiastolitic" andalusite in the black shale units is indicative of a medium-grade contact metamorphism. Cordierite is mainly found in the Fe- and Mg-rich beds, whereas andalusite is present in the more Al-rich black shale. These minerals commonly enclose sulfides.

The emplacement of dikes of porphyritic granite associated with Late Hercynian intrusions locally produced the remobilization of the earlier ores. In the Sant Bernat ravine, south of the Poblet Monastery, these dikes (usually barren) are enriched in sulfides along their contacts. The mineralization occurs as pseudomorphs of feldspars and mafic minerals, with similar mineralogy to that of the stratiform deposits (galena, pyrrhotite, chalcopyrite, sphalerite, scheelite), but also comprises some sulfur-rich minerals (pyrite, arsenopyrite). Therefore, the sulfidation process that led to replacement of löllingite by arsenopyrite and the remobilization of precious metals can be related to this stage.

A very late hydrothermal episode was produced at higher $f(S_2)$ (bird's-eye texture in pyrite) and at more oxidizing conditions (presence of barite in small cracks in the bird's-eye textures). In the bird's-eye cracks, other minerals that are common in the Atrevida late vein, as galena and acanthite, can be recorded. Therefore, this late stage of crystallization could be related to the circulation of the same fluids as those that formed the Ba–F–Pb–Ni–Co–Ag–As-bearing Atrevida vein.

Discussion

The occurrence of PGE-enriched sedimentary rocks has been reported in several environments, mostly directly related to black shales (Coveney *et al.* 1992, Fan *et al.* 1992, Hulbert *et al.* 1992, Pašava 1993, Kucha *et al.* 1993). Pd and Pt enrichments have also been reported from VMS deposits (*i.e.,* Pan & Xie 1992). These enrichments cause a considerable controversy over their origin, mainly owing to the absence at present of contemporary models. A problem for interpretation of the origin is the paucity of detailed descriptions of the PGE-bearing minerals and their textures in these sedimentary units. As an example, high concentrations of the PGE have been documented in black shale of the Bohemian Massif (Pašava *et al*. 1996), but the carrier phases have not been identified.

Some aspects of the deposits from the Prades Mountains, however, point out that these, at least, are of sedimentary-exhalative origin: 1) The mineralization is stratiform and is hosted by detrital sedimentary rocks. The first stage of ore mineralization is syngenetic with the sedimentary host-rocks. The mineralization displays the same deformation and metamorphic disturbances as the host sediments. 2) There are monomineralic strata of “abnormal” metasediments: feldspars, chert, phosphate, and sulfides. This is a typical pattern of many sedimentary-exhalative deposits in the Catalonian Coastal Ranges: in Cambrian – Ordovician deposits (Gimeno & Viladevall 1983, Ayora *et al.* 1990) or in Carboniferous deposits (Melgarejo 1992, Ayora *et al.* 1990, Canet 2001). Similar meta-exhalites also occur in Ordovician and Devonian stratiform deposits in the Pyrenées (Bois *et al.* 1976), and in the Proterozoic series of Bohemia (Gabriel 1991). 3) Although the host sequence of the mineralization contains black shale, the content of organic matter in the mineralized beds is low. 4) Volcanic rocks are not present in the Silurian series of the area. However, contemporaneous Silurian alkali basaltic rocks have been reported by Carmona & Viladevall (1983) at the eastern area of the Catalonian Coastal Ranges. 5) An extensional geotectonic setting in the area, active since the Silurian up to the Lower Carboniferous, is suggested by an intraplate alkali volcanism in the Lower Silurian series (Carmona & Viladevall 1983, Gil Ibarguchi *et al.* 1990) and in the Lower Carboniferous (Melgarejo & Martí 1989), and by the synsedimentary faulting that caused major changes in thickness and lithology in the upper Paleozoic series (Melgarejo 1992). All these characteristics are comparable to those used by Pouit (1984) to define sedex deposits and their geodynamic setting.

