



Geochemical evidences of sedimentary-exhalative origin of the shale-hosted PGE–Ag–Au–Zn–Cu occurrences of the Prades Mountains (Catalonia, Spain): trace-element abundances and Sm–Nd isotopes

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Abstract

The Llandoveryian black shales of the Prades Mountains, SW Catalanian Coastal Ranges, contain several metamorphosed stratiform sulfide deposits. The mineralized interval, up to 30 m in thickness, consists of interbedded sulfide-rich (mostly pyrrhotite) shales, feldspar-rich layers and apatite beds. The ore contains Zn, Cu, Pb, Au, Ag and PGE. Whole-rock trace-element analyses were performed by ICP-MS, and the results were normalized to NASC reference standard. The REE patterns show enrichment in Eu (La) and a strong depletion in Ce. This distribution is compatible with REE mostly inherited from seawater, but a significant hydrothermal component is inferred for Eu. Profiles of redox-sensitive trace elements show great V, Cr, Ni, Co, Mo and U enrichments with respect to NASC standard. Part of this enrichment could derive from a direct precipitation from seawater, favoured by the euxinic conditions of the Silurian basin. Nevertheless, V (up to 5444 ppm) and Cr (up to 640 ppm) contents would require additional sources. These elements could be scavenged from seawater by exhalative particles in a hydrothermal derived plume that finally accumulated on the seafloor. In contrast, high Ni, Co and Mo values could be of hydrothermal origin. Sm–Nd isotopic analyses of feldspar-rich layers yielded an isochron age of 437 ± 57 Ma (Llandoveryian). These results, as well as the fine-grained textures, the lack of evidences of replacement and the pre-deformational and pre-metamorphic character support the syngenetic origin of the mineralization. Trace-element geochemistry and Sm–Nd isotopes are consistent with a submarine-exhalative origin of the mineralization processes, and suggest that the feldspar-rich levels are metaexhalites.

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1. Introduction

In the northern section of the Prades Mountains (SW of the Catalanian Coastal Ranges, NE of Spain),

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several metamorphosed stratiform sulfide occurrences hosted in Silurian black shales have been found. The reserves comprise up to 30 Mt of low-grade ore. These occurrences have been classified as sedimentary-exhalative (Melgarejo, 1992; Canet, 2001), because of their stratiform character, the special relationship to unusual abnormal metasedimentary rocks, interpreted as metaexhalites, and the lack of volcanic rocks directly related to the orebodies.

A noticeable feature of the stratiform sulfide mineralizations in the Prades Mountains is their content in precious metals, including PGE (Melgarejo et al., 1994; Canet et al., 2003a). In addition, the sulfide-mineralized beds have unusual composition formed of interbedded sulfide-rich shales with feldspar-rich layers and apatite beds.

Striking geochemical characteristics of the studied deposits are their high values of V, Cr, Mo and U (Canet and Melgarejo, 2001). The high V and Cr values (V up to 5444 ppm, Cr up to 640 ppm) in the mineralized profile agree with the high contents of these elements in garnets, micas, amphiboles and pyroxenes found in these deposits (Canet et al., 2003b). V and Cr geochemical anomalies related to exhalative deposits are not unusual. High V and Cr contents have been reported in the massive sulfides of Sättra, Sweden (Vuorelainen and Kouvo, 1963). In addition, Jedwab et al. (1989) reported this kind of anomaly in some modern metalliferous sediments.

Another special characteristic of these sulfide deposits is their close association with microcrystalline feldspar-rich layers formed mostly of anorthite. Feldspar layers of different composition have been reported in several exhalative deposits worldwide, with ages ranging from Precambrian to Paleozoic. Many examples of albite occurrences are known: Thackaringa, in Australia (Plimer, 1977), Cinco Villas, in the Basque Country, Spain (Pesquera and Velasco, 1993), Sullivan, in Canada (Shaw and Hodgson, 1986), Foz-Barreiros, in Galicia, Spain (Roel, 1994), in Roná district, Czech Republic (Křibek et al., 2002), and in several deposits of the Caledonian–Appalachian Orogeny (Stephens et al., 1984). However, anorthite-bearing layers have only been reported in few deposits; the most known are in Dachang, China (Pan et al., 1993). Stratiform ore deposits containing K-feldspar layers occur at Dachang (Pan and Amstutz, 1993) and Howard Pass, Canada (Good-

fellow, 1984). Ba-feldspar rocks appear to be more common in exhalative ores; celsian forms thick monomineralic lenses, as in Aberfeldy, Scotland (Fortey and Beddoe-Stephens, 1982; Willan and Coleman, 1983). Celsian has been also reported in Arrens, Pyrenees (Pouit and Bois, 1986), and in Broken Hill, Australia (Lottemoster, 1989; Parr, 1992). In Zamora, Spain, Moro et al. (2001) reported celsian lenses with hyalophane and cymrite, interlayered in apatite and massive sulfide layers. In Andros Island, Greece, celsian is associated with manganese oxide distal deposits (Reinecke, 1982). Additionally, stratiform hyalophane deposits have been recognized in unusual paragenesis. For example, hyalophane has been found in relation to the Zn–Cu–Pb sedex deposits of Sudbury Basin, Canada (Whitehead et al., 1992), associated with barite in Roná, Bohemian Massif (Křibek et al., 1996), and in Rosh Pinah, Namibia, where hyalophane is associated to barite, norsethite and bentsonite (Page and Watson, 1976). Finally, there is a remarkable similarity between the occurrences of the Prades Mountains and the Cambrian Ni–Mo deposits from Southern China, that are also hosted by black shales, containing feldspar layers and significant amounts of PGE minerals (Shengrong and Zhenmin, 1996).

REE geochemistry has been used to constrain the genesis of fossil exhalative deposits, especially for the exhalites that are spatially associated with them (i.e. Lottemoster, 1989; Parr, 1992; Steiner et al., 2001). Thus, assuming immobility of REE in metamorphic processes (Muecke et al., 1979; Taylor et al., 1986), we infer that REE patterns of Prades Mountains are representative of the primary (pre-metamorphic and pre-deformative) processes that caused ore deposition.

Hence, the aim of this paper is to use redox-sensitive elements and REE data in order to obtain genetic information about the Silurian mineralizations of the Prades Mountains. In addition, Sm–Nd isotopes have been analyzed in feldspar-rich layers to determine their age. This technique has been typically used to date metamorphosed igneous protoliths (Dickin, 1995). In the studied case, the inferred protolith is of hydrothermal origin (feldspar-rich layers), with essential minerals analogous to the metamorphic rocks (gneiss) for which this method is effective. Nevertheless, it is necessary to consider that the feldspar-rich layers can contain detrital compo-

nents. This fact should not be an impediment for dating, since Sm–Nd isotopes also may date materials of mixed origin, i.e. volcano-sedimentary series (i.e. Frost and Schellekens, 1991).

