Chemical and mineralogical compositions of black shales (Middle Palaeozoic of the Central Pyrenees, Haute-Garonne, France)

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Abstract

The epicontinental sedimentary, epi- to mesozonal rocks of the Middle Palaeozoic of the Central Pyrenees host several economic Pb–Zn concentrations and numerous occurrences of these metals. The authors have endeavoured to recognize the original mineralogical nature of the epizonal host rocks in the concession of Baren (Haute-Garonne). Seventy-two whole-rock analyses were used for this purpose and interpreted by means of chemico–mineralogical diagrams.

These diagrams use parameters chosen so as to include in the projection planes the essential minerals forming the rocks under discussion. In this way, the nature and the possible initial mineralogical composition of the rocks, which are usually obliterated during metamorphism, are made visible. The chemical compositions of the different rock units are sufficiently typical to compensate for the absence of fossils and to allow stratigraphic identifications.

No volcanic contribution could be recognized in the pelites. The latter demonstrate the existence of a continent, undergoing a kaolinite-producing alteration, especially during the Silurian. The analysed trace elements (Ba, Cr, Cu, Ni, Pb, Rb, Sr, Th, U, V and Zn) are not enriched with respect to the clarkes for these rocks, except slightly in the case of U and Th and more strongly for Cr and V. The carbonate rocks contain predominantly calcite, with subordinate dolomite. They show a strong enrichment in Ba, whereas the content of the other trace elements is normal.

KEYWORDS: black shales, palaeogeographic reconstruction, geochemistry, sulphides, Pyrenees, France.

Introduction

Aim and scope. This publication* reports on chemical analyses of the metamorphic black shales in the Baren Pb–Zn exploration concession (Hautes Pyrénées), on the interpretation of major-element data by means of chemico–mineralogical

diagrams (see appendix for the explanation of the diagrams). The first aim was to determine the initial nature and composition of the black shales occurring near the Pb–Zn occurrences. Similar sulphide occurrences in other parts of the central Pyrenees were interpreted as being pene-contemporaneous with the sediments of Upper Ordovician or Lower Devonian age, and the metals were supposed to have been derived from a remote contemporaneous volcanism. This deduction was based on rocks interpreted as being interstratified tuffites and an attempt was therefore made to trace any volcanic parentage.

The conclusions of this paper do not apply to Pierrefitte–Nestalas (Hautes Pyrénées), which is
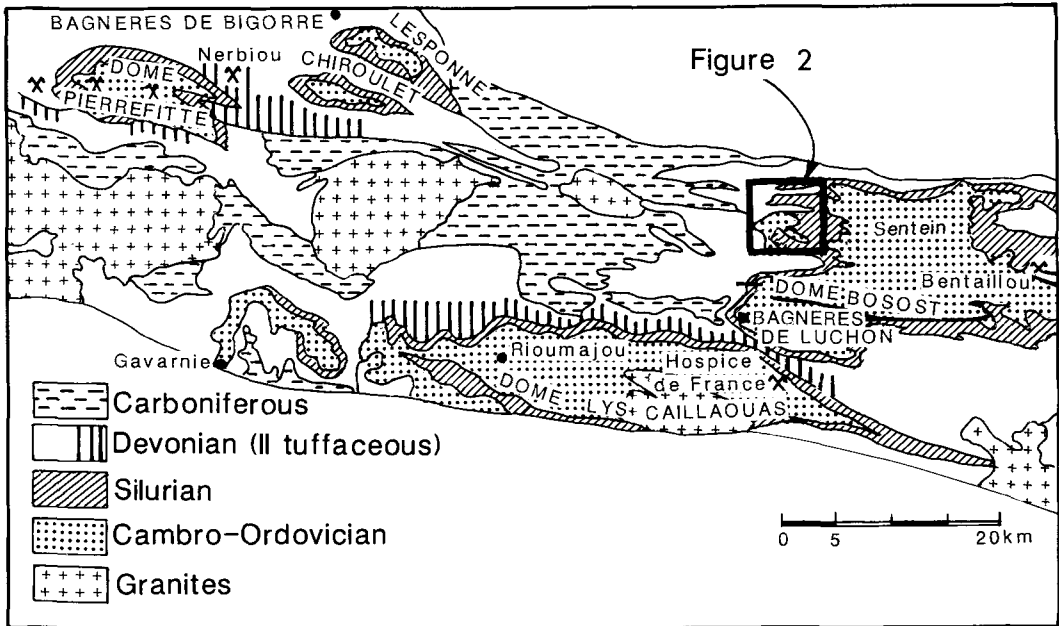
FIG. 1. Map showing the study area and the Pyrenean localities mentioned in the text (from Pouit and Alsac, 1978).

located 55 km W of the study area (Fig. 1) and is the only Pb–Zn deposit of the Pyrenees to be geometrically related to volcanic phenomena.

Regional setting. The area studied is located in the northern part of the Palaeozoic Axial Zone of the Pyrenees (Fig. 1). It includes metamorphic formations and igneous rocks (Mail de la Pique granite and microgranites) of Upper Ordovician to Middle Devonian age for the former, and probable Westphalian for the latter (Fig. 2). The area underwent Hercynian and Pyrenean orogenies.

Stratigraphy and petrography

The sedimentary sequence

Three major stratigraphic subdivisions were distinguished in the field (Vegas, 1982) (Fig. 3).

Ordovician. From bottom to top the following units can be recognized:

50 m of conglomerates (= 'niveau de base').