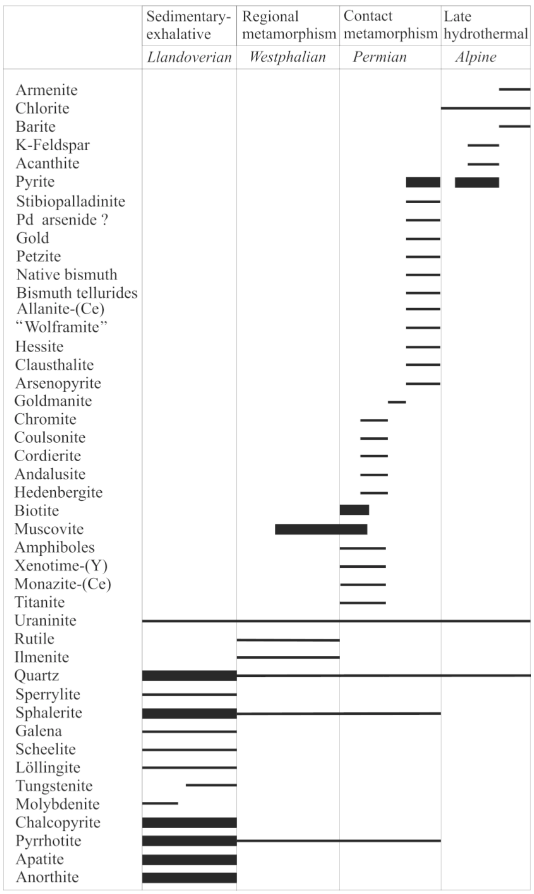


FIG. 9. Episodes and sequence of crystallization in the stratiform mineralization of the Prades Mountains.

Moreover, in the southern parts of the Catalonian Coastal Ranges, sedex deposits containing Mn–Pb–Zn–Cu–Ag are widespread throughout the Carboniferous series (Melgarejo 1992, Canet 2001). According to Pouit (1984), the continuous development of sedex deposits during a long period of time is common. Sedimentary-exhalative deposits are common throughout the Paleozoic series in other parts of the Catalonian Coastal Ranges (Ayora *et al.* 1990) and the Pyrenées (Pouit 1978, 1986, Ayora & Casas 1985). Although there are no data about PGE in these deposits, the association arsenopyrite – löllingite – gold has been reported in many of them (Oudin *et al.* 1988).

In some occurrences of black shale from the Czech Republic, there are PGE anomalies associated with phosphate and carbonate beds, as well as marked anomalies of Ni, Se, Y, Ni and Bi (Pašava 1993). Other associations of a more varied mineralogy can be found in the Catalan Lower Silurian, and similar phosphate mineralization has been reported in Silurian base-metal deposits from the Iberian Massif (Moro *et al.* 1992). Furthermore**,** phosphate precipitation takes place in present-day submarine exhalative environments, as was verified in the Punta Mita coastal vents, in Mexico (Prol-Ledesma *et al*. 2002).

The V–Cr–PGE association is not rare in exhalative deposits. Chromian spinel and vanadoan amphiboles, associated with Pd minerals, have been reported in Nairne, Australia (Graham 1978). The association of noble metals and V (as evidenced in the compositions of muscovite, phlogopite, pumpellyite, garnet, epidote, Sb-enriched vesuvianite and titanite) has also been reported in the Hemlo deposit, Ontario, Canada (Pan & Fleet 1992).

The origin of these deposits is still controversial, and the category "PGE in black shales" may include deposits with different origins. A hydrothermal origin, related to volcanism, was proposed to explain the high contents of base metals and PGE in black shales (Grauch *et al.* 1991, Pašava *et al.* 1993, 1996). Pašava (1993) suggested that PGE anomalies develop because of exhalative processes around volcanic centers in rift areas, with the participation of organic matter.

Conclusions

Textural relations among the ores and their accompanying minerals indicate that mineralization in the Prades Mountains originated in Silurian times, and the ore assemblages were formed and modified during three main events: Silurian, Permian and Alpine. The Silurian episode produced a stratiform mineralization in a euxinic basin, comprising an interbedding of V- and Cr-rich beds, feldspar-rich beds, black shale, massive sulfides and phosphates. Au, Ag and PGE minerals formed also at this stage. Pt concentrated in sperrylite and Pd in löllingite.

During the Permian, contact-metamorphism produced annealing of mineral associations, including the PGE mineralization. Sulfidation of the mineral association produced replacement of löllingite by arsenopyrite. During this process the arsenopyrite structure was unable to accommodate such high concentrations of Pd ; this element was thus redistributed as new Pd-rich minerals along the löllingite – arsenopyrite contact.

The PGE-bearing stratiform mineralization acts as a preconcentration for late metallogenetic events. Therefore, the possibility that PGE can be removed from the stratiform mineralizations to other associations of the area (skarns and low-temperature Alpine veins) must be envisaged.

