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V-RICH MINERALS IN CONTACT-METAMORPHOSED SILURIAN SEDEX DEPOSITS IN THE POBLET AREA, SOUTHWESTERN CATALONIA, SPAIN

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Abstract

The Lower Llandoverian metasedimentary rocks of the Prades Mountains, southwestern Catalonia, Spain, consist of interstratified anorthite-rich beds, chert beds, phosphate beds, sulfide-rich black shale (with mainly pyrrhotite and minor chalcopyrite), massive sulfide lenses and calc-silicate beds. These metasedimentary rocks are anomalously enriched in V and Cr, and have disseminated minerals of precious metals: mainly sperrylite and palladian löllingite. The V- and Cr-rich associations are the result of an isochemical metamorphism of V- and Cr-rich protoliths. The contact metamorphism of V-rich shale produced metapelitic hornfels with V-rich aluminosilicates and V–Cr oxides. The occurrence of V oxides in apparent equilibrium with V-rich silicates suggests a limit for the V and Cr contents in these aluminosilicates at the conditions of thermal metamorphism. On the other hand, metamorphism of anorthite- and V-,Cr-rich sedimentary rocks produced V- and Cr-rich silicates, such as goldmanite, V-rich amphiboles, V-rich titanite and V-rich allanite.

Keywords: vanadium oxides, vanadium silicates, chromium, sedex, black shale, Silurian, contact metamorphism, Catalonia, Spain.

Sommaire

Les roches métasédimentaires du Silurien Inférieur des montagnes de Prades, dans le sud-ouest de la Catalogne, en Espagne, contiennent des alternances de couches de roches à anorthite, des cherts, des niveaux à phosphates, des schistes noirs à sulfures (pyrrhotite surtout, avec chalcopyrite), des sulfures massifs et des calc-silicates. Ces roches métasédimentaires sont très riches en V et Cr, et elles contiennent des minéraux disséminés de métaux précieux: sperrylite et löllingite palladifère. Ces paragenèses à V et Cr sont le produit d'un métamorphisme isochimique de protolithes riches en V et Cr. Le métamorphisme de contact d'ardoises

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riches en vanadium a produit des cornéennes à aluminosilicates vanadifères, biotite vanadifère, et des oxydes de V–Cr. La présence locale des associations d'oxydes et des silicates de V apparemment en équilibre témoignerait d'une limite pour les activités de V et Cr dans ces silicates aux conditions du métamorphisme de contact. En plus, le métamorphisme de roches riches en anorthite, V et Cr a mené au développement de silicates de V et Cr, par exemple la goldmanite, les amphiboles vanadifères, la titanite vanadifère et l'allanite vanadifère.

Mots-clés: oxydes de vanadium, silicates de vanadium, chrome, gisement de type sedex, schistes noirs, Silurien, métamorphisme de contact, Catalogne, Espagne.

INTRODUCTION

The Paleozoic series of the Catalonian Coastal Ranges, in northeastern Spain, contains several sedex-type deposits (Ayora *et al.* 1990). Similar deposits occur in the Hercynian terranes of the Pyrenées, the Iberian Massif and the Montagne Noire district in southern France. Most of the reported occurrences occur in Carboniferous and Cambrian–Ordovician series, but the Silurian series also contain several deposits at its base. In some of these Silurian deposits in the Prades Mountains, near the monastery of Poblet, in the southern part of the Catalonian Coastal Ranges (Fig. 1), Pd and Pt minerals related to a V–Cr anomaly have recently been found (Melgarejo 1992, Melgarejo *et al.* 1994). In addition to the unusually high contents of precious metals, these metasedimentary rocks contain unusual associations of V- and Cr-rich minerals. Our aim in this contribution is to describe these mineral associations and their evolution during the geological history of the area.

GEOLOGY OF THE PRADES MOUNTAINS

The Prades Mountains are located at the southern part of the Catalonian Coastal Ranges (Fig. 1). They consist of a Hercynian basement unconformably covered by Mesozoic and Cenozoic series. The basement consists of Silurian and Devonian series unconformably overlain by Carboniferous rocks, essentially sedimentary in origin.

A stratigraphic profile of the Lower Paleozoic series from the Southern Catalonian Coastal Ranges is presented in Figure 2. The early Silurian series starts with a 20-m-thick unit made up of interbeddings of quartzite and black shale. Above, an ore-bearing unit (up to 30 m thick) contains a complex interbedding of various metasedimentary rocks: chert, phosphate, anorthite-rich beds, calc-silicate beds and sulfide-rich shales. On the basis of the graptolite fauna in the black shales, these lowest units have been regionally attributed to the Lower Llandoverian (Melgarejo 1992).

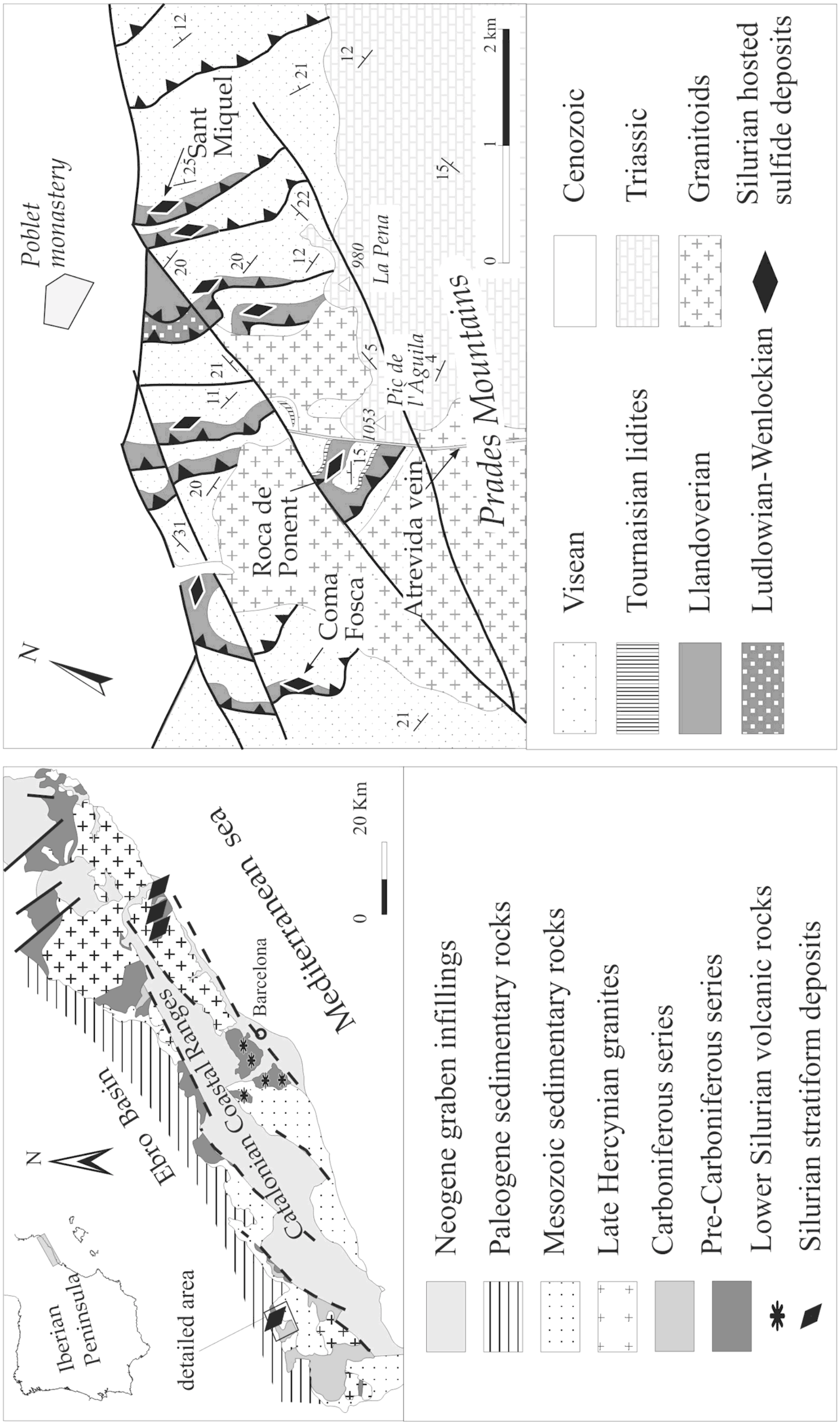
The intermediate units of the Silurian series essentially consist of 50 m of graptolite-rich black shale, dated by Ashauer & Teichmuller (1935) as Upper Llandoverian and Wenlockian. In spite of the fact that Ludlovian–Pridolian outcrops (mainly limestones) only appear in eastern areas of the Catalonian Coastal Ranges (García-López *et al.* 1990), the occurrence of limestone olistholiths of these ages within Carboniferous detrital series near the Prades Mountains seems to indicate that limestone sedimentation during the Upper Silurian and Early Devonian was also taking place in this area (Melgarejo & Martí 1989).

The above limestones are followed by a 100-m-thick sequence of marl interbedded with limestone, corresponding to the Gedinnian–Siegenian, and those units are overlapped by 80 m of alternating calcarenite and slate of Emsian age, which grade upward into black shale with quartzite beds corresponding to Eifelian–Famennian (up to 200 m thick) (Melgarejo 1992).