2. Geological setting

The studied deposits are located on the northern part of the Prades Mountains (*Muntanyes de Prades*), in the southern domains of the Catalonian Coastal Ranges. In this area, a Hercynian folded basement unconformably overlaid by Mesozoic and Cenozoic sedimentary series occurs (Fig. 1). The Hercynian basement is divided in two major sequences, Carboniferous and Pre-Carboniferous, separated by a stratigraphic unconformity (Melgarejo, 1992). In the studied area, Carboniferous outcrops dominate over Pre-Carboniferous ones.

The Pre-Carboniferous stratigraphic sequence is formed of Early Cambrian, Silurian and Devonian sedimentary series. East of the studied area, the oldest series locally outcrops in an anticline core near Valls.

On the basis of its fossil ichnofauna content, Sanz-López et al. (2000) determined an Early Cambrian age for these series.

The Silurian series starts with a basal, 20 m thick, interbedded pile of quartzites and black shales, overlain by the mineralized interval. This sequence is up to 30 m in thickness, and consists of an interbedding of chert, sulfide-rich shales, feldspar levels and massive sulfides. Based on graptolitic fossil fauna, the age of these units was ascribed to Lower Llandoveryan (Melgarejo, 1992). The intermediate Silurian series comprise about 50 m of black shales with abundant graptolite fossil fauna that indicates Upper Llandoveryan to Wenlockian ages (Solé Sugrañes, 1973). Rocks of Late Silurian age are only represented in the study area by limestone olistoliths hosted in detrital breccias at the base of the Carboniferous series (Melgarejo and Martí, 1989).

The Devonian series consists of an 80-m-thick unit of greenish shales and calc-schists (Emsian), followed by 200 m of black shales with interbedded quartzite and chert layers of Eifelian–Famennian age (Melgarejo, 1992).

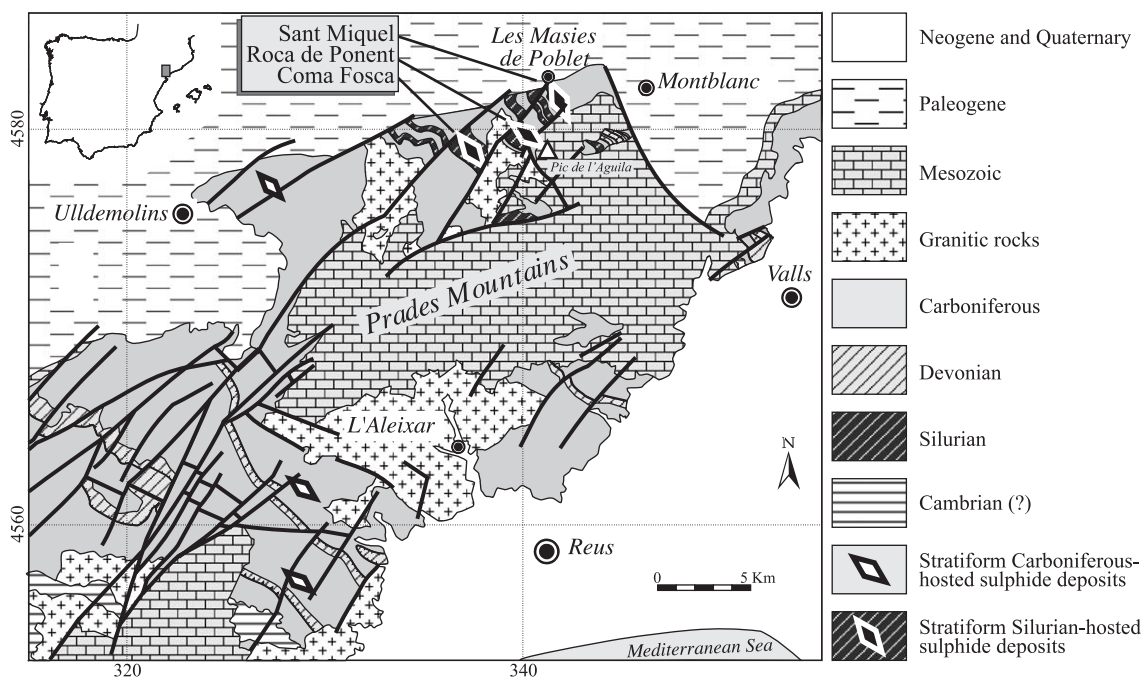


Fig. 1. Geological map of the studied area (after Melgarejo, 1992). The Silurian-hosted stratiform sulfide deposits of the Prades Mountains are labeled for Sant Miquel, Coma Fosca and Roca de Ponent locations.

The Carboniferous series, mainly composed of detrital rocks, unconformably overlie the above-mentioned units and are characterized by abrupt lateral facies and thickness changes (Melgarejo, 1992). In the Prades Mountains, the Carboniferous series starts with a 10-m-thick chert unit that is regionally ascribed to the Tournaisian in age (Melgarejo, 1992). Above, a thick sandy-pelitic sequence (of about 2000 m) of Visean to Lower Westphalian age occurs. Some Pb–Zn–Cu–(Ag) sulfide deposits and occurrences of sedimentary-exhalative affinity are hosted at the base of the Carboniferous sequence (Melgarejo, 1992; Canet, 2001).

The Paleozoic series were deformed in epizonal conditions during the Hercynian orogeny. The most important deformational episode took place during the Upper Carboniferous and produced NW–SE trending recumbent folds, with poorly developed cleavage. In addition, thrust structures developed in the flanks of the folds, and their detachment levels usually are the Silurian series (ore-bearing metasediments and black shales). Thus, the outcrops of Silurian rocks that contain the studied stratiform sulfide deposits define narrow belts approximately parallel to the folds and thrusts (N130). The Hercynian regional metamorphism was developed under low-grade conditions, corresponding to the lower part of the greenschist facies (Melgarejo, 1992).

Late Hercynian granitic stocks, ranging in composition from quartzdiorite to leucocratic granites, intruded all the Paleozoic series (Melgarejo and Ayora, 1984). These intrusions, of Permian age (Enrique and Debon, 1987), produced a contact metamorphic aureole, up to 500 m thick, ranging from pyroxene to amphibole hornfels facies (Serra and Enrique, 1989). The contact metamorphism produced cordierite dots in the shales and, in the case of the more aluminian black shales, andalusite poikiloblasts. A high number of dikes of porphyritic granitic rocks crosscut the ensemble. The main directions of these dikes are N030 and N110. The dikes are up to 2 km long, and up to 30 m wide. Related to these intrusions, scheelite-bearing quartz veins are found both into the granites and the surrounding rocks. A fluid inclusion study of these veins yields temperatures of about 400 °C and pressures of 0.8 kbars (Ayora et al., 1987).

A Triassic megasequence (Germanic facies), of 200 m in thickness, unconformably overlies the Paleozoic rocks. The limit between the Prades Mountains and

the Cenozoic sedimentary infillings of the Ebro and Prelitoral basins is defined by Alpine faults. Some of these faults favoured a hydrothermal circulation that formed Ba–F–Pb–Zn–Cu–Ni–Co–Ag low-temperature veins (Canals and Cardellach, 1997).