The reported characteristics show the similarity between the Prades Mountains deposits and many others emplaced in similar geodynamic contexts throughout the Hercynian massifs of western Europe. For instance, many Silurian deposits in the Iberian Massif (*e.g.*, Moro *et al.* 1995), and others of Ordovician and Devonian age in the Pyrenées (*e.g.*, Bois *et al.* 1976). As a result, these data open an interesting possibility for exploration for precious metals in sedimentary series and low-temperature Ni–Co–As veins in western Europe.

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References

Alfonso P., Canet, C., Melgarejo, J.C. & Fallick, A.E. (2002): Sulphur isotope composition of Silurian shale-hosted PGE–Ag–Au–Zn–Cu mineralisations of the Prades Mountains (Catalonia, Spain). *Mineral. Deposita* **38**, 192-212.

Ashauer, H. & Teichmuller, R. (1935): Die variszische und alpidische Gebirgbildung Kataloniens. *Abh. Ges. Wiss. Gott. math.-phys. Kl.* **3**, 1-79.

Ayora, C. & Casas, J.M. (1985): Mineralización estratiforme de Pb–Zn–Cu en el Paleozoico de Bassegoda (Pirineo Oriental). *Acta Geol. Hisp.* **20**, 233-239.

________, Soler, A. & Melgarejo, J.C. (1990): The Hercynian ore deposits from the Catalonian Coastal Ranges. *Acta Geol. Hisp.* **25**, 65-73.

Bois, J.P., Pouit, G., Gros, Y., Guérange, B. & Picot, P. (1976): Les minéralizations de Zn (Pb) de l'anticlinorium de Pierrefitte: un exemple de gisements hydrothermaux et sédimentaires associés au volcanisme dans le Paléozoïque des Pyrénées centrales. *Bull. Bureau de Recherches Géologiques et Minières* (*sér. II*) **6**, 543-567.

Cabri, L.J., Gervilla, F., Kojonen, K., Oberthür, T., Weiser, T., Johnason, B., Sie, S.H., Campbell, J.L., Teesdale, W.J. & Laflamme, J.H.G. (2002): Comparison of PGE trace analyses of pentlandite and some arsenides and sulpharsenides by EPMA and micro-PIXE. *9th Int. Platinum Symp., Program Abstr.*, 73-76.

Canals, A., Cardellach, E., Rye, D. & Ayora, C. (1992): Origin of the Atrevida vein (Catalonian Coastal Ranges, Spain): mineralogic, fluid inclusion and stable isotope study. *Econ. Geol.* **87**, 142-153.

Canet, C. (2001): *Dipòsits sedimentàrio-exhalatius del Paleozoic del SW dels Catalànides: model de dipòsit.* Ph.D. thesis, Universitat de Barcelona, Barcelona, Spain.

________, Alfonso, P., Melgarejo, J.C. & Jorge, S. (2003): V-rich minerals in contact-metamorphosed Silurian sedex deposits in the Poblet area, southwestern Catalonia, Spain. *Can. Mineral.* **41**, 561-579.

CARMONA, J.M. & VILADEVALL, M. (1983): Estudio geológico del sector oriental del macizo Paleozoico del Montnegre (Provincia de Barcelona). *Rev. Inv. Geol.* **36**, 83-96.

COVENEY, R.M., JR. & CHENG, N. (1991): Ni–Mo–PGE–Au rich ores in Chinese black-shales and speculations on possible analogues in the United States. *Mineral. Deposita* **26**, 83-88.

________, MUROWCHICK, J.B., GRAUCH, R.I., CHENG, N. & GLASCOCK, M.D. (1992): Field relations, origins, and resource implications for platiniferous molybdenum–nickel ores in black shales of South China. *Explor. Mining Geol.* **1**, 21-28.

FAN, D. (1983): Polyelements in the lower Cambrian black shales series in southern China. *In* The Significance of the Trace Metals in Solving Petrogenetic Problems and Controversies (S.S. Augustithis, ed.). Theophrastus Publ. S.A., Athens, Greece (447-474).

________, YE, J. & LUI, T. (1992): Black-shale series-hosted silver–vanadium deposits of the upper Sinian Doushantuo Formation, western Hubei province, China. *Explor. Mining Geol.* **1**, 28-38.

GABRIEL, Z. (1991): Upper Proterozoic chert-hosted Au–Ni–V–Cr–Ba mineralization. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). Proc. 25th SGA Anniversary Meeting, Balkema, Rotterdam, The Netherlands (41-43).