300 m of quartz-phyllites, quartzites and phyllites with an interstratified discontinuous limestone horizon of less than 15 m (sometimes containing faint occurrences of sphalerite). This horizon is the lateral equivalent of the 'calcaire de Bentaillou' (Fig. 1) and grades upwards into phyllites and quartzites (= 'serie du Caradoc').

30 m of shales (= 'serie de transition I', elsewhere called 'schistes bleus'). Ten metres of a fossiliferous limestone (= 'horizon troué', also known as 'grauwacke à Orthis' or as 'calcaire en sandwich') are interstratified in these shales near Granges de Coumagnès. This unit hosts the only important sphalerite and pyrite occurrence in the Upper Ordovician. It is the lateral equivalent of a lenticular limestone horizon, found extensively over the Iberian Peninsula (Saupé, 1971; Tamain, 1971), where it is dated as Ashgill in the Sierra Morena (Fuganti and Serpagli, 1968). In the latter region, it frequently contains non-economic Pb–Zn occurrences.

Silurian. The carbonaceous shales of the Pyrenees are traditionally considered to be of Silurian age, although palaeontological evidence is frequently lacking (Destombes, 1953). They are up to 100 m thick. Graptolite shales, like those found 45 km WNW of Baren at the Fontaine de Labassère, near Bagnères de Bigorre (Francois, 1983), differ chemically and macroscopically from the classical black shales of the Pyrenees (Report to the DGRST in preparation, later referred to as A.C. report). The lateral extension of these formations is large, extending from the Sahara to Thuringia (G.D.R.), without synchronicity (Saupé, 1973). Moreover, black shales occurring at different

ALLUVIUM AND DEBRIS

CHLORITOID SCHIST

CRINOID-BEARING LIMESTONE

RHYTHMIC SHALE-LIMESTONE ALTERNANCES

"SERIE DE TRANSITION II"

MIDDLE

DEVONIAN

LOWER

CARBONACEOUS SHALES   SILURIAN

"SERIE DE TRANSITION I"

"HORIZON TROUE"

QUARTZ PHYLLITES, PHYLLITES AND QUARTZITES

"CALCAIRE RUBANE"

"NIVEAU DE BASE"

UPPER ORDOVICIAN

γ GRANITE OF "MAIL DE LA PIQUE"

μ MICROGRANITES

FAULT

BEDDING

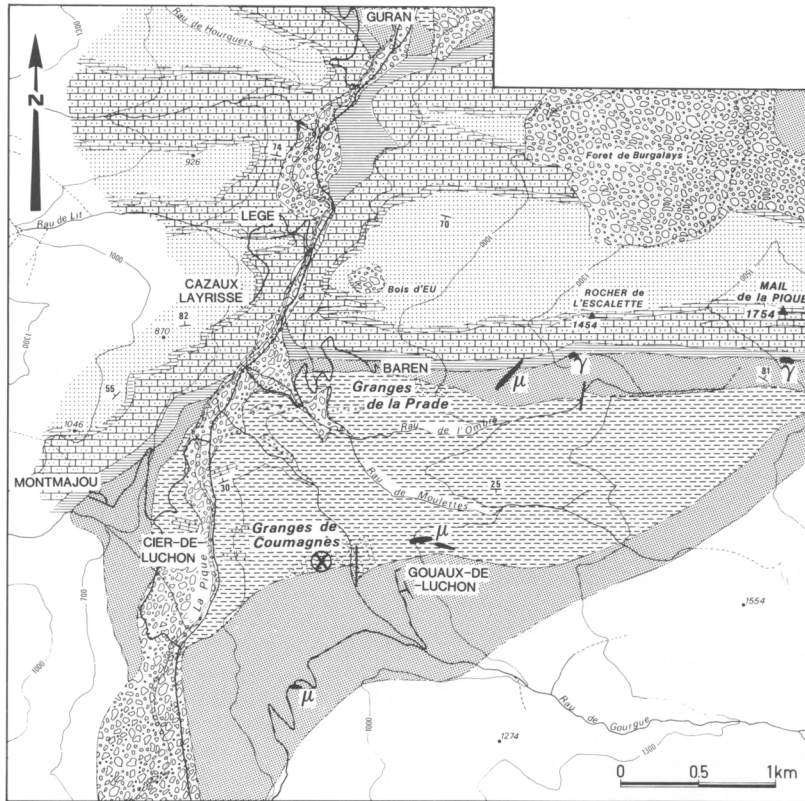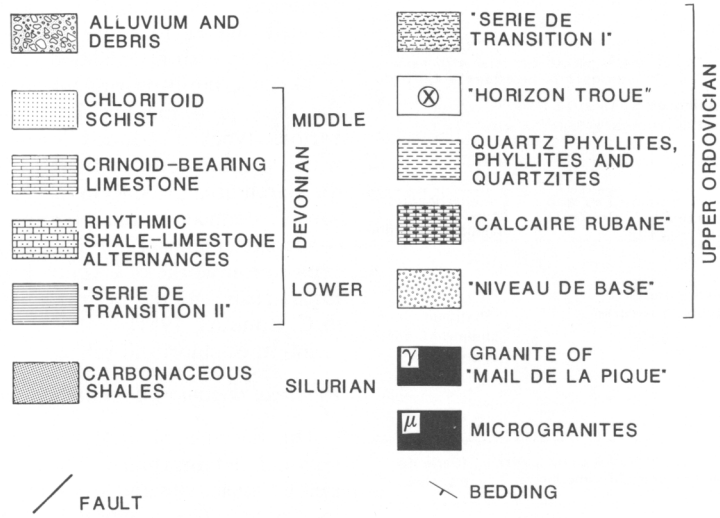Dess. A. LEGROS-CRPG-Avril 1984