The Carboniferous series unconformably lies above the Silurian and Devonian rocks. In the Prades Mountains, the base of the Carboniferous series consists of chert beds ("lidites"). These beds, up to 10 m thick, are regionally attributed to the Tournaisian, and they contain several Mn deposits of sedimentary-exhalative affinity (Melgarejo & Ayora 1992). A thick sequence of detrital series (up to 2 km), ranging in age from Visean to Lower Westphalian, contains many sedimentary-exhalative stratiform Pb–Zn–Cu–(Ag) deposits (Melgarejo 1992, Canet 2001).

The above rocks have been deformed at several stages during the Hercynian Orogeny. Regional metamorphism and deformation took place in the epizone. The main phases of deformation gave NW–SE folds with an axial plane dipping toward the northeast; cleavage usually is poorly developed, and thrust structures were formed in the flanks of folds. The Silurian sediments (ore-rich sediments and black shales) and the Upper Devonian black shales acted as the detachment levels of the Hercynian thrusts. A second phase of deformation produced chevron folds trending NW–SE with an axial plane dipping to the southwest. Hercynian regional metamorphism in the southwest of Catalonia attained in the lowest part of the greenschist facies (Melgarejo 1992).

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).


Iberian Peninsula
detailed area
N
Ebro Basin
Catalonian Coastal Ranges
Barcelona
Mediterranean sea
0
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
N
Poblet monastery
Sant Miquel
Roca de Ponent
Coma Fosca
Atrevida vein
Pic de l'Àguila
La Pena
Prades Mountains
980
1053
12
21
12
25
22
20
20
12
15
5
4
21
11
15
20
31
21
0
1
2 km
Visean
Tournaisian lidites
Llandoverian
Ludlowian-Wenlockian
Cenozoic
Triassic
Granitoids
Silurian hosted sulfide deposits

Late Hercynian granitic rocks, ranging in composition from quartz diorite to leucogranite, intruded all of the above series, and produced a contact-metamorphic aureole up to 500 m wide (Melgarejo 1992, Serra & Enrique 1989). A suite of porphyritic granitic dikes, mainly NW–SE- and NE–SW-trending, cross-cuts the above granites and the Paleozoic metasedimentary series. Scheelite-bearing quartz veins occur into these granites. Fluid inclusions in quartz and scheelite indicate conditions that agree with the epizonal emplacement of these granitic rocks (400°C and 0.8 kbar; Ayora *et al.* 1987).

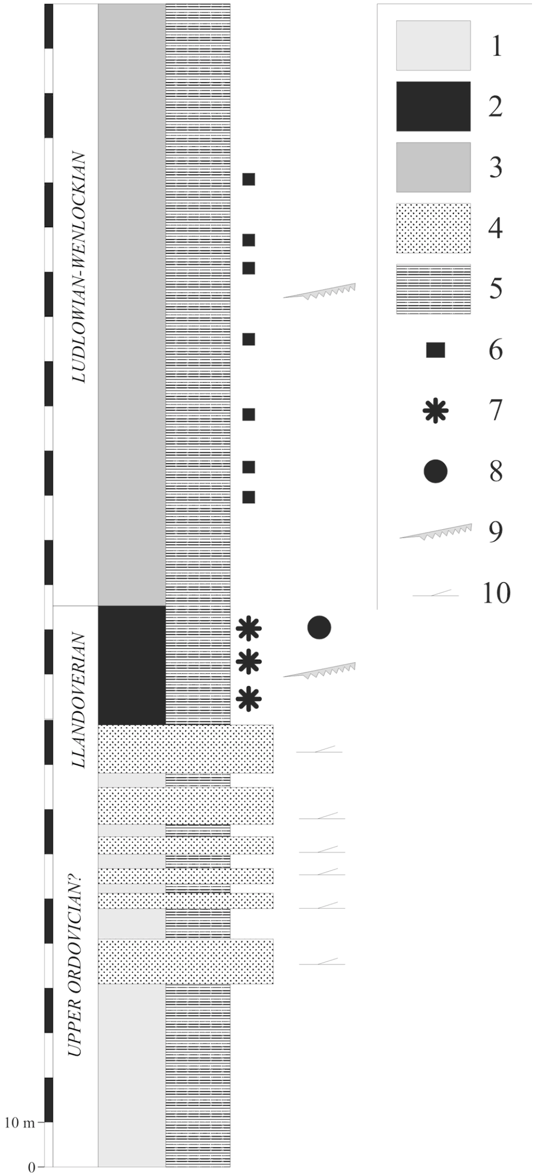


FIG. 2. Stratigraphic profile of the Lower Paleozoic series in the study area. 1. Grey shale, 2. sulfide-rich shale, 3. black shale, 4. quartzite, 5. planar lamination, 6. disseminated pyrite, 7. disseminated pyrrhotite, 8. PGE mineralization, 9. graptolites, 10. cross-lamination.

Contact metamorphism produced mineral associations up to the pyroxene hornfels facies in the proximity of the granite intrusions. Andalusite poikiloblasts developed in the Silurian black shale, whereas cordierite was mainly produced in Carboniferous metapelite and metagreywacke. The occurrence of almandine + biotite in pelitic hornfels, and of diopside in the calc-silicate hornfels, suggests temperatures higher than 500°C in the innermost aureole.

A Triassic megasequence (Germanic facies), up to 200 m thick, unconformably overlies the Paleozoic basement. The boundary between the Prades Mountains and the Cenozoic Ebro and Prelitoral basins consists of faults of Alpine age. Some of these faults host low-temperature Ba–F–Pb–Zn–Cu–Ni–Co–Ag veins, as at the Atrevida mine, the largest Ba deposit in the southwestern Catalonian Coastal Ranges (Melgarejo & Ayora 1985a, b, Canals *et al.* 1992).

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

Many Llandoverian-hosted stratiform deposits and showings have been discovered on the northern slopes of Prades Mountains. Usually, the Llandoverian metasedimentary units acted as detachment horizons of Hercynian thrusts, and therefore, they crop out as thin belts approximately parallel to the direction of the folds and thrusts of the first tectonic phase (N130°). Furthermore, these Llandoverian series were affected by various grades of thermal metamorphism. The most important ore-bearing outcrops in extent, thickness, and mineral contents are Roca de Ponent, Coma Fosca and Sant Miquel (Fig. 1).

The stratigraphy of the ore-bearing interval can be described as an interbedding of roughly monomineralic beds: anorthite-rich beds, phosphate beds, sulfide-rich shales, massive sulfides and more unusual calc-silicate beds. The thickness of individual beds ranges from some millimeters to several decimeters. An example of the distribution of these units is provided by the Roca de Ponent occurrence (Fig. 3).

The contact between these units is sharp and concordant. No evidence of replacements of precursor rocks has been found. The lateral continuity of the stratiform mineralization is on the scale of tens or hundreds of meters.

CONDITIONS OF ANALYSIS

The mineral associations have been studied in thin and polished sections. Scanning electron microscope (SEM) images and qualitative analyses were produced using a JEOL scanning electron microscope and a Cambridge Stereoscan 120 at the Serveis Científico-Tècnics de la Universitat de Barcelona (Spain). The samples were carefully examined in the back-scattered electron (BSE) mode, in order to examine the distribution of minerals containing heavy elements. The minerals were quantitatively analyzed with a JEOL electron microprobe in the energy-dispersion mode at Carleton University, Ottawa, Canada, and by wavelength-dispersion mode using a CAMECA SX–50 electron microprobe at the Serveis Científico-Tècnics of the University of Barcelona, and a CAMEBAX electron microprobe at the Muséum d'Histoire Naturelle, at Paris. Conditions of analysis for the ore minerals were: 15 keV, 20 nA (except in hydrated silicates), beam diameter of 1 μm, and a counting time of 10 s. We used the following standards: orthoclase (Si$K\alpha$, Al$K\alpha$, K$K\alpha$), rutile (Ti$K\alpha$), chromium oxide (Cr$K\alpha$), V metal (V$K\alpha$), scandium metal (Sc$K\alpha$), hematite (Fe$K\alpha$), rhodonite (Mn$K\alpha$), wollastonite (Ca$K\alpha$), albite (Na$K\alpha$), nickel oxide (Ni$K\alpha$), barite (Ba$L\alpha$), silver chloride (Cl$K\alpha$), corundum (Al$K\alpha$), LaB_6 (La$L\alpha$), CeO_2 (Ce$L\alpha$), YAG (Y$L\alpha$), ThO_2 (Th$M\alpha$), ZnS (Zn$K\alpha$, S$K\alpha$), ZrO_2 (Zr$L\alpha$), and cobalt metal (Co$K\alpha$).

MINERALOGY OF THE ANORTHITE-RICH BEDS

The anorthite-rich fine-grained metasedimentary rocks are common in all the occurrences, and in the Roca de Ponent outcrop, they attain up to 1 m in thickness. They consist mainly of anorthite, with lesser amounts of quartz and K-feldspar. The proportion of quartz is very variable, but normally smaller than that of anorthite. K-feldspar is usually associated with quartz. Other minerals found in anorthite-rich beds are: V-rich titanite (very common), smaller amounts of V-bearing amphiboles, goldmanite [the V-dominant garnet: $Ca_3(V,Cr,Al,Fe^{3+})_2(SiO_4)_3$] and muscovite. Rutile, ilmenite and coulsonite [V-bearing spinel: $(Fe,Mn)(V,Cr)_2O_4$] are also abundant. Monazite-(Ce), xenotime-(Y), thorianite and uraninite occur in lesser amounts, generally enclosed in the above-mentioned minerals as small inclusions (1–5 μm in diameter).