3. Methodology

Mineral associations of the Prades Mountains occurrences have been studied in thin and polished sections. SEM images acquired in BSE mode were produced using a Cambridge Stereoscan 120 electron microscope at the Serveis Científic-Tècnics de la Universitat de Barcelona.

Selected minor and trace elements have been analyzed in 24 whole-rock samples representative of the lithologies of the studied deposits (11 feldspar-rich layers, 8 sulfide bearing shales, and 4 sterile host black-shales). All the analyses were performed in the ACTLABS laboratories of Canada, by a combination of different analytical methods: neutron activation, ICP-MS and X-ray fluorescence. Samples were crushed in a tungsten carbide rings mill. The analyzed elements and its detection limits are: Be (5 ppm), Sc (0.1 ppm), V (0.5 ppm), Cr (1 ppm), Ni (1 ppm), Co (1 ppm), Cu (1 ppm), Zn (1 ppm), As (2 ppm), Se (3 ppm), Br (1 ppm), Rb (1 ppm), Mo (5 ppm), Ag (0.2 ppm), Cd (1 ppm), Sb (0.2 ppm), Ta (1 ppm), Cs (0.5 ppm), La (0.5 ppm), Ce (3 ppm), Nd (5 ppm), Sm (0.1 ppm), Eu (2 ppm), Tb (0.5 ppm), Hf (0.5 ppm), Bi (1 ppm), Pb (2 ppm), Hg (1 ppm), Th (0.5 ppm), U (0.5 ppm). Trace-element contents (La, Ce, Nd, Sm, Eu, Tb, Cr, Mn, Co, Ni, As, Th and U) were normalized to NASC standard (North American Shale Composite), established by Gromet et al. (1984), whereas V was normalized to Marine Shale of Ruhr (Degens et al., 1958) and Mo was normalized to Recent Sediments (Wedepohl, 1974). Sc was also normalized (to NASC) due to its association to V, and Ti and Zr were also included as reference elements. The Eu anomaly was obtained according the equation: $Eu_{NASC}/Eu^*_{NASC} = (3 \times Eu_{sample}/Eu_{NASC}) / (2 \times Sm_{sample}/Sm_{NASC} + Tb_{sample}/Tb_{NASC})$.

Ten Sm–Nd isotopic analyses have been performed on feldspar-rich samples. The analyzed samples are representative of the three studied occurrences (four from Sant Miquel, four from Coma Fosca and

two from Roca de Ponent), and they were selected on the basis of its high content in feldspar and the absence of alteration. The purity of these samples was tested by X-ray diffraction. The isotopic analyses were performed in the Institute of Precambrian Geology and Geochronology of Saint Petersburg, Russia. The ϵ parameter (430 Ma) was calculated with *CHUR* reference values (Chondritic Uniform Reservoir): $^{147}\text{Sm}/^{144}\text{Nd}=0.1967$, and $^{143}\text{Nd}/^{144}\text{Nd}=0.512638$.

4. Mineralogy and structure of the ore deposits

On the basis of its ore mineral content, the thickness of the mineralized interval and the outcropping conditions the three most important occurrences are Roca de Ponent, Coma Fosca and Sant Miquel.

The Sant Miquel occurrence is located 100 m south of Les Masies de Poblet hamlet (Fig. 1). This is the only Silurian sulfide deposit that preserves vestiges of an ancient mining activity, which consists of two short galleries and an open pit in a sulfide-bearing meta-sedimentary unit of 5 m in thickness.

The Roca de Ponent occurrence is located 2 km southwest of the Sant Miquel occurrence, near of the Pic de l'Àguila summit (1035 m; Fig. 1). The mineralized unit is up to 30 m thick.

The Coma Fosca occurrence is about 4 km far from Roca de Ponent. The mineralized unit attains 15 m in thickness.

The stratiform sulfide occurrences are in all cases hosted in black shales of Lower Llandoveryan age and have the same stratigraphic position.

The three sulfide occurrences are unequally affected by the thermal metamorphism: amphibole hornfels facies in Sant Miquel, and pyroxene hornfels in Coma Fosca and Roca de Ponent. Contact metamorphism produced granoblastic textures and an increase of the grain size in all the studied occurrences. Locally, it also produced the redistribution of some elements into new-formed minerals. In particular, high concentrations of REE occur in a mineral of the crichtonite group and in allanite (Canet et al., 2003b). However, the sulfur isotopic equilibrium was not achieved among the sulfides (Alfonso et al., 2002).

In detail, the mineralized units consist of an interbedding of anchi-monomineralic layers (feldspar-rich layers, shales with disseminated sulfides, apatite beds,

massive sulfides and less abundant calc-silicate layers; Fig. 2). The thickness of individual laminae is usually lower than 1 mm, but it can reach up to several centimeters. The contact between the different lithological units is always sharp and concordant, and in no case textural evidences of replacement of previous lithologies are observed. Neither underlying discordant mineralization nor alteration complex has been

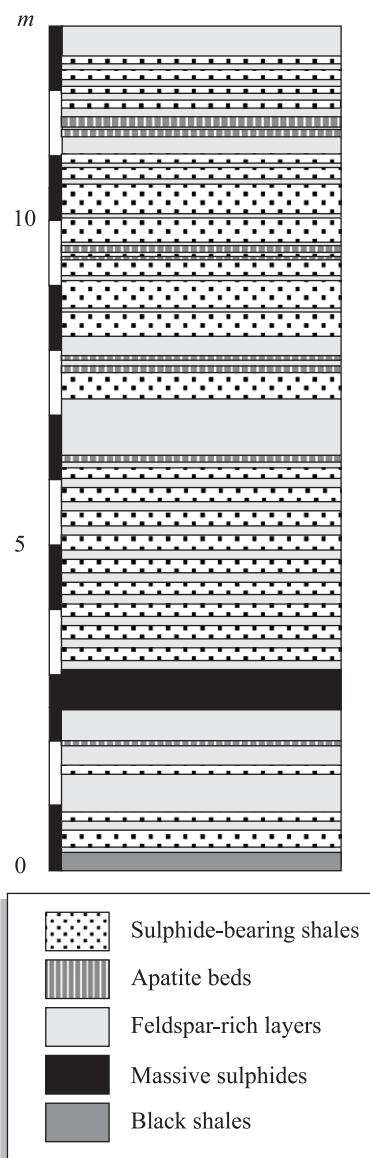


Fig. 2. Lithological column of the mineralized interval from Sant Miquel occurrence, showing the distribution of lithofacies.

observed in relation to the studied shale-hosted sulfide deposits.

4.1. Sulfide-bearing units

The sulfide-bearing units consist of sulfide-rich shales, with disseminated ore minerals, and massive sulfide beds, the first being much more important in volume.