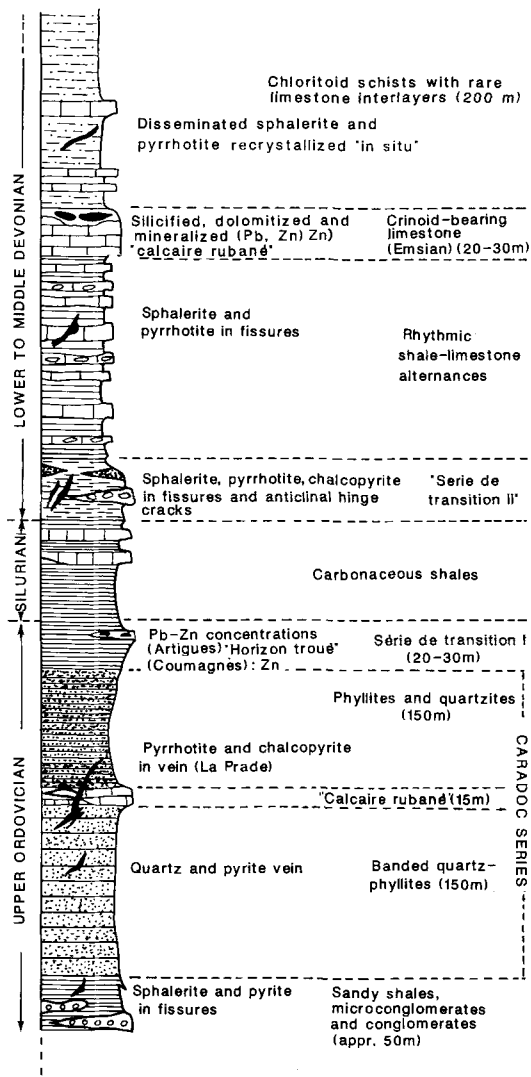Fig. 2. Detailed geological map of the Baren area (Haute-Garonne).

FIG. 3. Stratigraphical column of the Baren area.

stratigraphical levels have sometimes been confused with each other, especially if they are pyrite-bearing and limonitized. Fossiliferous calc-schists are intercalated in the upper levels and are considered to be of Wenlock age, by analogy with similar rocks dated elsewhere in the central Pyrenees (e.g. Destombes and Vaysse, 1947).

Devonian. The uppermost units are divided from bottom to top as follows:

50 m of dark, carbonate shales, containing up to 4 or 5% C_{org} (Vegas, 1982) (= 'serie de transition II');

200 m of rhythmic shale-carbonate alternations,

beginning with feldspathic sandstones, passing to banded shales, to more or less marly banded calc-schists with intercalated vacuolar limestones;

30 m of crinoid-bearing limestone of Emsian age; the base is a massive limestone, grading into various types of banded limestones at the top, which contain most of the Pb–Zn occurrences of the Baren area (= 'CRGS' or 'calcaire rubané gris souris', defined in the Nerbiou (Fig. 1) mining concession, Dallas, 1980); the CRGS found near the exploration works of Cazaux-Layrisse is dated as Emsian using conodonts (pers. comm. of D. Stoppel to C. Bouquet, 1981);

200 m of chloritoid schists.

Regional metamorphism and contact metamorphism

The Baren area underwent a weak, two-stage regional metamorphism. The first stage, characterized by muscovite and secondary calcite, is related to the first Hercynian deformation phase. This phase gave an isoclinal, axial-plane schistosity that obliterates the bedding in most places. The second metamorphic episode can be related to the second Hercynian deformation phase and is marked by the formation of a crenulation schistosity in the silty layers.

The contact metamorphism of the Mail de la Pique granite gave muscovite and actinolite in the Silurian shales and muscovite, biotite, actinolite and tremolite in the Lower Devonian carbonate horizons.

Major-element data and their interpretation

All the rock types were chemically analysed except for the Upper Ordovician conglomerates and the feldspathic sandstones of the lowermost rhythmic series of the Lower Devonian. The analyses were performed by automated emission spectrography using a microwave-plasma source (Govindaraju et al., 1976). The 72 analyses are available upon request from the EDTA Service of the CRPG. Analyses of representative samples are given in Tables 1 (clastic rocks) and 4 (limestones).

The isochemical metamorphism recognized in the following may need justification. During diagenesis, important chemical exchanges occur between the porous sediments and the interstitial waters. As porosity decreases with increasing diagenesis and later with incipient metamorphism, the solutions become less abundant and thus, the chemical compositions of the rocks tend to be preserved (von Engelhardt, 1967). In an active geothermal system, like Salton Sea (California, USA), with porous sediments and a high geothermal gradient inducing an intensive fluid circulation, Na and Mg tend to be fixed in the

solids, and K and Ca to be enriched in the fluids (Degens and Chillingar, 1967). A mass balance calculation of these exchanges, based on experimental data on the equilibrium between alkali feldspars and alkali chloride vapours, shows that at 600 °C and 2 kbar, only 0.02% Na is replaced by the corresponding amount of K in the rocks of Salton Sea (Bartholomé, 1965). Similarly, the formation of glaucophane and of jadeite in the Franciscan 'melange' is only pressure controlled (Ernst, 1971). In less extreme cases, the absence of chemical re-equilibration and of visible trends has been repeatedly shown for clastic sediments passing from phyllites to mica schists in the regional metamorphism (Shaw, 1956; Zwart, 1963; de La Roche, 1965; Moine, 1974). Thus, an isochemical metamorphism is the rule for massive clastic rocks. On the contrary, chemical exchanges occur during metamorphism of thin alternating sequences (e.g. flyschs in general, or in the studied sequence, the Devonian rhythmic shale-carbonate alternations transformed by regional metamorphism into the so-called 'barregiennes') or in the event of hydrothermal phenomena.