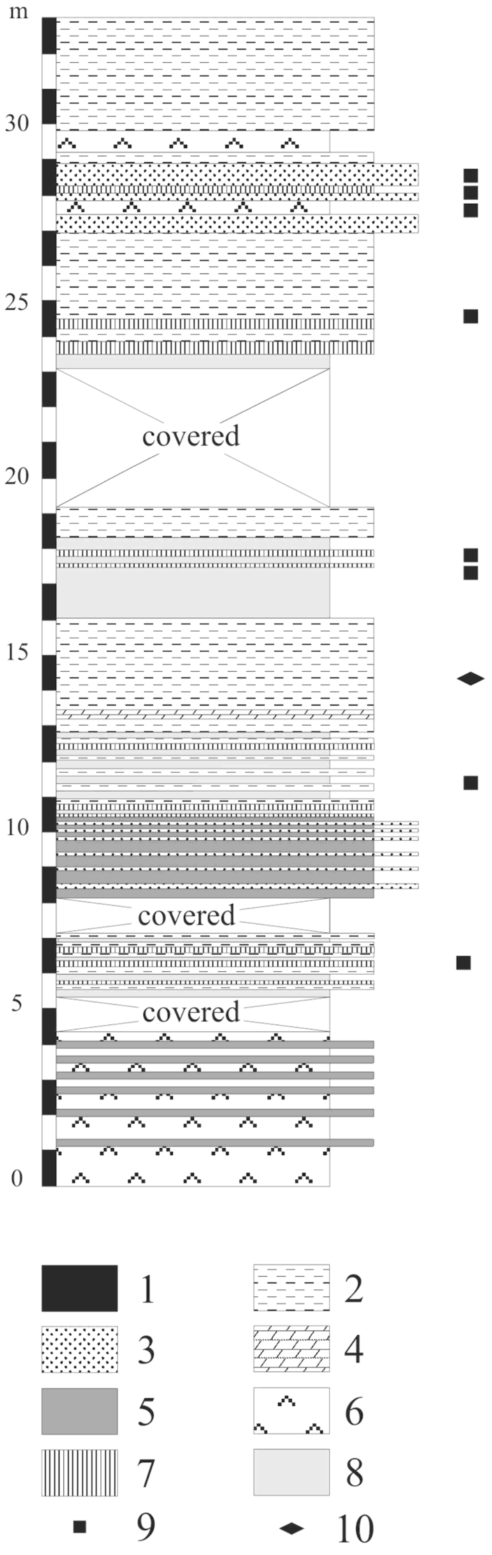


FIG. 3. Stratigraphic profile of the Roca de Ponent occurrence, indicating the distribution of the mineralization facies. 1. Massive sulfides, 2. sulfide-rich shale, 3. quartzite, 4. calc-silicate rocks, 5. black shale, 6. chert, 7. apatite-rich beds, 8. feldspar beds, 9. disseminated sulfides, 10. arsenopyrite-rich horizon.

Sulfides are not common in these beds, and pyrrhotite is the most abundant among them. The pyrrhotite, usually in anhedral disseminated grains in some cases included in V-bearing silicates, is locally replaced by late pyrite (bird's-eye texture).

Textural features in these feldspathic beds indicate that they have been affected by the Hercynian episode of deformation and metamorphism. Tight folds are well developed, in addition to axial plane cleavage. The anorthite-rich beds that are hosted by sulfide-rich schists usually display boudinage structures, indicating a more rigid behavior than the host sediments during the regional metamorphism and deformation. Anorthite, quartz and most of the above-mentioned minerals display annealing and granoblastic textures (with rounded grain-boundaries and triple points) due to the Late Hercynian thermal metamorphism.

Some anorthite-rich beds are partly replaced by white mica.

Quartz

In some cases, quartz is scarce and occurs disseminated in the anorthite groundmass, but in other cases, it constitutes more than the 50% of the rock. Its grain size also is variable, although generally close to 50 μm across, and the crystals have a polygonal texture.

Anorthite

Anorthite occurs as anhedral grains that generally display polysynthetic twinning. Usually, these grains have an elongate shape, and their *c* axis defines a lineation. The grain size, up to 50 μm, strongly depends on the metamorphic grade that affected each occurrence. Anorthite-rich beds affected by low- to medium-grade metamorphism are very fine-grained, but in those affected by high-grade contact metamorphism, as in Roca de Ponent and Coma Fosca occurrences, anorthite develops a coarse granoblastic texture with quartz and pyrrhotite. This metamorphic recrystallization overprints the Hercynian foliation (Fig. 4). In addition, anorthite fills open spaces in the necking zones of boudinage structures, thus suggesting a recrystallization during the Hercynian regional metamorphism. The chemical composition of anorthite from all the occurrences ranges between $An_{96.9}$ and $An_{99.5}$, with an average composition of $An_{98.5}$.

K-feldspar

K-feldspar is less common than anorthite; it is also fine-grained (up to 200 μm) and it is associated with enhanced amounts of quartz. K-feldspar is generally rich in inclusions of anorthite and organic matter. Rutile is

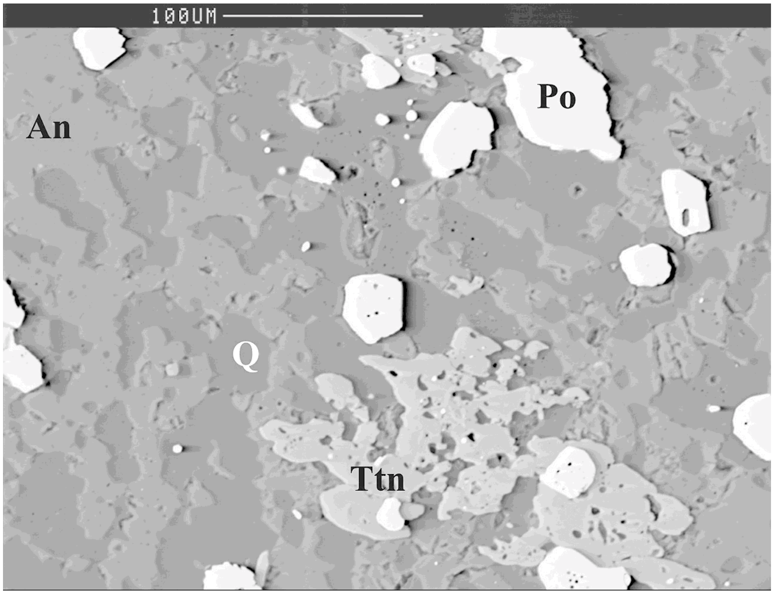


FIG. 4. Textural pattern of the anorthite-rich beds annealed during thermal metamorphism: granoblastic aggregates and rounded borders involving quartz (Q), anorthite (An), pyrrhotite (Po) and titanite (Ttn). SEM, BSE image. Scale bar: 100 μm.

also found as small inclusions (up to 5 µm). Most of the crystals correspond to a rather pure low-temperature microcline, with a very low Na content but a noticeable Ba-celsian content (up to 2 wt.% BaO, usually about 1 wt.%, Table 1). The K-feldspar crystals are unaffected by either deformation or schistosity, thus suggesting a formation related with the Alpine low-temperature Ba-veins, common in the vicinity of these deposits.

TABLE 1. CHEMICAL COMPOSITION AND STRUCTURAL FORMULAS OF SELECTED SILICATES FROM THE LOWER SILURIAN SERIES, PRADES MOUNTAINS, CATALONIA, SPAIN