GERVILLA, F., MAKOVICKY, E., MAKOVICKY, M. & ROSE-HANSEN, J. (1991): Los arseniuros de níquel como portadores de elementos del grupo del platino. Resultados experimentales en el sistema Ni–As–Pd a 790°C y 490°C. *Bol. Soc. Esp. Min*. **14**, 17-18.

GIL IBARGUCHI, J.I., NAVIDAD, M. & ORTEGA, L.A. (1990): Ordovician and Silurian igneous rocks and orthogneisses in the Catalonian Coastal ranges. *Acta Geol. Hisp.* **25**, 23-30.

GIMENO, D. & VILADEVALL, M. (1983): Las mineralizaciones estratiformes en Fe–Pb–Zn–F–Cu–(W) y en Pb del Cambro-Ordovícico del macizo de Les Guilleries. *Rev. Inv. Geol.* **36**, 121-133.

GRAHAM, J. (1978): Manganochromite, palladium antimonide, and some unusual mineral associations at the Nairne pyrite deposit, South Australia. *Am. Mineral.* **63**, 1166-1174.

GRAUCH, R.I., MUROWCHICK, J.B., COVENEY, R.M., JR. & CHENG, N. (1991): Extreme concentration of Mo, Ni, PGE and Au in anoxic marine basins, China and Canada. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). Proc. 25th SGA Anniversary Meeting, Balkema, Rotterdam, The Netherlands (531-534).

HULBERT, L.J., CARNE, R.C., GRÉGOIRE, D.C. & PAKTUNC, D. (1992): Sedimentary nickel, zinc, and platinum-group element mineralization in Devonian black shales at the Nick property, Yukon, Canada: a new deposit type. *Explor. Mining Geol*. **1**, 39-62.

KUCHA, H., PRZYBYLOWICZ, W., LANKOSZ, M., VAN LANGEVELDE, F. & TRAXEL, K. (1993): EPMA, micro-PIXE, synchrotron microprobe and TEM study of visible and invisible accumulations of Au and PGE in black shale and organic matrix, Kupferschiefer, Poland. *Mineral. Mag*. **57**, 103-112.

LARGE, D.E. (1983): Sediment-hosted massive sulphide lead–zinc deposits. *In* Sediment-Hosted Stratiform Lead–Zinc Deposits (D.F. Sangster, ed.). *Mineral. Assoc. Can., Short Course Handbook* **9**, 1-29.

MELGAREJO, J.C. (1992): Estudio geológico y metalogenético del Paleozoico del Sur de las Cordilleras Costeras Catalanas. *Mem. Inst. Tecnol. Geomin. España* **103**.

________ & AYORA, C. (1984): Mineralización filoniana de tungsteno en rocas graníticas del sector S de las Cordilleras Costeras Catalanas. *Bol. Geol. Min. Esp*. **95**, 235-245.

________ & ________ (1985a): La Mina Atrevida (Ba,F,Pb, Zn,As,Ni,Co,Ag), Cadenas Costeras Catalanas: un ejemplo de filón triásico de zócalo-cobertera. *Rev. Inv. Geol*. **40**, 87-102.

________ & ________ (1985b): Mineralogía, paragénesis y condiciones de formación de la mina "Atrevida", Cadenas Costeras Catalanas**.** *Rev. Inv. Geol.* **41**, 47-65.

________ & ________ (1992): Mineralización exhalativo-sedimentaria de manganeso en los tramos basales de la serie carbonífera del Priorato – Sierra de Miramar (Cataluña). *Bol. Geol. Min. Esp.* **103**, 544-550.

________, JORGE, S., TAYLOR, R.P. & JONES, P. (1994): The occurrence of platinum group and Ag–Au–V–Cr–REE minerals in Lower Silurian sedimentary-exhalative (sedex) sulphide mineralization, Poblet, Catalonia, Spain. *Int. Mineral. Assoc., 16th Gen. Meeting* (*Pisa*), *Abstr. Program*, 274.

________ & MARTÍ, J. (1989): El vulcanisme bàsic del Carbonífer Inferior de la Serra de Miramar. *Acta Geol. Hisp*. **24**, 131-138.

MORO, M.C., FERNÁNDEZ-FERNÁNDEZ, A., CEMBRANOS, M.L. & TIMÓN, S.M. (1995): The sulphide mineralization of the Silurian black shales of the Zamora Province (Spain). *In* Mineral Deposits: from their Origin to their Environmental Impacts (J. Pašava, B.B. Kríbek & K. Zák, eds.). Balkema, Rotterdam, The Netherlands (961-965).