The sulfide-rich shales are fine-grained, and are mostly composed of V-rich biotite, muscovite, quartz and pyrrhotite, with variable amounts of anorthite, chalcopyrite, sphalerite, titanite and Ti–V–Cr oxides. Furthermore, bismuth tellurides, native bismuth, löllingite, arsenopyrite, clausthalite (PbSe), altaite (PbTe), monazite, xenotime, wolframite, scheelite, uraninite and zircon may occur as accessory minerals.

A very notable mineralogical characteristic is the occurrence of disseminated Pd, Pt, Au and Ag bearing minerals (Pd-rich löllingite, sperrylite, native Pd, electrum and Au–Ag tellurides) in close association with the sulfide mineralization. Canet et al. (2003a) reported up to 0.6 ppm of Pd, 0.2 ppm of Au and Pt, and 6 ppm of Ag in the Sant Miquel occurrence.

All the mentioned mineral associations are affected by the regional cleavage and thermal metamorphism, which produces annealing textures and develops cordierite and andalusite poikiloblasts. Though scarce,

concordant massive sulfide lenses are found in the mineralized interval. They can attain 20 cm in thickness, and are basically composed of pyrrhotite, sphalerite, pyrite and chalcopyrite.

4.2. Apatite beds

Apatite beds are very common, and usually are interlayered within sulfide-rich and feldspathic layers. Their thickness ranges from tens of microns to some centimeters. These beds are almost totally composed of cryptocrystalline apatite, though accessory amounts of pyrrhotite, quartz, muscovite, monazite and uraninite occur.

4.3. Calc-silicate layers

They consist in fine-grained beds (up to 5 cm thick) essentially composed of Ca pyroxenes that form granoblastic aggregates. Titanite is present in minor amounts.

4.4. Feldspar-rich layers

The feldspar-rich layers consist of fine-grained metasedimentary rocks of chert appearance. They are made up essentially of anorthite, with minor amounts of quartz, chlorite and V-rich minerals. The

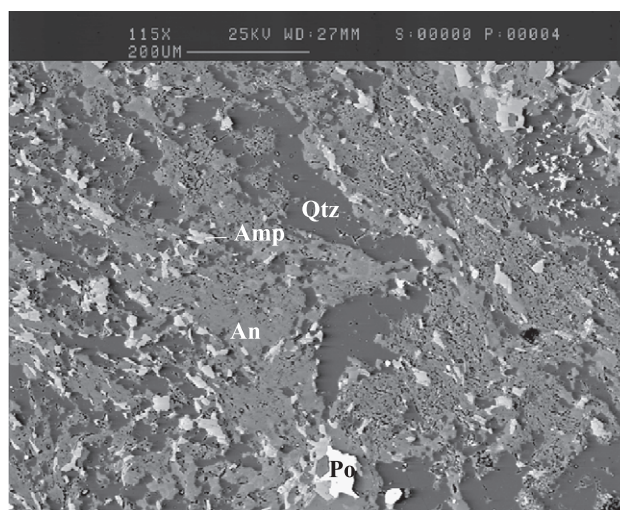


Fig. 3. Detail of the texture of a feldspar-rich layer, with cleavage development in sulfide and feldspar grains. Qtz, quartz; An, anorthite; Amp, tremolite; Po, pyrrhotite. SEM-BSE image.

Table 1

Trace and minor element contents (in ppm) in the analyzed samples from Sant Miquel (M) and Coma Fosca (Ag) sulfide occurrences (n.a. = not analyzed)

Sample	Black shales				Feldspar-rich layers												Sulfide bearing shales						
	M 1	M 2	M 13	M 14	M 3	M 4	M 5	M 6	M 7	M 8	M 11	M 12	M 20	M 21	M 22	M 17	M 18	M 23	M 24	M 25	Ag 14	Ag 17	Ag 18
Ag	1	1	2	1	1	1	1	4	4	1	1	2	3	3	4	1	2	2	3	1	0	0	0
As	5	10	17	9	5	8	14	53	45	7	16	8	40	24	42	10	12	17	44	0	0	0	0
Be	3	5	2	5	4	4	6	2	0	6	5	5	2	5	0	6	6	13	4	3	n.a.	n.a.	n.a.
Bi	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Br	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	n.a.	n.a.	n.a.
Cd	0	0	0	0	0	0	0	3	3	1	3	0	3	5	2	0	5	2	4	3	3	3	6
Co	9	42	49	77	30	47	47	55	63	30	53	23	51	82	68	77	68	44	68	51	333	368	212
Cr	150	170	150	170	120	94	200	560	330	130	550	320	300	320	640	180	390	550	440	110	n.a.	n.a.	n.a.
Cs	6	9	8	8	12	10	12	6	10	13	10	14	5	3	7	9	7	10	8	10	n.a.	n.a.	n.a.
Cu	19	132	122	96	149	171	177	1034	707	136	164	31	724	566	849	98	345	203	734	32	669	717	461
Hf	5	5	4	5	5	5	5	4	4	5	4	8	4	4	4	4	4	6	4	4	2	0	6
Hg	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	n.a.	n.a.	n.a.
Mn	155	929	310	465	1007	929	1239	929	852	1162	774	542	542	387	929	465	697	1007	774	1704	1433	3563	821
Mo	8	6	11	0	0	5	7	17	26	0	56	17	10	24	22	5	40	14	39	6	31	125	14
Ni	6	71	20	34	17	58	107	335	342	33	87	7	367	237	326	71	185	110	251	28	310	801	306
Pb	17	23	41	45	51	10	14	25	16	23	28	57	18	6	14	11	16	10	14	7	285	18	48
Rb	191	193	146	165	228	131	173	122	137	221	142	257	110	23	125	173	96	129	99	147	n.a.	n.a.	n.a.
Sb	4	1	1	1	1	1	1	1	2	2	3	4	1	1	1	1	2	1	1	0	0	0	1
Sc	15	18	14	17	21	17	20	16	16	19	15	25	15	13	15	17	14	25	16	16	8	8	16
Se	21	0	7	6	0	0	0	53	48	0	0	0	36	32	41	0	0	6	25	0	n.a.	n.a.	n.a.
Ta	2	2	3	2	2	2	2	1	1	3	1	3	2	2	0	2	2	2	2	3	n.a.	n.a.	n.a.
Th	8	13	6	12	14	12	15	8	9	15	8	15	8	7	8	11	8	16	8	13	10	10	30
U	6	5	3	5	2	1	5	14	10	3	38	9	7	15	14	4	40	11	30	2	36	21	2
V	289	359	333	388	192	134	244	1073	959	164	2125	1091	427	597	1093	478	1576	700	838	95	3862	5444	592
Zn	9	135	42	68	50	189	79	867	1011	74	501	47	697	965	595	140	1233	411	643	372	88	35	120
La	57	64	37	70	72	64	75	82	55	69	74	64	55	61	62	59	79	93	64	38	69	99	65
Ce	80	90	43	91	114	100	11	73	58	116	76	75	62	61	59	77	83	107	63	77	69	103	153
Nd	36	51	25	57	65	57	60	66	29	60	53	34	45	44	56	48	73	79	57	31	47	75	46
Sm	6	8	3	10	11	10	10	11	6	11	10	4	8	9	10	6	14	13	11	6	10	14	8
Eu	1	2	1	2	2	2	2	3	2	2	3	1	2	4	3	1	4	4	5	1	2	3	1
Tb	1	1	1	2	2	2	1	2	1	2	2	1	1	2	2	1	3	2	2	1	2	2	1

thickness of the individual layers extends from some millimeters to few meters. The grain size is usually $< 5 \mu\text{m}$, however, the annealing produced by thermal metamorphism locally can increase it up to $50 \mu\text{m}$.