	Amp (1)	*Amp* (2)	*Glm* (1)	*Glm* (2)	*Glm* (3)	*Glm* (4)	*Bt* (1)	*An* (1)	*Kfs* (1)	*Aln* (1)	*Ttn* (1)	*Ttn* (2)
SiO_2 wt.%	45.65	43.75	36.74	36.71	36.45	35.70	35.68	44.43	65.66	31.33	30.50	30.25
TiO_2	0.19	0.31	0.08	0.16	0.15	0.54	3.70	-	0.03	0.36	26.69	30.15
Al_2O_3	6.65	9.51	7.01	6.30	2.03	4.18	15.84	35.80	18.61	19.04	3.39	3.02
Sc_2O_3	0.02	0.01	-	-	-	-	0.01	-	-	-	-	-
V_2O_3	3.76	2.13	13.07	17.83	20.26	20.69	4.38	-	-	0.41	8.37	5.52
Cr_2O_3	0.55	0.74	5.91	2.47	4.74	3.28	0.52	-	-	0.94	0.48	0.22
FeO	15.34	18.50	-	-	-	-	13.85	-	-	-	-	-
Fe_2O_3	-	-	1.30	1.93	1.86	3.92	-	0.14	-	11.08	0.98	0.25
SnO_2	-	-	0.07	0.04	0.02	0.00	-	-	-	-	-	-
MgO	11.48	9.29	0.03	0.06	0.00	0.36	10.47	-	-	-	0.29	-
CaO	11.78	11.05	33.89	34.49	33.74	29.91	0.00	18.45	0.01	13.68	25.69	27.33
MnO	0.73	0.98	0.34	0.31	0.38	1.62	0.55	-	-	0.18	0.15	0.08
SrO	-	-	-	-	-	-	-	0.07	0.07	-	-	-
BaO	-	-	-	-	-	-	-	0.06	1.20	-	-	-
Na_2O	0.62	0.75	0.06	-	-	-	0.14	0.43	0.22	-	-	-
La_2O_3	-	-	-	-	-	-	-	-	-	6.93	-	-
Ce_2O_3	-	-	-	-	-	-	-	-	-	8.75	-	-
Pr_2O_3	-	-	-	-	-	-	-	-	-	0.64	-	-
Nd_2O_3	-	-	-	-	-	-	-	-	-	2.54	-	-
ThO_2	-	-	-	-	-	-	-	-	-	0.49	-	-
K_2O	0.68	0.50	-	0.02	-	-	9.09	0.56	14.26	-	0.05	-
H_2O	2.05	2.04	-	-	-	-	4.33	-	-	1.64	3.38	3.44
total	99.48	99.54	98.50	100.29	99.55	100.20	98.56	99.94	100.06	98.00	99.99	100.25
Si *apfu*	6.878	6.657	3.003	2.965	3.013	2.922	4.945	2.056	3.017	2.765	1.032	1.021
Ti	0.021	0.035	0.005	0.010	0.009	0.033	0.385	-	0.001	0.024	0.679	0.765
Al	1.179	1.702	0.674	0.599	0.197	0.402	2.583	1.953	1.008	1.981	0.068	0.060
Sc	0.003	0.002	-	-	-	-	0.001	-	-	-	-	-
V	0.454	0.259	0.855	1.153	1.341	1.356	0.486	-	-	0.029	0.227	0.149
Cr	0.065	0.088	0.381	0.157	0.309	0.212	0.057	-	-	0.066	0.013	0.006
Fe^{2+}	1.930	2.351	-	-	-	-	1.603	-	-	-	0.007	0.007
Fe^{3+}	-	-	0.080	0.117	0.116	0.241	-	0.011	-	0.736	0.027	0.007
Sn	-	-	0.002	0.001	0.001	-	-	-	-	-	-	-
Mg	2.575	2.103	0.004	0.007	-	0.044	2.161	0.000	-	-	0.015	-
Ca	1.898	1.799	2.962	2.979	2.983	2.618	0.000	0.915	-	1.294	0.932	0.988
Mn	0.092	0.126	0.023	0.021	0.027	0.112	0.065	-	-	0.014	0.004	0.002
Sr	-	-	-	-	-	-	-	-	0.002	-	-	-
Ba	-	-	-	-	-	-	-	0.010	0.022	-	-	-
Na	0.090	0.110	0.009	-	-	-	0.037	0.007	0.020	-	-	-
La	-	-	-	-	-	-	-	-	-	0.226	-	-
Ce	-	-	-	-	-	-	-	-	-	0.283	-	-
Pr	-	-	-	-	-	-	-	-	-	0.021	-	-
Nd	-	-	-	-	-	-	-	-	-	0.080	-	-
Th	-	-	-	-	-	-	-	-	-	0.010	-	-
K	0.130	0.096	0.000	0.002	-	-	1.604	0.025	0.836	-	0.002	-
OH^-	2.000	2.000	-	-	-	-	4.000	-	-	0.964	0.380	0.380

Symbols: *Amp*: amphiboles (structural formula based on 23 O,OH); *Glm*: goldmanite (structural formula based on 12 O); *Bt*: biotite (structural formula based on 24 O,OH); *An*: anorthite (structural formula based on 8 O); *Kfs*: K-feldspar (structural formula based on 8 O); *Aln*: allanite (structural formula based on 12 O,OH), *Ttn*: titanite (structural formula based on 5 O,OH).

Titanite

Titanite develops euhedral to subhedral crystals, widely distributed in the anorthite-rich beds. Titanite grains from these deposits display a strong reddish black pleochroism, are slightly radioactive, and possess a thin metamict aureole. The mineral is very rich in small inclusions of Ti oxides (rutile and ilmenite). In addition, titanite also occurs as a rim around ilmenite crystals. Therefore, titanite can be interpreted as having formed by a metamorphic reaction between ilmenite or rutile and the host anorthite. The titanite is vanadoan (up to 8.37 wt.% V_2O_3) and chromian (up to 0.6 wt.% Cr_2O_3; Table 1). Titanite can accommodate variable amounts of V, as described in Hemlo, Canada (Harris 1989, Pan & Fleet 1992) and in Andros Island, Greece (Bernau & Franz 1987). Assuming that all the vanadium is trivalent in titanite, and in absence of significant replacement of Ca, the OH content is expected to be high, as a result of the coupled substitution $Ti^{4+} + O^{2-} = (Al^{3+} + Fe^{3+} + V^{3+} + Cr^{3+}) + OH^-$. Nb and Ta, mentioned in other deposits, are absent in titanite at this locality. The association of titanite with the above-mentioned oxides and anorthite strongly suggests that it formed during contact metamorphism. This interpretation could also explain the V content, because the rutile grains of these deposits have significant contents of vanadium.

Vanadoan amphiboles

Vanadoan amphiboles develop mainly at the Roca de Ponent and Coma Fosca occurrences, where the metamorphic grade is higher (amphibole to pyroxene hornfels facies). They form poikiloblastic subhedral crystals of prismatic habit, up to two centimeters in length. These crystals include anorthite and biotite grains, whereas inclusions of V–Ti oxides are rarer. The crystals are randomly oriented, and in some cases, they form veins. These amphiboles probably formed during contact metamorphism related to the Late Hercynian granitic intrusive bodies that crop out near the occurrences sampled. They are calcic amphiboles according to the classification of Leake *et al.* (1997). The ferroactinolite and tschermakite components are very variable at all scales: district, deposit and individual grain (Fig. 5, Table 1). As a distinctive feature, most of the amphiboles from the Prades Mountains occurrences have high levels of V (ranging between 0.6 and 5.8 wt.% V_2O_3, 1.5 wt.% on average) and Cr contents (0.1–0.6 wt.% Cr_2O_3). Moreover, the Sc content is relatively high (up to 0.05 wt.% Sc_2O_3). Vanadium occupies the octahedral sites in the structure, and has a negative correlation with Si, thus suggesting a mechanism of substitution of the type: ${}^{IV}Si^{4+}\,{}^{VI}Fe^{2+} = {}^{IV}Al^{3+}\,{}^{VI}V^{3+}$. The crystals are irregularly zoned; the external part is the

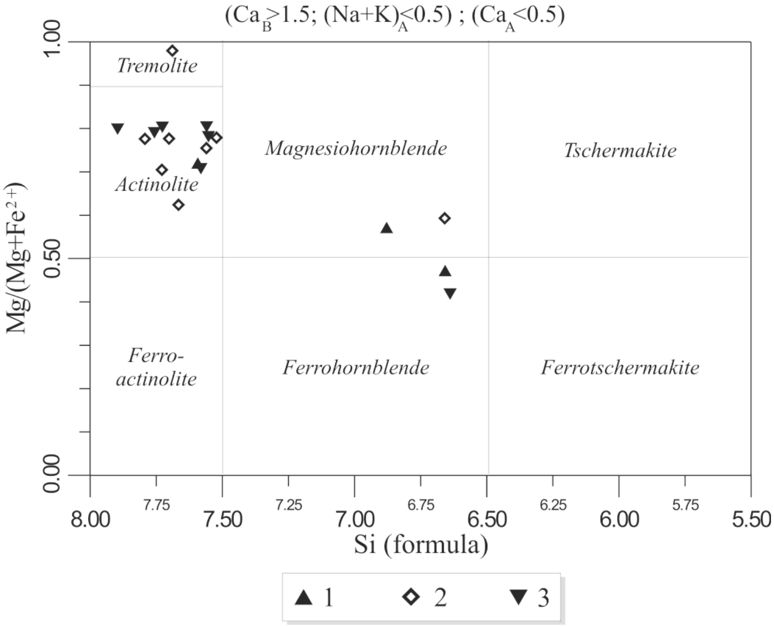


FIG. 5. Classification of the calcic amphiboles from the occurrences studied. 1. Coma Fosca, 2. Roca de Ponent, 3. Sant Miquel. Amphibole diagram of Leake *et al.* (1997).

richest in V and Cr and the poorest in Si. Therefore, this V-enrichment occurs mainly in the ferrohornblende domain.

Goldmanite

Goldmanite, $Ca_3(V,Cr,Al,Fe^{3+})_2(SiO_4)_3$, occurs exclusively within the anorthite-rich bands; the crystals are green, up to 2 mm across, and develop as poikiloblastic anhedral domains (Fig. 6) that include anorthite, V-rich amphibole, pyrrhotite, chalcopyrite and vanadium oxides. Its chemical composition is very variable, as commonly reflected in the concentric or patchy zoning, and can be expressed in terms of the end members: $Gm_{55–81}Uv_{7–29}And_{5–20}Gr_{20–30}$. In the zoned crystals, the core is richer in the grossular end-member, and the rim, in goldmanite and uvarovite. Similar V-enrichment in the external part of calc-silicate crystals was reported in the Hemlo gold deposit, Canada (Pan & Fleet 1992).