Pelitic rocks (Table 1)

Ordovician. The 'niveau de base' had a common initial mineralogical composition: detrital quartz and clay minerals (Fig. 5), the other constituents being subordinate, as shown by the elongate shape of the representative cluster, parallel to and close to the quartz-(illite, chlorite) line. The other diagrams (Figs. 4 and 7) show that the chlorites were subordinate, except to a small extent for sample 101. The illite of sample 45 does not differ much from muscovite. Among all the rocks examined, those of the 'niveau de base' have the highest maturity, especially sample 44 with approximately 70% quartz.

The 'serie du Caradoc' shows distinctly less chemical homogeneity (Figs. 4-6), and consists of two petrographic types: phyllites and quartz-phyllites (Vegas, 1982). The representative cluster of this group surrounds the origin of the coordinates and is elongate towards the illite-muscovite pole in the Al/3 = f(Al/3 − K) diagram (Fig. 5). The sandstones of this group are less mature than those of the 'serie de base'. Quartzo-phyllites (underlined
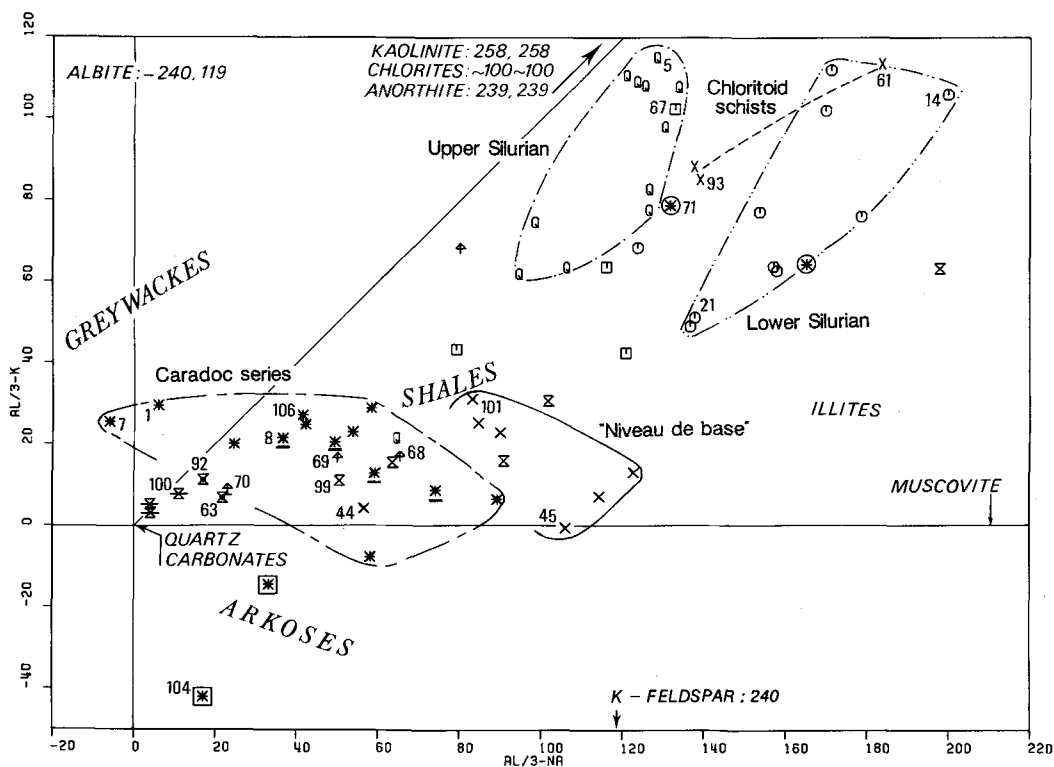

FIG. 4. Al/3 − K = f(Al/3 − Na) diagram.

Table 1 - Selected chemical analyses of Middle Palaeozoic detrital rocks from the Baren area (Haute-Garonne)