Anorthite (An_{95-98}) is the most common mineral in these layers, followed by quartz, which is usually

disseminated within feldspar grains. Its abundance is extremely variable, but usually lower than 30 modal%. Feldspar layers contain disseminated sulfides, mainly pyrrhotite, V-rich titanite, V-rich tremolite, goldmanite (V garnet), muscovite, V-rich allanite, apatite, rutile and ilmenite (both typically mantled

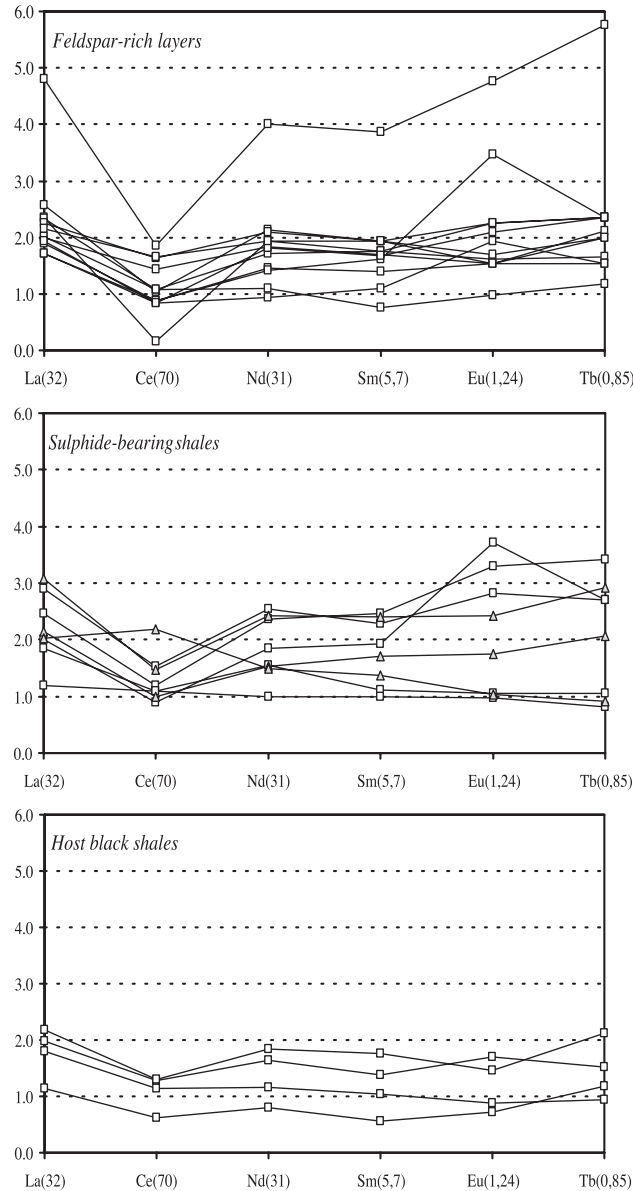


Fig. 4. REE concentrations of different lithologies of the studied ore deposits normalized to NASC (Gromet et al., 1984) (Normalization values shown in parentheses). White squares mark the 20 samples from Sant Miquel occurrence, and gray triangles mark the 3 samples from Coma Fosca.

by a reaction rim of V-rich titanite) and V oxides (Canet et al., 2003b).

Several textural features register the effects of the Hercynian deformation and metamorphism in feldspar layers (Fig. 3). Granoblastic textures are locally developed as a result of thermal metamorphism, characterized by an increase of grain size, and development of curved boundaries between anorthite, quartz and sulfide grains.

Likewise, similar feldspar-rich rocks have been found in almost all the sedimentary-exhalative deposits hosted in Carboniferous series of the SW Catalonian Coastal Ranges (Canet, 2001).

5. Results

5.1. Trace-element abundances

Contents in several trace-elements in whole rock samples from the studied deposits and occurrences are shown in Table 1.

5.1.1. REE elements

The mineralized units have moderately high LREE (La, Ce, Nd, Sm, Eu, Tb) contents. The mean content of LREE is 205 ppm in feldspar-rich layers, 217 ppm in the sulfide-bearing shales from Sant Miquel and

256 ppm in the sulfide-rich shales from Coma Fosca. These values are significantly higher than the LREE content of the regional host shales, which have a mean value of LREE of 170 ppm.

The North American Shale Composite (NASC) normalized LREE contents of the analyzed samples are shown in Fig. 4. The obtained profiles in samples from the feldspar-rich layers show a significant enrichment in some LREE, especially in Eu and La. Nevertheless, Ce exhibits a conspicuous negative anomaly. Eu shows a weak positive anomaly ($Eu_{NASC}/Eu^*_{NASC}=0.8-1.8$). REE patterns from samples of the sulfide-bearing shales are similar to those from the feldspar-rich layers; they show a Ce depletion and its Eu anomaly is also low but significant ($Eu_{NASC}/Eu^*_{NASC}=0.8-1.7$). Finally, the REE profiles of the regional host shales are nearly flat, similar to the international shale patterns. In this case, the Eu anomaly is not significant ($Eu_{NASC}/Eu^*_{NASC}=0.8-1.2$).

5.1.2. Redox-sensitive trace elements

The normalized contents of some redox-sensitive trace elements (RSE) together with Sc, Ti and Zr in the analyzed samples are shown in Fig. 5.