Goldmanite is the rare vanadium-dominant end-member of the garnet group. V-rich garnet has been reported in many environments, such as metamorphosed uranium–vanadium deposits (Moench & Meyrowitz 1964), skarns or skarnoids (Benkerrou & Fonteilles 1989, Mueller & Delor 1991), and metamorphosed black shales (Jeong & Kim 1999). In all cases, it occurs in association with carbonaceous sediments (Uher *et al.* 1994, and references therein). Ito (1965) synthesized goldmanite at temperatures above 450°C in a reducing atmosphere. These conditions are compatible with the metamorphic conditions inferred for the Prades Mountains and the carbonaceous nature of the Silurian series. The compositions obtained in our study area are similar to those reported worldwide (Fig. 7, Table 1).

Hedenbergite

Fe-rich members of the diopside–hedenbergite series have been found only in the occurrences affected by the highest metamorphic grade, such as at Roca de Ponent. The crystals occur sparsely disseminated in the anorthite groundmass. Hedenbergite is anhedral and occupies the interstices between the anorthite grains, or forms poikiloblastic crystals rich in anorthite inclusions. Hedenbergite is devoid of significant amounts of V, Cr or Sc.

Muscovite

There are two generations of muscovite. The first one is related to early metamorphic processes, and is one of the main components of the pelitic rocks that host the ore-bearing horizons. The second generation of muscovite is fine grained and occurs close to late fractures, as a result of replacement of anorthite.

The muscovite structure can accommodate significant amounts of Ba and Cr (*e.g.*, Pan & Fleet 1991a, Chabu & Boulègue 1992) and V (*e.g.*, Kazachenko *et*

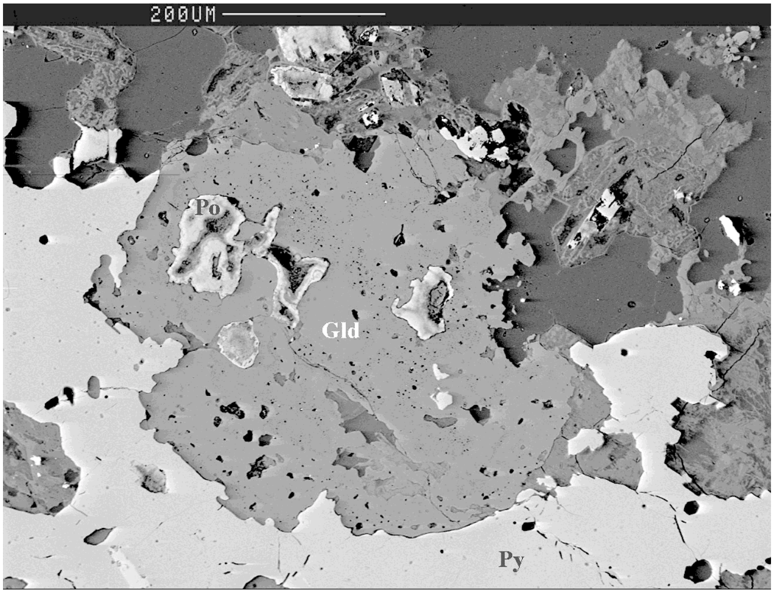


FIG. 6. Poikiloblastic goldmanite (Gld) enclosing pyrrhotite grains (Po). Pyrite (Py) replaces the association. SEM, BSE image. Scale bar: 200 μm.

al. 1993). As a result, we systematically analyzed muscovite for these elements, but only negligible amounts were found.

Allanite-(*Ce*)

Allanite-(Ce) is very common in the Coma Fosca and Roca de Ponent occurrences. The crystals are usually zoned and display different shades of pale rose to salmon pink. Allanite-(Ce) occurs in the feldspathic beds as euhedral poikiloblastic crystals, up to 300 μm across, displaying concentric zoning, or as a product of infilling in late undeformed veins. In these veins, allanite-(Ce) is associated with calcite and epidote. The V and Cr contents are noticeable (up to 0.4 wt.% Cr_2O_3 and 1.5 wt.% V_2O_3); much higher Cr contents have already been reported in Outukumpu, Finland (up to 5 wt.% Cr_2O_3, Treloar & Charnley 1987), and Pan & Fleet (1991b) reported up to 7.8 wt.% V_2O_3 in allanite-(La) and 8.5 wt.% V_2O_3 in allanite-(Ce) from Hemlo, Canada. Allanite-(Ce) from the Prades Mountains is rich in all the light rare-earths (Table 1). The allanite occurrence can be interpreted in terms of *REE*-, V- and Cr-remobilization during thermal metamorphism.

Ilmenite

Ilmenite is a rather common component of the anorthite-rich beds and, as mentioned above, it has been partly replaced by titanite. The crystals are poikiloblastic and include small grains of scheelite (up to 2 μm in size), which excludes a detrital origin (Fig. 8). The pyrophanite and geikielite components are absent in these crystals.

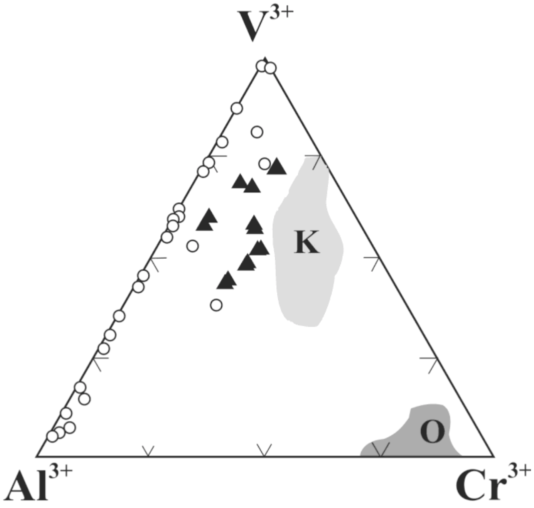


FIG. 7. Compositions of goldmanite from the Silurian occurrences of the Prades Mountains (black triangles) and world occurrences reported in Uher *et al.* (1994) (circles). Dashed areas represents the compositional fields reported: O: Outukumpu, K: Malé Karpaty.

MINERALOGY OF THE SULFIDE-RICH SHALES

The sulfide-rich shale horizons contain fine-grained minerals: V-rich biotite, muscovite, quartz and pyrrhotite. Accessory amounts of chalcopyrite, Ti–V oxides and titanite are present, as well as lesser contents of native bismuth, bismuth tellurides, sphalerite, löllingite, arsenopyrite, clausthalite (PbSe), altaite (PbTe), monazite, xenotime, wolframite, scheelite, uraninite and zircon. The sulfides occur disseminated or as thin discrete beds (less than 1 mm). All these minerals are affected by the regionally developed cleavage. In these beds, the thermal metamorphism led to recrystallization and development of cordierite and andalusite.

These beds provide the highest concentrations in precious metals; in the Sant Miquel deposit, they contain up to 0.6 ppm Pd, 0.2 ppm Au and 0.1 ppm Pt. These elements have been found in the following situations: a) as discrete grains disseminated in the sulfide-rich shale matrix (sperrylite, hessite), b) in the löllingite structure, *i.e.*, Pd-bearing löllingite, c) as native elements, arsenides, tellurides and selenides related to the löllingite sulfidation process, and d) as late vein infillings (acanthite).

Vanadoan biotite

Vanadoan biotite is the most common mineral in the sulfide-rich beds. In contrast, biotite is nearly absent in the other units of the deposits. It occurs as reddish brown subhedral tabular crystals of about 100 μm across. Generally, these crystals are arranged according to the regional schistosity associated with Hercynian folds, except in the zones most affected by thermal metamorphism. Biotite from the sulfide-rich beds has high vanadium contents (more than 4 wt.% V_2O_3 and up to 0.5 wt.% Cr_2O_3). The level of vanadium may even exceed that of titanium (Table 1). These vanadium contents are relatively high, although higher vanadium contents in phlogopite (up to 10.1 wt.% V_2O_3) were reported in Hemlo, Canada (Pan & Fleet 1992). The biotite crystals from the ore horizons are very rich in small inclusions of radioactive minerals (uraninite, zircon, monazite), which produce metamict aureoles.

Andalusite

Andalusite occurs as euhedral prismatic crystals, corresponding to the variety "chiastolite". It is sparsely distributed in bands of Al-rich black shale interbedded within the sulfide-rich bands. Andalusite is usually altered to white mica and kaolinite. The crystals are randomly oriented; thus, they are related to the post-tectonic contact metamorphism.