________, GIL AGERO, M., CEMBRANOS, M.L., PÉREZ DEL VILLAR, L., MONTERO, J.M., FERNÁNDEZ FERNÁNDEZ, A. & HERNÁNDEZ SÁNCHEZ, E. (1992): Aluminofosfatitas silúricas de la Península Ibérica: síntesis preliminar. *Bol. Soc. Esp. Mineral.* **15**, 227-232.

NEUMAYR, P., CABRI, L.J., GROVES, D.I., MIKUCKI, E.J. & JACKMAN, J.A. (1993): The mineralogical distribution of gold and relative timing of gold mineralization in two Archean settings of high metamorphic grade in Australia. *Can. Mineral.* **31**, 711-725.

OUDIN, E., POUIT, G. & TOLLON, F. (1988): Les minéraux en trace de Ni–Co, Sn, Ge–Ga, Pb–Sb, Ag et Au témoins de l'évolution de l'hydrothermalisme de l'Ordovicien au Dévonien dans les minéralizations zincifères des Pyrénées centrales. *Bull. Minéral.* **111**, 49-63.

PAN, YUANMING & FLEET, M.E. (1992): Mineral chemistry and geochemistry of vanadian silicates in the Hemlo gold deposit, Ontario, Canada. *Contrib. Mineral. Petrol*. **109**, 511-525.

________ & XIE, Q. (1992): Extreme fractionation of platinum group elements in volcanogenic massive sulfide deposits. *Econ. Geol*. **96**, 645-651.

PAŠAVA, J. (1993): Anoxic sediments – an important environment for PGE; an overview. *Ore Geol. Rev*. **8**, 425-445.

________, HLADÍKOVÁ, J. & DOBES, P. (1996): Origin of Proterozoic metal-rich black shales from the Bohemian Massif, Czech Republic. *Econ. Geol*. **91**, 63-79.

________, SULOVSKY, P. & KOVALOVÁ, M. (1993): Geochemistry and mineralogy of Proterozoic metal-rich blackshales from the Bohemian Massif, Czech Republic, with a description of possible new molybdenum selenide and telluride phases. *Can. Mineral.* **31**, 745-754.

PÉREZ, R.G. & MELGAREJO, J.C. (1998): El yacimiento Matahambre (Pinar del Río, Cuba): estructura y mineralogía. *In* Geología y Metalogenia de Cuba: una Introducción (J.C. Melgarejo & J. Proenza, eds.). *Acta Geol. Hisp.* **33**, 133-152.

PESQUERA, A. & VELASCO, F. (1993): Ore metamorphism in sulfide mineralizations from the Cinco Villas Massif (western Pyrenees, Spain). *Econ. Geol.* **88**, 266-282.

POUIT, G. (1978): Différents modèles de minéralisation "hydrothermale sédimentaire" à Zn (Pb) du Paléozoïque des Pyrénées centrales. *Mineral. Deposita* **13**, 411-421.

________ (1984): Les gisements à sulfures massifs exhalatifs-sédimentaires: une mise au point sur leur classification et la méthodologie de leur recherche. *Chron. Rech. Min.* **476**, 31-34.

________ (1986): Les minéralisations Zn–Pb exhalatives sédimentaires de Bentaillou et de l'anticlinorium Paléozoïque de Bosost (Pyrénées ariégeoises, France). *Chron. Rech. Min.* **485**, 3-16.

PROL-LEDESMA, R.M., CANET, C., MELGAREJO, J.C., TOLSON, G., RUBIO-RAMOS, M.A., CRUZ-OCAMPO, J.C., ORTEGA-OSORIO, A., TORRES-VERA, M.A. & REYES, A. (2002): Cinnabar deposition in submarine coastal hydrothermal vents, Pacific margin of central Mexico. *Econ. Geol.* **97**, 1331-1340.

SCOTT, S.D. (1983): Chemical behaviour of sphalerite and arsenopyrite in hydrothermal and metamorphic environments. *Mineral. Mag.* **47**, 427-435.

SERRA, P.R. & ENRIQUE, P. (1989): The Late-Hercynian intrusives from southern Catalonian Coastal Ranges (NE Spain), and their epiplutonic to subvolcanic level of magma emplacement. *Rend. Soc. Ital. Mineral. Petrol.* **43**, 817-829.

VALDÉS-NODARSE, E.L., DÍAZ CARMONA, A., DAVIES, J.F., WHITEHEAD, R.E. & FONSECA, L. (1993): Cogenetic sedex Zn–Pb and stockwork Cu ore, western Cuba. *Explor. Mining Geol.* **2**, 297-305.

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