The obtained profiles exhibit a general V enrichment. V contents reach up to 5444 ppm in Coma Fosca, and 2100 ppm in Sant Miquel, which is more

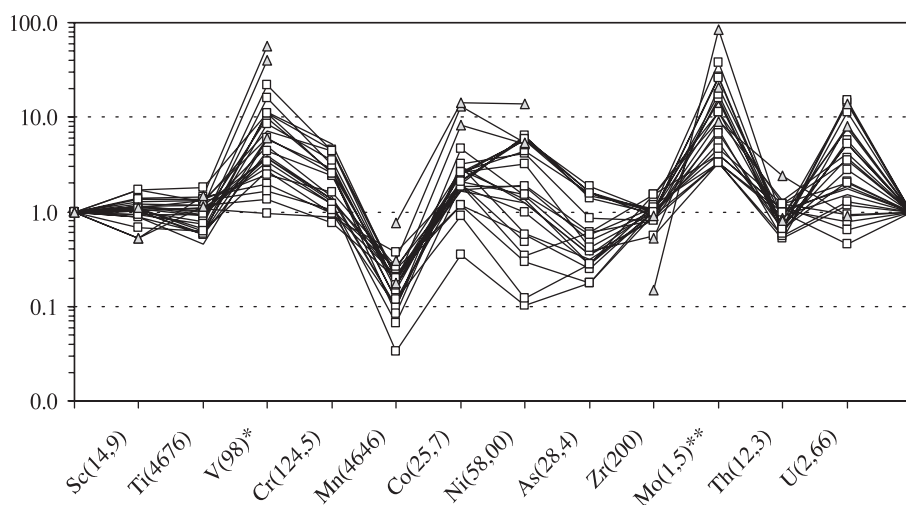


Fig. 5. Concentrations of some redox-sensitive elements (V, Cr, Mn, Co, Ni, As, Mo, Th, U), as well as Ti, Sc and Zr. The values were normalized to NASC (Gromet et al., 1984), except V*, which is normalized to Marine Shale of Ruhr (Degens et al., 1958), and Mo**, to Recent Sediments (Wedepohl, 1974).

Table 2
Sm–Nd isotope results from samples of feldspar-rich layers

Sample	[Sm]	[Nd]	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2δ	ϵ	T(DM)	T(DM2)
AG-11	4.486	24.788	0.1095	0.51198	14	–7.2	1651	1781
AG-22	1.040	6.303	0.0999	0.51199	11	–7.4	1760	1801
AG-24	81.931	297.656	0.1665	0.51217	11	–7.4	3143	1801
AG-27	57.327	237.57	0.1460	0.51212	16	–7.5	1813	1807
M-7	11.552	61.805	0.1131	0.51200	15	–7.4	1556	1797
M-12	11.855	61.226	0.1171	0.51203	14	–7.3	2314	1793
M-13	7.339	36.892	0.1203	0.51204	15	–7.6	2147	1816
M-14	10.668	58.682	0.1100	0.51203	10	–7.7	2640	1827
MT-20	38.224	167.398	0.1381	0.51208	12	–8.0	1707	1850
MT-21	10.738	42.023	0.1546	0.51212	12	–7.9	1744	1841

ϵ parameter was calculated with Chondritic Uniform Reservoir (CHUR) reference values: $^{147}\text{Sm}/^{144}\text{Nd}=0.1967$ and $^{143}\text{Nd}/^{144}\text{Nd}=0.512638$. T(DM) and T(DM2) were calculated with the parameters: $^{147}\text{Sm}/^{144}\text{Nd}=0.2136$ and $^{143}\text{Nd}/^{144}\text{Nd}=0.513151$. Ag: Coma Fosca, M: Sant Miquel and Mt: Roca de Ponent.

than 20 times the normalization value (98 ppm of V in Marine Shale of Ruhr, Degens et al., 1958).

Cr also is significantly enriched; it attains up to 640 ppm in Sant Miquel. Nevertheless, there is not a significant Sc enrichment (8 to 25 ppm).

All the analyzed samples show a negative anomaly in Mn; the mean value of the Mn content is 155 ppm.

Co and Ni are significantly enriched in the most part of the samples. The highest Ni and Co concentrations correspond to the sulfide-bearing shales from Coma Fosca (up to 800 ppm of Ni and up to 368 ppm

of Co). As exhibits a wide range of values (up to 53 ppm).

The Mo content is always high with respect to the normalization values. The mean value is 20 ppm, with a maximum value of 125 ppm corresponding to one sample of sulfide-bearing shale from Coma Fosca. U is enriched in all the samples, also in the host black shales.

Independently of the lithology and occurrence, the different RSE profiles show analogous trends of enrichment and impoverishment.

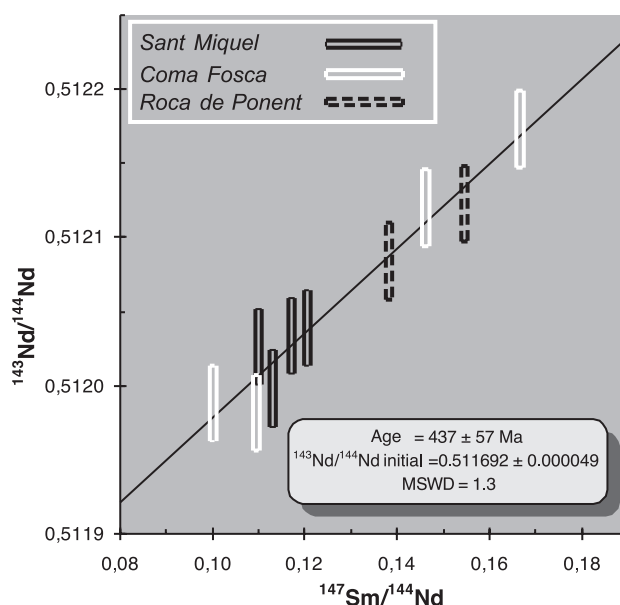


Fig. 6. $^{147}\text{Sm}/^{144}\text{Nd}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ isochron for the feldspar-rich layers.

5.2. Sm–Nd isotopic ratios

The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Sm}/^{144}\text{Nd}$ isotopic ratios obtained in the feldspar-rich layers are exposed in Table 2. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio ranges from 0.0999 to 0.1546 and the $^{143}\text{Sm}/^{144}\text{Nd}$ ratio is from 0.51198 to 0.51217.

Assuming that the different samples of the feldspar-rich beds are cogenetic, since all of them come from an equivalent interval in the sedimentary Silurian series, an isochron can be plotted using $^{147}\text{Sm}/^{144}\text{Nd}$ versus $^{143}\text{Sm}/^{144}\text{Nd}$ ratios (Fig. 6).

The obtained isochron indicates an age of 437 ± 57 my, corresponding to the Llandoveryan, with a MSWD (Mean Squares of Weighted Deviates) of 1.3. This age is in agreement with that obtained from the paleontological data (Solé Sugrañes, 1973).

6. Discussion

6.1. Trace-element geochemistry

There are several well-known examples of PGE in sedimentary rocks. In most cases worldwide, the PGE occurrences in sedimentary rocks are closely related to black shales (i.e. Grauch et al., 1991; Coveney et al., 1992; Hulbert et al., 1992; Whitehead et al., 1992; Lott et al., 1999). Furthermore, stratiform exhalative sulfide deposits usually have high Pd and Pt contents (Sawlowicz, 1993). However, the origin of these PGE is still controversial, though several authors suggest hydrothermal contributions (i.e. Pašava, 1993; Lott et al., 1999).