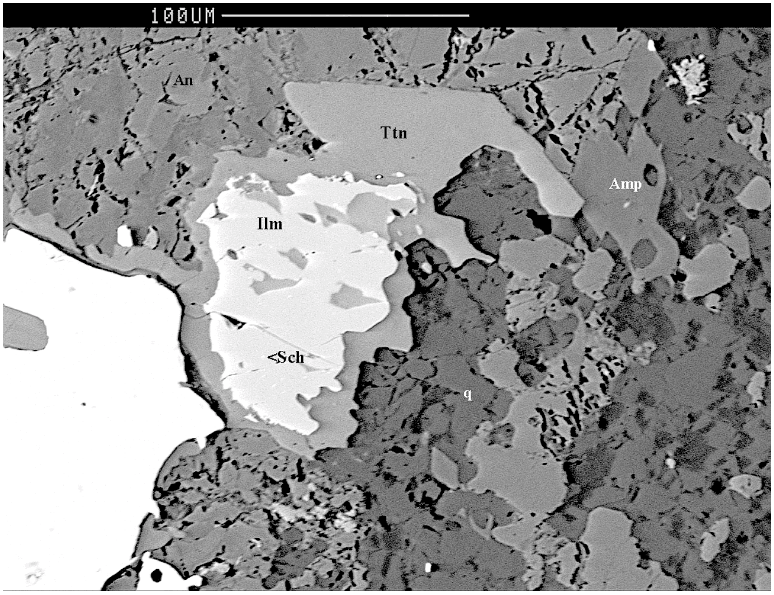


FIG. 8. Ilmenite crystal (Ilm) containing tiny inclusions of scheelite (Sch). Notice the subhedral rim of titanite (Ttn) at the contact between ilmenite and the silicate matrix, composed of quartz (q), amphibole (Amp) and anorthite (An). SEM, BSE image. Scale bar: 100 μm.

Cordierite

Cordierite only occurs in the Roca de Ponent and Coma Fosca occurrences. It develops anhedral poikiloblastic crystals, up to 250 μm in diameter. This mineral formed during an episode of thermal metamorphism, as indicated by the random arrangement of the crystals. Cordierite is strongly altered to white mica, and does not show an abnormal composition (*e.g.*, V or Cr enrichment).

Rutile

Rutile develops subhedral prismatic crystals, sparsely distributed in the pelitic matrix. Most of rutile grains from occurrences in the Prades Mountains contain noticeable contents of V (up to 3 wt.%) and Cr (up to 0.4 wt.%, Table 2).

Coulsonite

Coulsonite, (Fe,Mn,Zn)V_2O_4, a rare member of the spinel group, is rather abundant in the Sant Miquel deposit, where it develops anhedral poikiloblastic grains scattered in the pelitic bands. These crystals may attain 100 μm across. Fe is the main cation in tetrahedral positions, unlike the classic Mn-rich vuorelainenite from the Sätra deposit, Sweden (Zakrzewski *et al.* 1982). However, coulsonite from Sant Miquel is very rich in Cr and Zn, though its contents are not as high as those reported by Dimitrieva *et al.* (1990) (Table 2, Fig. 9). These crystals are poikiloblastic and contain many inclusions of quartz, micas and sulfides; therefore, a detrital origin can certainly be discarded. The analyzed grains show small compositional variations, but they are internally homogeneous.

Chromite

Chromite is very rare, and only a few grains in a sample from the Sant Miquel deposit have been found up to now. These are anhedral and fine-grained (up to 40 μm). Although the Fe/(Fe + Mn) and V/(V + Cr) values are very similar to those reported from the Rampura Agucha massive sulfide deposit (Höller & Stumpfl 1995), chromite crystals from Sant Miquel have higher Zn contents (Table 2, Fig. 9).

High proportions of the zincochromite component are typical of many chromite occurrences in sedimentary rocks worldwide (*e.g.*, Weiser & Hirdes 1997, and references therein). In many cases, chromite of comparable compositions has been attributed to metamorphic processes affecting chromite of ultramafic provenance in placer deposits (Challis *et al.* 1995, López Sánchez-Vizcaíno *et al.* 1995), or to alteration zones developed at the expense of basic rocks (Bernier 1990, Béziat &

TABLE 2. CHEMICAL COMPOSITION AND STRUCTURAL FORMULAS OF Ti OXIDES FROM THE LOWER SILURIAN SERIES, PRADES MOUNTAINS, CATALONIA, SPAIN

	Cou (1)	*Cou* (2)	*Chr* (1)	*Rt* (1)	*Rt* (2)	*Brd* (1)	*TiV* (1)	*TiV* (2)	*TiV* (3)	*TiV* (4)	*TiV* (5)
SiO_2 wt.%	-	-	0.07	0.03	0.02	-	-	0.03	0.03	0.18	0.04
TiO_2	0.20	0.40	1.99	97.11	94.24	37.60	60.40	53.74	54.26	52.55	52.23
ZrO_2	-	-	-	-	-	-	-	1.48	1.72	1.15	1.88
Al_2O_3	-	0.50	13.32	0.01	0.09	1.00	2.18	1.57	1.56	1.92	1.43
Sc_2O_3	-	-	0.03	0.04	-	-	3.52	1.02	0.99	0.39	0.93
Cr_2O_3	25.40	25.90	38.40	0.20	0.39	7.90	1.50	1.91	2.21	1.23	2.56
V_2O_3	42.20	39.90	11.15	1.10	2.71	47.90	20.35	20.40	19.58	19.94	20.60
Y_2O_3	-	-	-	-	-	-	-	1.01	0.67	0.46	0.67
Nb_2O_5	-	-	-	-	-	-	-	0.10	0.05	-	0.11
FeO	21.40	21.30	22.34	0.26	0.19	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	4.40	6.47	7.04	7.40	5.99	6.42
MnO	9.40	9.20	5.10	-	0.05	-	0.60	0.54	0.66	0.88	0.76
ZnO	3.30	3.10	6.95	-	-	-	-	0.76	0.77	0.69	0.39
MgO	-	-	0.48	-	-	-	0.41	0.47	0.35	1.05	0.64
UO_2	-	-	-	-	-	-	-	1.01	0.48	4.46	2.75
CaO	-	-	0.04	-	0.36	-	2.56	0.81	0.77	0.74	0.82
La_2O_3	-	-	-	-	-	-	-	2.64	2.75	3.43	2.83
Ce_2O_3	-	-	-	-	-	-	0.47	2.53	2.43	2.45	2.79
Nd_2O_3	-	-	-	-	-	-	-	0.74	0.75	0.39	0.80
Dy_2O_3	-	-	-	-	-	-	-	0.11	0.33	0.14	0.08
SrO	-	-	-	-	-	-	-	0.57	0.62	0.49	0.69
PbO	-	-	0.14	-	-	-	-	0.97	1.04	0.88	0.42
K_2O	-	-	0.02	-	-	-	-	0.07	0.06	0.08	0.01
BaO	-	-	-	-	-	-		0.29	0.26	0.20	0.27
Na_2O	-	-	-	-	-	-	0.03	0.00	0.00	0.00	0.00
total	101.90	100.30	100.02	98.74	98.06	98.80	98.49	99.81	99.74	99.70	100.10
Si *apfu*	-	-	0.002	-	-	-	-	0.009	0.008	0.054	0.012
Ti	0.004	0.009	0.049	0.983	0.959	0.881	12.776	11.901	11.990	11.892	11.680
Zr	-	-	-	-	-	-	-	0.213	0.247	0.169	0.273
Al	-	0.018	0.519	-	0.001	0.037	0.721	0.544	0.540	0.680	0.502
Sc	-	-	0.001	-	-	-	0.862	0.262	0.253	0.103	0.241
Cr	0.599	0.624	1.003	0.002	0.004	0.194	0.334	0.446	0.513	0.293	0.602
V	1.499	1.447	0.439	0.018	0.044	1.775	4.588	4.818	4.614	4.813	4.913
Y	-	-	-	-	-	-	-	0.158	0.106	0.073	0.106
Nb	-	-	-	-	-	-	-	0.014	0.007	-	0.016
Fe^{2+}	0.534	0.542	0.617	0.003	0.002	-	-	-	-	-	-
Fe^{3+}	-	-	-	-	-	0.115	1.522	1.561	1.636	1.357	1.438
Mn	0.238	0.237	0.143	-	0.001	-	0.144	0.134	0.164	0.224	0.191
Zn	0.073	0.070	0.169	-	-	-	-	0.164	0.167	0.154	0.085
Mg	-	-	0.024	-	-	-	0.170	0.207	0.151	0.472	0.283
U	-	-	-	-	-	-	0.000	0.066	0.033	0.299	0.187
Ca	-	-	0.001	-	0.005	-	0.770	0.254	0.243	0.238	0.261
La	-	-	-	-	-	-	-	0.287	0.298	0.381	0.310
Ce	-	-	-	-	-	-	0.048	0.272	0.261	0.270	0.303
Nd	-	-	-	-	-	-	-	0.078	0.079	0.042	0.085
Gd	-	-	-	-	-	-	-	0.010	0.032	0.014	0.007
Sr	-	-	-	-	-	-	-	0.097	0.106	0.085	0.118
Pb	-	-	0.001	-	-	-	-	0.077	0.082	0.071	0.034
Ba	-	-	-	-	-	-	-	0.034	0.030	0.024	0.032
K	-	-	0.001	-	-	-	-	0.027	0.023	0.031	0.005
Na	-	-	-	-	-	-	0.016	-	-	-	-
total	2.947	2.947	2.969	1.006	1.016	3.002	21.954	21.633	21.582	21.738	21.683

Symbols: *Cou*: coulsonite (structural formula based on 4 O); *Chr*: chromite (structural formula based on 4 O); *Rt*: rutile (structural formula based on 2 O); *Brd*: berdesinskiite (structural formula based on 5 O); *TiV*: Ti–V oxide of the crichtonite group (structural formula based on 38 O). Fe^{2+} and Fe^{3+} calculated according to stoichiometry.