	AB 101	AB 45	AB 44	AB 1	AB 106	AB 8	AB 104	AB 68	AB 69	AB 71	AB 14	AB 21	AB 5	AB 17	AB 67	AB 49	AB 61	AB 93
	×	×	×	✳	✳	✳	⊠	↑	↑	⊛	◔	◔	Q	Q	▣	▣	×	×
SIO2	59.20	70.93	84.22	75.02	59.23	73.50	64.47	57.89	42.55	62.02	41.93	52.56	57.46	66.83	48.00	27.73	40.11	48.69
AL2O3	13.89	17.02	8.85	13.25	16.93	15.03	14.47	10.50	8.30	24.97	34.73	24.07	26.17	18.90	29.03	13.07	33.92	22.93
FE2O3 T	12.56	1.61	1.80	1.59	7.73	1.67	6.88	4.70	2.97	0.29	2.94	3.09	0.17	0.86	4.62	3.99	8.51	8.75
MNO	0.11	0.02	0.02	0.03	0.04	0.03	0.10	0.08	0.08	0.03	0.05	0.03	0.01	0.02	0.03	0.21	0.04	0.09
MGO	1.84	0.73	0.42	0.66	3.09	0.42	1.70	1.24	1.29		1.27	1.30	0.16	0.32	1.67	1.77	2.25	1.49
CAO	2.65			0.67	0.43		1.29	13.06	22.05*	0.47	1.87	0.17	1.59	0.19	0.19	23.90	0.45	5.38
NA2O	0.14	0.16	0.04	2.50	1.86	1.91	1.27	0.10	0.13	0.98	0.85	0.61	1.35	0.92	1.77	0.19	1.21	0.36
K2O	2.71	5.25	2.51	2.68	3.60	3.60	3.32	2.42	1.76	3.97	5.69	4.99	2.69	2.95	4.11	1.97	5.15	3.10
TIO2	0.61	0.97	0.48	0.76	1.17	0.73	0.83	0.50	0.38	1.26	1.70	1.11	1.45	0.91	1.13	0.61	1.61	0.90
P2O5	1.95	0.20		0.23	0.58	0.11	0.19	0.01	0.05		0.13	0.17		0.03	0.15	0.17	0.23	0.24
P.F.	3.70	3.28	1.81	1.84	4.19	2.05	3.99	9.28	19.25	5.69	7.62	11.37	8.63	7.81	9.67	24.92	6.32	8.50
TOTAL	99.36	100.17	100.15	99.23	98.85	99.05	98.51	99.78	98.81	99.68	98.78	99.47	99.68	99.74	100.37	98.53	99.80	100.43
CO2 M	0.05	0.02	0.02	0.00	0.19	0.04	1.21	8.87	17.68	0.15	0.28	0.00	0.21	0.25	0.00	21.37	0.05	5.08
C ORG	0.27	0.36	0.05	0.02	0.25	0.08	0.13	0.13	0.24	1.29	1.82	4.21	4.55	3.80	0.95		0.30	0.25
H2O T	4.31	2.72	1.64	2.05	4.20	1.82	3.22	2.44	2.05	4.14	5.54	3.48	4.26	3.10	5.60	3.27	6.49	3.92
S T	<0.01	0.04	0.04	0.90	0.02	0.11	0.31	4.26	0.16	<0.02	0.03	0.71	0.02	0.02	0.49	0.09	0.02	0.14
BA	251	555	240	347	472	450	689	230	227	590	920	609	545	440	844	827	906	667
CR	59	117	41	69	114	73	92	55	58	170	206	137	129	99	198	118	199	104
CU	<10	<10	<10	<10	30	29	<10	27	<10	<10	54	11	<10	42	33	<10	<10	23
NI	66	27	22	24	53	31	45	52	39	23	38	86	17	29	119	57	91	94
SR	81	35	25	48	46	22	48	87	209	221	139	119	248	142	856	822	693	125
V	87	184	44	87	179	105	137	54	84	394	453	423	281	424	412	176	252	126
RB	85	211	82	85	144	93	120	71	64	239	393	231	144	206	220	80	236	117
PB	13		3		20	15	10	32	17	26	189	20	23	20	42		21	25
ZN	97		8		61	69	38		527	7	59	103	6	11	142		157	125
U											11	9	5	9				
TH											19	14	15	14				

Analytical techniques - Major elements (%) : automatically recorded micro-wave excited emission spectography (Govindaraju et al., 1976) - Carbonate CO_2, C_{org}, total H_2O and total S : impulsion coulometry organic CO_2 deducted, impulsion coulometry after elimination of carbonates, gravimetry (Penfield) and coulometry - Trace elements : automatically recorded ICP emisssion spectrography (Govindaraju et al., 1976)

Samples - Ordovician : 1) "Serie de base" (101 - chlorite schists; 45 - muscovite schist; 44 - quartz phyllite)
2) Caradoc series (1 - albite phyllite; 106 - phyllite; 8 - quartz phyllite; 104 - schist interlayer in the "calcaire rubané")
3) "Horizon troue" (68 and 69 - mineralized, detrital facies)
4) "Serie de transition I" (71 - schist)

Silurian : 1) Lower Silurian (14 and 21 - carbonaceous schists)
2) Upper Silurian (5 and 17 black shales)

Devonian : 1) "Serie de transition II" (67 - phyllosilicate type; 49 - carbonate type)
2) Chloritoid schists (61 and 93)

stars) are less variable than phyllites and have chemical compositions similar to those of the rocks of the 'serie de base', slightly diluted by other minerals (Fig. 5).

The latter can be identified as albite, Fig. 6 (up to 21% in sample 1, the richest of all), and an Fe–Mg mineral, possibly biotite (Fig. 7). Indeed, in this diagram the points representing the pelites associated with the banded limestones (104 and 105) and two points representative of phyllites extend along a line with a slope of 0.5, corresponding to a constant K/(Fe + Mg) ratio. This value has no simple explanation because the line does not pass through a point representing a specific mineral, except possibly for a mixture of orthoclase and biotite, especially since the ratio Fe_2O_3/MgO is highly variable for these samples (in this diagram the theoretical biotite end members are distributed between the point (1.25,0.5) for eastonite and siderophyllite and the point (3,1) for annite and phlogopite). Such an alignment is probably not fortuitous and implies chemical exchanges which are likely because the rocks of these formations are composed of thin layers. In Fig. 7 all the other points representative of the 'serie du Caradoc' are closely grouped, showing that the relative proportions of sheet silicates are rather constant.

The 'serie de transition I' differs markedly from the two other Ordovician formations but is underrepresented taking into account its larger variability, although exaggerated by the differences in losses on ignition. The eccentric position of two points in Fig. 4 indicates a higher kaolinite content (Figs. 5–7), also corresponding to mature rocks.