Several studies carried out for PGE in ophiolites show that those elements could mobilize during metamorphism and fixed by pre-existing sulfides (Vatin-Perignon et al., 2000; Malitch et al., 2001). In the Prades Mountains occurrences, textural relations among the ores indicate that a PGE enrichment process took place before the contact metamorphism, although during metamorphism part of these elements were redistributed and formed new minerals in relation to the replacement of löllingite by arsenopyrite (Canet et al., 2003a). Therefore, the mineralization of base and noble metals (PGE–Ag–Au–Zn–Cu) of the Prades Mountains can be attributed to a syngenetic exhalative hydrothermal supply in the sea floor.

6.1.1. Rare earth elements (REE)

The most distinctive features of the REE patterns of the sulfide-rich shales and feldspar-rich layers are the light enrichment in LREE, especially in Eu–La ($\text{Eu}_{\text{NASC}}/\text{Eu}^*_{\text{NASC}} = 0.8–1.8$), and a conspicuous negative anomaly of Ce. Otherwise, the host black shales do not show any significant anomaly.

As mentioned above, Ce negative anomaly is distinctive of the REE patterns of the Prades Mountains shale-hosted deposits. Likewise, seawater is depleted in Ce (Sotto and Yoshiyuki, 1999). This impoverishment is explained by the oxidation of Ce^{3+} (soluble) to Ce^{4+} (insoluble) and accumulation in the sediments as CeO_2 . Furthermore, in present-day metalliferous sediments the REE acquisition is also governed by scavenging from seawater (Ruhlin and Owen, 1986). Consequently, Ce negative anomaly of the Prades Mountains samples could be inherited from seawater.

The Eu–La enrichment in the mineralization is in agreement with the occurrence of REE bearing minerals (monazite, allanite, xenotime). Furthermore, anorthite, that is the main component of the feldspar layers, is able to concentrate Eu^{2+} (Rollinson, 1993). The Eu–La anomaly can be caused by hydrothermal activity. The mobility of Eu strongly depends on the redox and temperature conditions: Eu enrichments involve hot (>250 °C) and reduced fluids, whereas Eu negative anomalies imply cold and oxidizing fluids (Parr, 1992). The first mentioned conditions are coherent with the hydrothermal activity responsible for exhalative submarine deposits (i.e. Large, 1981). Among the REE, Eu is the only significantly mobile element in hydrothermal vent fluids (Michard et al., 1983). In fact, the hydrothermal supply is confirmed by the Eu enrichments in present-day vent fluids (Manikyamba et al., 1993). Likewise, Barret and Jarvis (1988) reported La enrichments in present-day exhalative sediments. In the same way, Eu enrichments have been documented in several BIF deposits (Derry and Jacobsen, 1990). In contrast, present-day geothermal fluids related to orogenic and continental environments are depleted in Eu (Michard and Albarède, 1986). Therefore, the Eu anomaly found in the Prades Mountains deposits agrees with the enrichment reported in many present-day and fossil exhalative submarine ore deposits, presumably originated by hot and reducing hydro-

thermal fluids, and it cannot be explained by continental hydrothermal fluids.

In summary, the obtained REE patterns show a marine signature for this group of elements, in spite that the hydrothermal activity might have appreciably contributed in REE distribution, since this explains the Eu–La enrichment. Therefore, these results suggest that the mineralization was originated by venting of hot (>250 °C) and reduced fluids at the sea floor.

6.1.2. Redox-sensitive trace elements

Most of the analyzed samples of the Prades Mountains deposits and occurrences show significant enrichment of V, Cr, Co, Ni, Mo and U, relative to NASC standard. High concentrations of Ni, Mo, V, Cr, U, Cd, Zn and Ag are not unusual in black shales elsewhere. The reduced conditions and the abundance of organic matter are the main causes of the accumulation of these elements (Brumsak, 1986). According to the criteria defined by Thomson et al. (1993) and Quinby-Hunt and Wilde (1994), V, Mo and U enrichments indicate a sedimentary anoxic environment. In addition, sulfur isotope studies of Alfonso et al. (2002) agree with a sedimentary-exhalative origin within an anoxic basin for the Prades Mountains deposits.

All the studied samples have high V and Cr values, which agree with the abundance of V and Cr bearing minerals (V-rich titanite, V-rich tremolite, goldmanite, V-rich allanite and V–Cr oxides) in the analyzed samples (Canet et al., 2003b). V is more soluble in oxidizing conditions (Wehrli and Stumm, 1989). So, V accumulations in sediments are indicative of an anoxic sedimentary environment (François, 1988). Consequently, the reducing conditions of the Silurian basin, evidenced by the occurrence of black shales, favoured the V accumulation. However, some analyses yielded high values (up to 0.80 wt.% of V₂O₃) that cannot be fully explained by a direct precipitation from seawater. The highest values are comparable to those found in metalliferous sediments of the Red Sea (1.3 wt.% of V₂O₃, Jedwab et al., 1989). In these sediments, V is mostly concentrated as authigenic vanadomagnetite crystals. Even higher values have been registered in black shale hosted sedex deposits from China (up to 5 wt.% of V₂O₃, Coveney and Nanseng, 1991). The highest Cr concentrations from the Prades Mountains (up to 640 ppm of Cr₂O₃) are

similar to those analyzed by Loukola-Ruskeeniemi (1991) in black shales from Outokumpu deposit (up to 520 ppm of Cr₂O₃).

Krauskopf (1956) demonstrated experimentally the efficiency of the Fe oxide particles to scavenge the V dissolved in water by adsorption. This fact supports the recognized importance of exhalative particles of the hydrothermal plumes in the V scavenging from seawater (Trefry and Metz, 1989). In this way, scavenging from seawater by exhalative particles far away from the vent zones (in the hydrothermal plume) may represent an important contribution to V enrichment in the Prades Mountains deposits, added to the distinctive enrichment of an anoxic pelitic sedimentation. The lack of underlying discordant mineralization and the scarcity of massive sulfides, which suggest a distal mineralization, support this hypothesis. The underlying mineralization complexes, interpreted as feeder zones to stratiform ore deposits (Goodfellow et al., 1993), are absent in near 80% of sedex deposits worldwide (Sangster and Hillary, 2000). Lydon (1995) considered those exhalative deposits that are not underlain by feeder zones as vent-distal deposits that formed away from vent zones.

A scavenging from seawater also would explain the Cr enrichment; since Cr adsorption by particles of Fe oxides has been experimentally demonstrated by Murray et al. (1983).

Most of analyzed samples show a considerable Ni and Co enrichment with respect to NASC standard. Ni–Co enrichment is distinctive of black shales elsewhere and has been reported in some present-day metalliferous sediments (i.e. TAG, Shearme et al., 1983). In addition, Ni–Mo sedimentary-exhalative deposits hosted in black shales are known in Canada (Grauch et al., 1991) and in China (Lott et al., 1999; Steiner et al., 2001). Thus, Ni–Co enrichment could be partially attributed to hydrothermal activity. Although average Mo concentration in sulfide bearing shales (34 ppm) is not greater than in black shales anywhere (i.e. 70 ppm according to Wedepohl, 1974), the highest concentrations (up to 125 ppm in Coma Fosca) could imply a hydrothermal contribution. These high values agree with the occurrence of small molybdenite crystals disseminated within the shales.