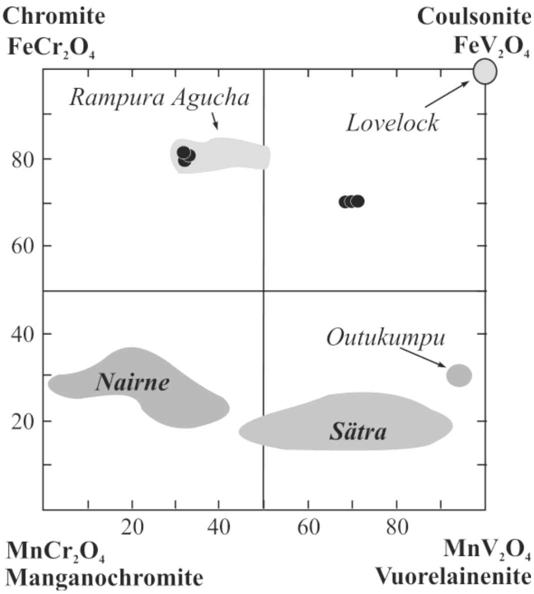


FIG. 9. Compositions of the Cr–V spinel in the deposits studied (black circles) plotted in the diagram of Höller & Stumpfl (1995).

Monchoux 1991). In other cases, hydrothermal processes without a magmatic chromite precursor are well established (von Knorring *et al.* 1986, Ashley & Martyn 1987, Mogessie *et al.* 1988, Hottin & Aloub 1990, Bermanec *et al.* 1999). In our case, the magmatic chromite precursor is lacking, and the formation of chromite may well be due to the metamorphism of Cr-rich black shales.

Berdesinskiite

Berdesinskiite, V_2TiO_5, is very rare, and occurs as small grains up to 25 μm across dispersed in the schists. Its chemical composition (Table 2) shows higher Cr contents than the type-locality material reported from Kenya (Bernhardt *et al.* 1983).

Ti–V–Cr–Sc–REE–U phase

The structural formula derived for what may be a new species, $(Ca,La,Ce)(U, Sc)(Ti,V,Fe,Cr,Mg)_{20}O_{38}$, is close to the general formula of the crichtonite group. However, the Sc-, V- and Cr-contents are higher than those reported for crichtonite-group members (Table 2). This phase is rather common throughout all the deposit, in roughly subhedral tabular poikiloblastic crystals (Fig.10). In polished section, it has a low reflectance, similar to that of sphalerite, and displays a brownish hue. The grain size (lesser than 100 μm) and the intimate intergrowth with the silicate matrix and sulfides do not allow us to obtain structural information.

Rutile

Rutile is very common in these beds, and forms single anhedral, poikiloblastic crystals. Its size varies between 30 and 200 μm. It is rich in inclusions of pyrrhotite, quartz and micas. Thus, a detrital origin is excluded. Rutile from these beds is enriched in V and Cr (Table 2).

Uraninite

Uraninite develops small euhedral cubes or rounded grains, up to 5 μm in size. Uraninite is abundant in some beds. In most cases, it is included in pyrrhotite crystals, but it can also occur as inclusions in pyrite crystals from late veins. In spite of its small size, uraninite crystals have inclusions of other minerals. Uraninite crystals have a variable composition, and some of them are Th-rich.

Zircon

Zircon is rather common as a detrital mineral, and occurs as small crystals (about 5 μm) included in biotite, in which it produces a metamict aureole.

Apatite

Anhedral crystals of an apatite-group mineral, up to 50 μm across, are rather widespread in the pelitic matrix. These apatite grains commonly contain inclusions of a monazite-group mineral.

Monazite

A monazite-group mineral is very abundant in some discrete beds, where it forms clouds of small anhedral crystals (usually less than 5 μm in diameter, but in some cases up to 100 μm). It generally it is included into biotite, apatite and sulfide grains. The monazite is Th-poor.

Xenotime

A xenotime-group mineral occurs at the same beds as monazite, but it is less common. As the monazite, it forms anhedral crystals, less than 50 μm in diameter.

MINERALOGY OF THE PHOSPHATE BEDS

Phosphate beds are very common in the sulfide-rich units of the Lower Llandoverian series of all the Catalonian Coastal Ranges. In most localities, they consist of an apatite-group mineral, with the exception of the Gavà and Montcada areas (central part of the Ranges), where aluminous and ferroan phosphate beds, consisting of variscite and strengite, are interbedded with apatite beds (Costa *et al.* 1993, Camprubí *et al.* 1994). In the Prades Mountains deposits, these Al- and Fe-phosphates are absent, and minerals of the apatite group are found as the dominant components of the phosphate beds. The phosphate beds can be interbedded within sulfide-rich bands or anorthite-rich beds. Their thickness is very variable, from some tens of micrometers up to a few centimeters. The apatite beds are almost monomineralic, but minor amounts of pyrrhotite, quartz, muscovite, monazite and uraninite also occur (Fig. 11). Uraninite crystals are rather common as disseminations through the phosphate beds. Uraninite is fine-grained (up to 5 μm), and usually euhedral (cubes). Unclassifiable fossil remains occur in rare cases into these beds, and they probably correspond to highly recrystallized radiolarian skeletons.

Although the apatite-group mineral is usually cryptocrystalline, it can increase slightly in grain size in the deposits affected by a higher metamorphic grade. The phosphate beds acted as rigid units during the deformation in comparison to the more ductile sulfide-rich shales, and therefore they are usually affected by boudinage structures. In this case, the necking-down zones between the apatite boudins are infilled by a second generation of apatite (as euhedral short prismatic crystals, up to 50 μm in length), together with quartz, anorthite, pyrite, uraninite and monazite.

MINERALOGY OF THE CALC-SILICATE BANDS

Calcic clinopyroxenes (Fe-rich members of the diopside–hedenbergite series) are the most common minerals in the calc-silicate beds. They occur as fine-grained crystals (up to 50 μm) that form granoblastic aggregates, with minor contents of titanite (scarce in these bands). A late association of minerals replaces the pyroxene grains along the rim of the grains, and consists of quartz, grossular–andradite garnet (with up to 20% of the spessartine end-member), epidote or an allanite-subgroup mineral in zoned crystals, calcite and actinolite. All these minerals clearly developed during the thermal metamorphism produced by the emplacement of bodies of Late Hercynian granite.

The silicates from the calc-silicate bands, in contrast with those from the anorthite or sulfide-rich shales, never contain noticeable amounts of V, Cr or Sc, and their chemical composition is very close to that of calc-silicates from many skarns worldwide.

MINERALOGY OF THE QUARTZITE BEDS

Quartzites consist mainly of quartz, with lesser amounts of fine-grained micas located at the borders of the quartz grains. Sulfides are very scarce. Pyrrhotite occurs in the interstices between quartz grains, and the mineral association show textural evidence of re-equilibration during the thermal metamorphism.

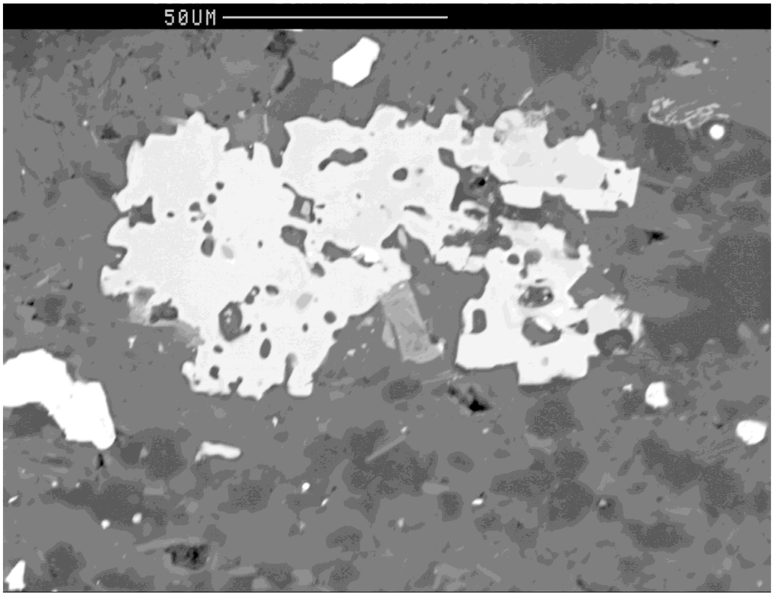


FIG. 10. Poikiloblastic development of a possible Cr-, V- and Sc-rich member of the crichtonite group. SEM, BSE image. Scale bar: 50 μm.