In the 'horizon troue' the following four different facies are distinguished (Vegas, 1982): (a) normal (70, see below); (b) brecciated; (c) silicified and (d) mineralized. It contains some calc-schist interlayers, either bearing pyrite and sphalerite (68) or barren (69).

The position of the points in the overlap zone of the shale and greywacke fields (Fig. 5) is misleading.
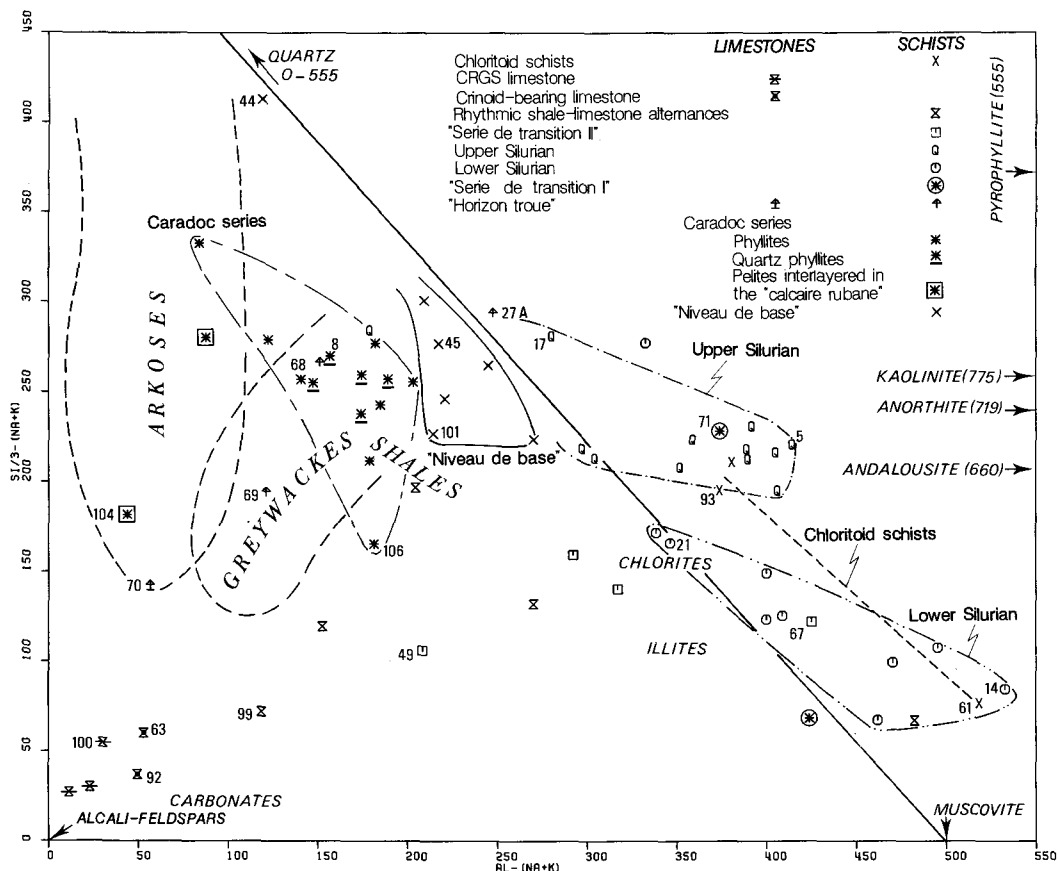
QUARTZ
0 - 555

44×

Chloritoid schists
CRGS limestone
Crinoid-bearing limestone
Rhythmic shale-limestone alternances
"Serie de transition II"
Upper Silurian
Lower Silurian
"Serie de transition I"
"Horizon troue"

LIMESTONES   SCHISTS
X

Caradoc series
Phyllites
Quartz phyllites
Pelites interlayered in
the "calcaire rubane"
"Niveau de base"

PYROPHYLLITE (555)

Caradoc series

ARKOSES

× 45   ＋ 27 A   Upper Silurian

KAOLINITE (775)
ANORTHITE (719)

Niveau de base

ANDALOUSITE (660)

GREYWACKES SHALES

104

×101

Chloritoid schists

69

*106

CHLORITES

Lower Silurian

70

67

ILLITES

14

49

99

61 X

100

63

92

CARBONATES
ALCALI-FELDSPARS

MUSCOVITE

SI/3 - (NA+K)

AL - (NA+K)

FIG. 5. Si/3 − (Na + K) = f(Al − (Na + K)) diagram.

They do not correspond to greywacke compositions as seen from Figs. 4, 6 and 7. If the position of the points is recalculated after deduction of Ca as calcite, the points fall near the quartz–sheet-silicate line and near point 27A. Further, the representative points are aligned in the other diagrams, showing that the original composition was binary and consisted of (1) a mixture of quartz, chlorite, kaolinite and illite in rather constant proportions, and (2) variable amounts of calcite.

Silurian. The representative points of the Silurian rocks form two distinct clusters, which correspond to Lower and Upper Silurian (Vegas, 1982). These subdivisions are not mappable. In neighbouring areas, of higher metamorphic grade, this distinction could not be verified (François, 1983; Brula, 1984).

The initial material of both Silurian groups of Baren was highly mature (Fig. 4) and consisted of kaolinite and illite in nearly equal amounts, with more detrital quartz in the upper group. The strongly elongate shape of the clusters cannot be explained by binary mixtures. It rather expresses an illite/muscovite–chlorite–quartz mixture in variable proportions, with additional kaolinite.