U is another element enriched in most analyzed samples, while Th concentration is close to normal

values (12.3 ppm according to Gromet et al., 1984). The U content is due to the occurrence of small crystals of uraninite in the analyzed samples. In anoxic conditions, U^{6+} (soluble) is reduced to U^{4+} (insoluble) (Cochran et al., 1986), favouring the accumulation in the sediments as UO_2 (uraninite). Moreover, it is necessary to consider that high U concentrations are reported in relation to present-day vent activity (Bloch, 1980). In these environments, U shows an isotope signature derived from seawater and accumulates as consequence of bacterial activity (Mills et al., 1994), or for adsorption by sulfide particles (Butler and Nestbitt, 1999). These arguments can justify the fact that some of the U-richer analyses of the Prades Mountains correspond to the sulfide richest samples.

Although Mn is usually related to submarine hydrothermal venting (Klinkhammer et al., 1983), all the analyzed samples are depleted in this element. To justify these low Mn values, it is necessary to consider that the studied deposits formed in a euxinic basin where anoxic conditions favoured the reduction

to the more soluble Mn^{2+} (Libes, 1992). So, Mn could not be fixed in the sediments.

In summary, the redox-sensitive trace-elements abundances suggest that ore deposition took place in an anoxic sea floor by fall-out of exhalative particles from a hydrothermal plume, but distal from the vent sites.

6.2. Sm–Nd isotopes: age of mineralization

The isochron obtained from feldspar-rich layers provides an age of 437 ± 57 Ma. The MSWD value is 1.3. Therefore, considering that strictly the isochrons has $MSWD \leq 1$ (Rollinson, 1993), in fact, a pseudo-isochron has been calculated. The dispersion of values that creates this error can be attributed to the presence of significant amounts of detrital grains that could affect the initial $^{147}Sm/^{144}Nd$ values. This contamination must be especially due to zircon detrital grains (capable to host REE). The two samples most separated from the isochron (M-14 and Ag-11) contain biotite, which possibly is to some degree of detrital origin.

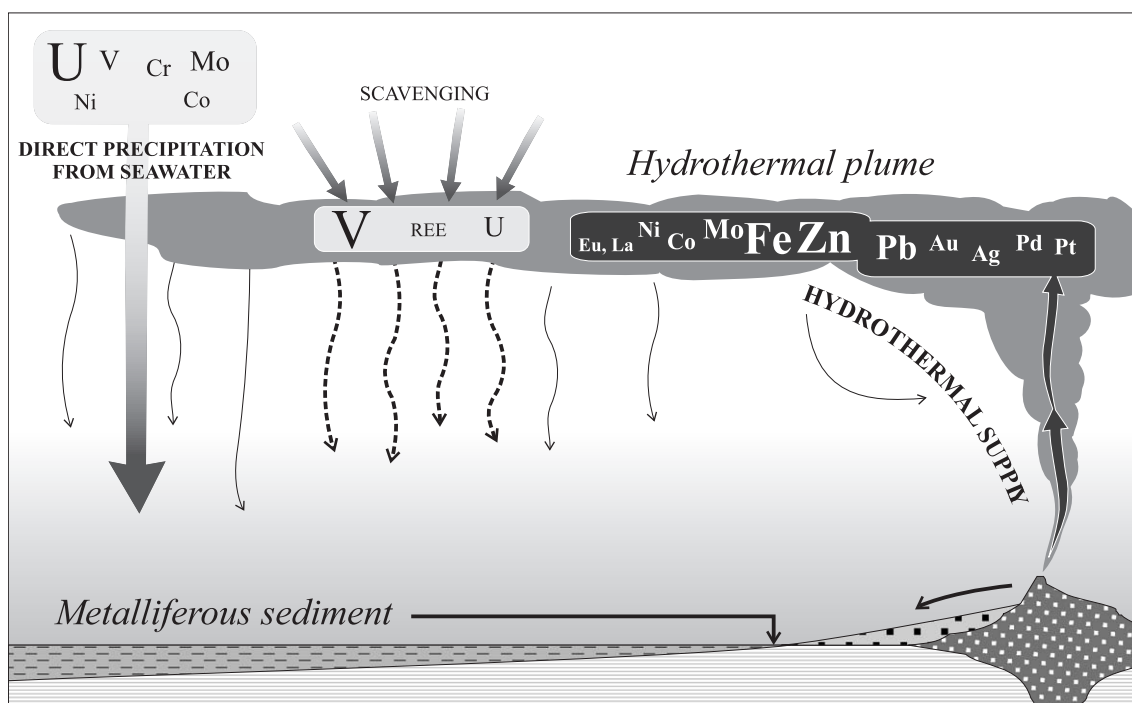


Fig. 7. Schematic reconstruction of the submarine hydrothermal system showing the origin of different enriched elements.

Furthermore, late processes, as sericite alteration that affected the feldspar-rich layer in variable degree, can modify the results. Late processes could supply or remobilize REE, and consequently, they could modify Sm–Nd isotope ratios.

In spite of the induced error, the resultant age (437 Ma) coincides with the age of the host shales (Llandoveryan). Consequently, feldspar-rich layers (or its precursor) must have a syngenetic origin in relation to the host sediment. This fact agrees with the fine granulometry of the feldspar-rich layers, the absence of textures that suggest replacement of previous lithologies and its pre-deformative and pre-metamorphic character.

7. Conclusions

Geochemical analyses provide information about the origin of the complex mineral associations of the V–Cr–PGE and base metals occurrences from the Prades Mountains.

The REE patterns are probably essentially inherited from seawater, suggesting a major marine origin for these elements, though there could be a substantial hydrothermal supply for Eu and La.

The concentration in some redox-sensitive trace elements (V, Cr, Co, Ni, Mo and U) is anomalously high. This enrichment is inferred to be partially due to a direct precipitation from seawater favoured by anoxic conditions. However, most V and Cr could have been fixed from seawater by means of a scavenging process by exhalative oxide particles in a hydrothermal plume. The enrichment of Ni, Co and Mo could imply a hydrothermal contribution for these elements.

Sm–Nd results indicate that the mineralization is contemporaneous to the host sediments (437 ± 57 Ma, Llandoveryan). This age is consistent with the pre-deformative and pre-metamorphic origin as suggested by the textural criteria. So, these results suggest that feldspar-rich layers are metaexhalites.

In summary, this geochemical study suggests a submarine exhalative origin for the sulfide deposits and occurrences of the Prades Mountains. The ore deposition could have taken place far away from the vent area, by accumulation of particles settling down from a distal hydrothermal plume in an anoxic basin (Fig. 7).

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