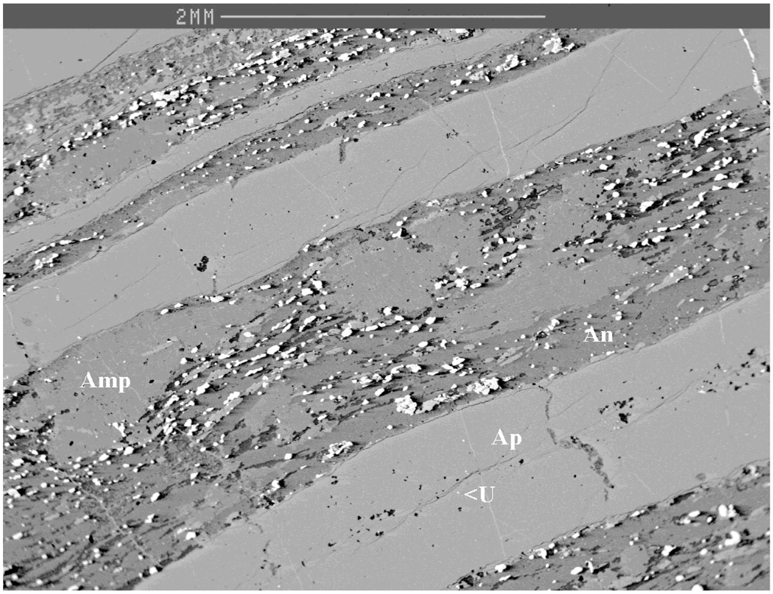


FIG. 11. Apatite-rich phosphate beds (Ap), interbedded with an anorthite-rich band composed of anorthite (An), amphibole (Amp) and pyrrhotite (brighter grains). Notice the presence of small grains of uraninite (U) disseminated in the phosphate beds. SEM, BSE image. Scale bar: 2 mm.

PARAGENETIC SEQUENCE

The V- and Cr-rich minerals occur disseminated among Llandoverian sulfide-rich metasedimentary units. The textural patterns indicate that most of these minerals formed or re-equilibrated during the regional or contact metamorphism.

The regional metamorphism (Westphalian in age) produced the recrystallization of many minerals; however, the regionally developed cleavage is only preserved in the outermost parts of the contact aureole. Muscovite is largely produced at that stage. Moreover, textural relationships suggest that ilmenite and rutile also may be formed at that stage. Firstly, they cannot be considered as detrital minerals, since they have inclusions of the accompanying minerals (for example, sulfides in rutile, and scheelite in ilmenite). Moreover, these poikiloblasts are arranged along the schistosity and, therefore, they are anterior to the Late Hercynian contact metamorphism.

The intrusion of the Late Hercynian granitic magma (Serra & Enrique 1989) produced contact metamorphic aureoles. The occurrence of cordierite and andalusite in the black shales is indicative of a medium-grade contact metamorphism, in the amphibole hornfels facies. Cordierite is mainly found in the Fe- and Mg-rich beds, whereas andalusite formed in the Al-rich black shales. These minerals enclose sulfides. The contact metamorphism produced the textural re-equilibration of the pre-existing mineral associations, the recrystallization of micas and the annealing of the sulfide associations (development of granoblastic decussate textures). Contact metamorphism also caused changes in the mineral associations. In the innermost part of the contact aureoles, biotite appears as randomly oriented grains. On the other hand, many poikiloblastic V- and Cr-minerals occur in this stage. The mineral association encountered depends on the average composition of the protolith. In the vanadium-rich shales, the V phases are oxides and biotite, whereas in the anorthite-rich rock, the minerals are principally V-rich calc-silicates (garnet, amphibole). As a rule, the highest V and Cr contents of amphibole and garnet grains are found in the outermost part of the crystals. This distribution of V and Cr in the silicates suggests that the equilibrium was not achieved during the thermal metamorphism, and that V and Cr were contributed from the host sediments. Goldmanite occurs in areas of higher metamorphic grade, and it formed after the V-rich amphiboles.

A more detailed paragenetic sequence of these mineral associations, that also comprises the ore minerals, is found in Canet *et al.* (2003).

DISCUSSION

The Lower Llandoverian sulfide-rich metasedimentary rocks of the Prades Mountains show V and Cr enrichment related to a noticeable PGE mineralization of sedimentary-exhalative primary origin (Melgarejo 1992, Melgarejo *et al.* 1994). The association V–Cr–PGE has been reported in some exhalative deposits. For example, chromian spinel and vanadoan amphiboles, associated with Pd minerals, have been described in Nairne, Australia (Graham 1978).

The V content in the Llandoverian sulfide-rich metasedimentary rocks of the Prades Mountains attains 0.54 wt.% V in the Coma Fosca outcrop (Canet & Melgarejo 2001). The V–Cr distribution in the minerals has been modified by metamorphic recrystallization. Vanadium (and Cr) were probably linked to the organic matter in the sedimentary protoliths, or to sheet silicates, as observed in many other V- and Cr-rich sediments related with hydrothermal deposits (*e.g.*, Pouit & Bois 1986, Meyer & Robb 1996). These elements presumably were accommodated in the structure of Ca-rich silicates (vanadoan garnet, amphiboles, *etc.*) during the contact metamorphism, when the sheet silicates equilibrated with anorthite-rich sediments.

Geochemical anomalies in V and Cr are not exceptional in exhalative deposits and have also been reported in present-day metalliferous sediments. Damman (1988) described Mn and V geochemical anomalies in sedex-type deposits, and concluded that the vanadium enrichments are representative of facies near the emitting center, whereas Mn-rich facies occur at more distal positions. High concentrations of V, leading to the presence of vuorelainenite, occur in the massive sulfide deposits at Sätra, Sweden (Long *et al.* 1963, Zakrzewski *et al.* 1982). Cr–V spinels also occur in the Rampura Agucha Pb–Zn–(Ag) deposit in Rajasthan, India (Höller & Stumpfl 1995). Moreover, although V-rich sedimentary rocks are rare in relation to stratiform mineralization in the Pyrenean deposits, chromian muscovite ("fuchsite") and Ti–Cr oxides are common in some deposits (Bois *et al.* 1976, Melgarejo 1992). Therefore, these minerals can give rise to a wide variety of mineral species during the regional or contact metamorphism. Gabriel (1991) described an interesting association of cherts with disseminations of crandallite (with Ba, Pb, Cr and V), florencite-(Ce), monazite-(Ce) and cerium oxides in the low-grade metamorphosed Proterozoic series from Bohemia. Veins with roscoelite and barite (with native gold and nickel in the gangue) cut the assemblage. Other V oxides are common in massive sulfide ores, like karelianite in Outukumpu, Finland (Long *et al.* 1963). Bermanec *et al.* (1999) described a case of stratiform sulfide mineralization containing hyalophane and chromite in Bosnia. Finally, it is worth mentioning the occurrence of authigenic V oxides in recent metalliferous sediments from the Red Sea (Jedwab *et al.* 1989). In our opinion, the textural patterns of V- and Cr-rich minerals indicate a premetamorphic origin. The V and Cr enrichment could be syngenetic with respect to the formation of the sulfide-bearing sediments.

The hydrothermal supply of V and Cr seems to be problematic owing to the apparent immobility of these elements; these elements could be enriched in the exhalative particles by a scavenging process. However, hydrothermal transport of Ti–U–V–Cr–Ba–*REE*–(Au) and sulfides by the same fluid is already known to occur in some hydrothermal veins (Johan *et al.* 1995), and Treloar & Charnley (1987) pointed out that the Cr immobility at Outukumpu seems established in metamorphic environments, but not in hydrothermal systems.

In the Prades Mountains deposits, V and Cr were immobilized by new minerals produced during metamorphism at short distances from the precursor mineral: in coronas (titanite, garnet) and veinlets (allanite). A similar conclusion can be reached concerning U and the *REE*.

Otherwise, the common occurrence of uraninite in the Prades deposits suggests that oxidizing fluids acted as carriers of these elements to a reducing sea bottom. Moreover, the role of such oxidizing brines in the transport of metals during the formation of Ba-poor sedex deposits has recently been envisaged (Cooke *et al.* 2000).

Another unusual occurrence in these showings is that of the feldspathic beds. The occurrence of massive Na-, K- and Ca-rich feldspar horizons is common in many exhalative deposits worldwide. They have been attributed to metamorphism of tuffaceous sediments (Plimer 1977), to diagenetic processes (Goodfellow 1984), or to reaction of alkaline marine water in Pre-Carboniferous seas with acid hydrothermal fluids (Russell 1988). Moreover, Ba-rich feldspar occurs in many metamorphosed exhalative deposits. These occurrences have been explained as a product of metamorphism of barite protoliths in environments of reduction (Chabu & Boulègue 1992).

CONCLUSIONS

The V- and Cr-rich mineral associations from the southwestern part of the Catalonian Coastal Ranges are the result of the regional and contact isochemical metamorphism. Contact metamorphism took place in epizonal conditions, and produced mineral associations typical of amphibole to pyroxene hornfelses. The mineral associations produced are a function of the precursor sedimentary rocks. Therefore, the composition of the metamorphic rocks can be described in terms of the protoliths. The metamorphism of rocks containing abundant organic matter favored the development of V^{3+}- and Cr^{3+}-bearing minerals.

Contact metamorphism of V-rich aluminous shales produces the development of V-rich aluminosilicates (mainly biotite) and V oxides. The presence of V oxides in apparent equilibrium with V-rich silicates suggests a upper limit for the V and Cr activities in these aluminosilicates at the conditions of the thermal metamorphism. Furthermore, both in medium- to high-grade contact metamorphism, V and Cr tend to be partitioned in the biotite structure, and muscovite does not seem to accommodate these elements.

Metamorphism of anorthite- and V-, Cr-rich sedimentary rocks led to the development of V- and Cr-rich calc-silicates, such as goldmanite, vanadoan tremolite, V-rich titanite and V-rich allanite-(Ce).

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