At Baren, the Lower Silurian averages 7.4% C_{org} and the Upper Silurian only 3.7% with a smaller spread for both figures. It is also noticed that the Upper Silurian is slightly enriched in CaO, compared to the Lower Silurian (1.07% for 13 samples, compared to 0.38% for 9 samples of which 4 are below the detection limit of 0.02%). This trend can be related to the presence of limestone interlayers and to occasional margarite in these formations. The high Al_2O_3 content of some samples is remarkable. The maximum 34.73% (14) is unusual for schists and corresponds to a high initial proportion of illite and kaolinite.

Paragonite, considered a marker mineral for Silurian strata in the Pyrenees (Escande *et al.*, 1981), was clearly identified by X-ray diffractometry in the sample (36: Upper Silurian) having the highest Na_2O content (1.58% Na_2O) and can still
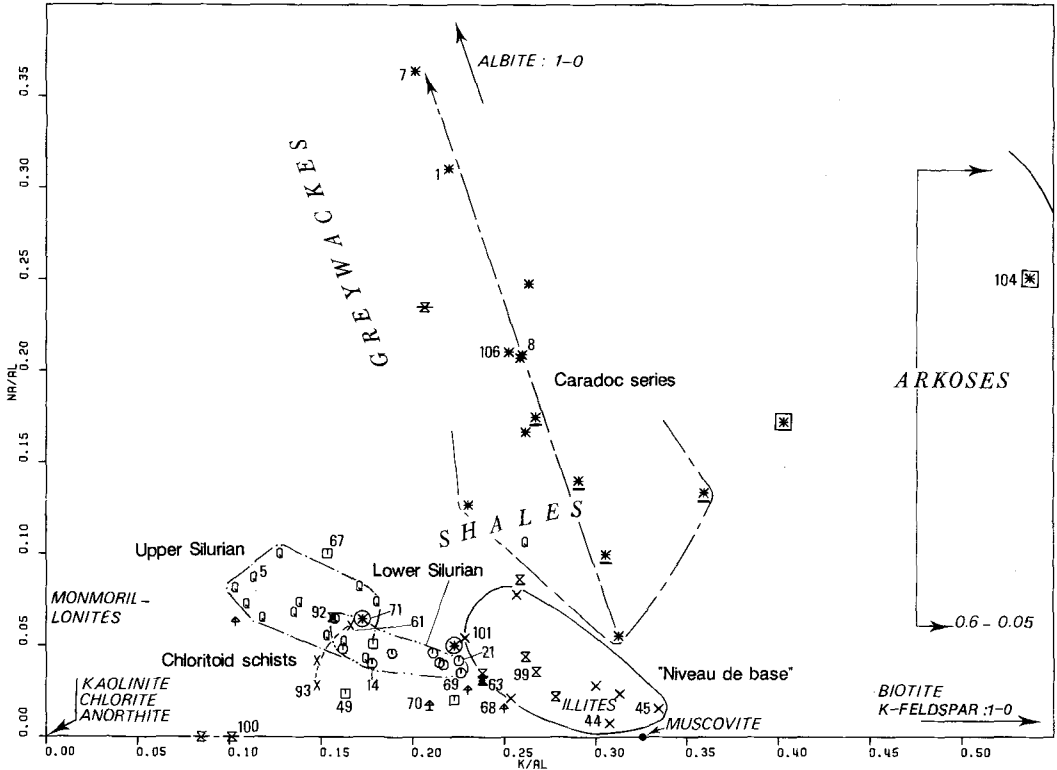
FIG. 6. Na/Al = f(K/Al) diagram.

be identified if the Na_2O content is lower (0.90% in sample 109: Upper Silurian). In both samples it is associated with muscovite, chlorite and quartz.

Margarite was determined by diffractometry in a number of Silurian samples. Its grain size is too small to permit a microscopical identification, but on a SEM image the Ca-rich zones are always seen to fall within high-Al areas. A mineral association of paragonite and margarite, with subordinate chloritoid was described for the Silurian of Sentein (Fert, 1976) (Fig. 1).

Devonian. The horizons of the lowermost Devonian (= 'série de transition II') were given an important role in the interpretation of the Pb/Zn sulphide occurrences of the central Pyrenees because they were thought to be tuffaceous (Pouit and Alsac, 1978). The distribution of these rocks (map in Pouit and Alsac, 1978; Fig. 1) is however limited to the areas of medium-grade metamorphism. The rocks of Baren, because of their low-grade metamorphism, offer an interesting comparison. The chemical constitution of the 'série de transition II' is similar to that of the so called tuffites, but no plagioclase is developed. Two

petrographic trends were observed in this 'série de transition II':

argillaceous type, consisting of kaolinite, sericite, chlorite and some detrital quartz grains, with subordinate pyrite, sphalerite and trails of organic matter (67).

carbonate type, formed by cm-thick alternations of calcite layers and detrital layers, containing illite, organic matter and heavy minerals (rutile, zircon). Sample 49 contains 23.90% CaO, which represents over 42% theoretical calcite. Noteworthy is the abundance of organic matter in these rocks (and as a consequence, that of sulphides) and the absence of plagioclase.

The 'schistes à chloritoide' are the youngest stratigraphic formation of the area studied. They contain muscovite, chlorite, quartz and chloritoid, determined microscopically and by diffractometry. The lack of kaolinite was checked by heating the preparations to 500 °C. Pyrophyllite was only suspected and not proven: a weak peak at 9.20 Å was observed in the sample having the highest chloritoid content (93). This pyrophyllite peak
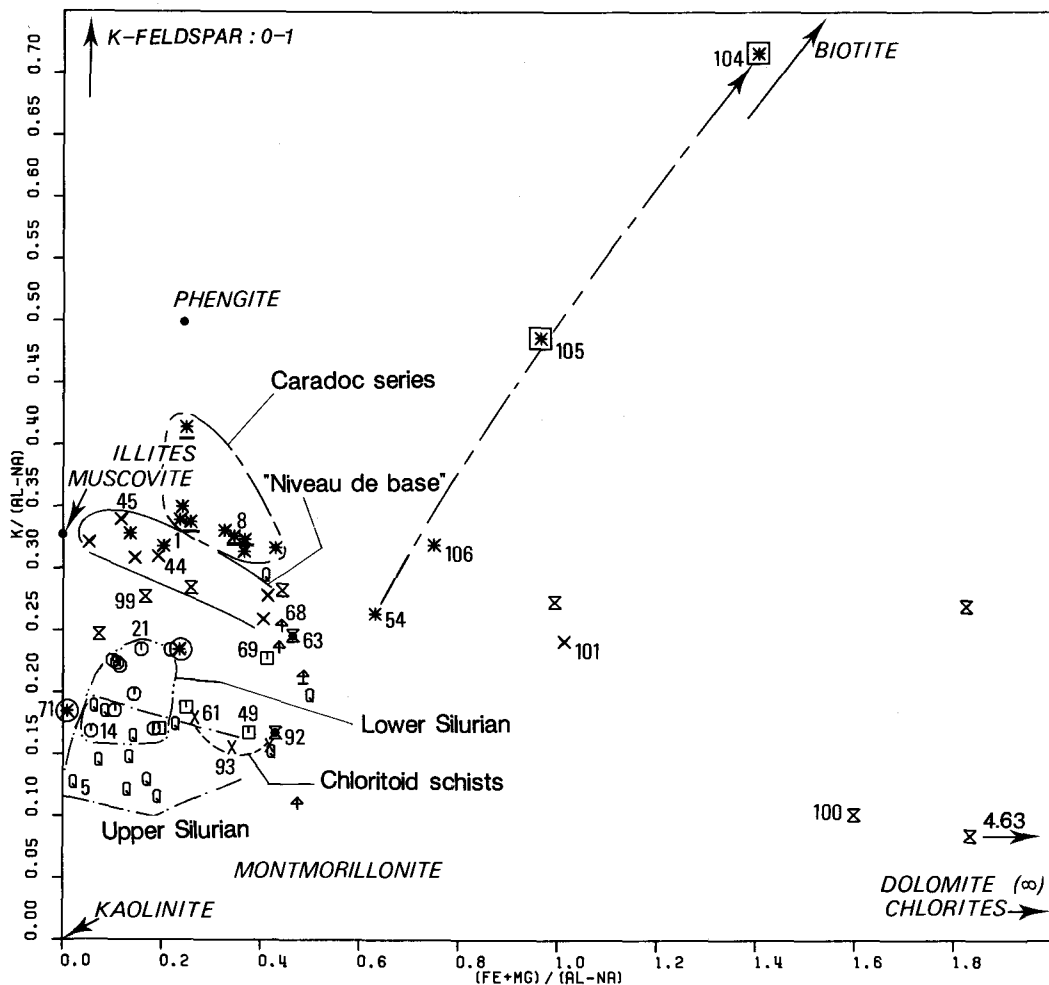
K-FELDSPAR : 0-1

104 ⊠ BIOTITE

PHENGITE

⊠ 105

Caradoc series

ILLITES
MUSCOVITE "Niveau de base"

45
×
× × 1
× 44 ×
99 ⊠

"Niveau de base"

8
*

* 106

* 54

⊠
× 101

⊠

21
99 ⊠

68
× ⊠
69 ⊡ ⊠ 63

71 ⊛
⊙ 14
5

61 49
× ⊠ 92
93

Lower Silurian

Chloritoid schists

Upper Silurian

100 ⊠

⊠ 4.63 →

MONTMORILLONITE

DOLOMITE (∞)
CHLORITES →

KAOLINITE

K/(AL−NA)

(FE+MG) / (AL−NA)

0.0   0.2   0.4   0.6   0.8   1.0   1.2   1.4   1.6   1.8

FIG. 7. K/(Al − Na) = f(Fe + Mg)/(Al − Na) diagram.

could not be strengthened by grain-size separation.

In sample 93, calcite and dolomite are finely dispersed throughout the rock (carbonate CO_2 = 5.08%). In the heavy fraction of this sample, only chloritoid and pyrite are concentrated, pyrrhotite being conspicuously absent. In other samples, pyrite and pyrrhotite coexist (Vegas, 1982). The association of Fe-sulphides and of chloritoid was not mentioned for metamorphic rocks (Halferdahl, 1961). It is known only for hydrothermal veins and their alteration aureoles.

Chloritoid forms thin laths. Its composition, determined by microprobe on two samples (14 measurements) is remarkably constant (Table 2). This mineral is known from other Pyrenean

localities but is rare. A characteristic mineral of the epizone, chloritoid points to peculiar chemical rock compositions (cf. Sagon, 1976). It exists only in rocks having high Al_2O_3 and FeO contents, where low Na_2O, K_2O and CaO prevent the formation of feldspars. A high p_{S_2} would give pyrite at the expense of chloritoid. Three analysed chloritoid schists contain an average of 8.83% total Fe_2O_3 (Table 3), compared to 1.80% in those of the Silurian schist devoid of pyrite and their S content is below detection limit (0.02% S).

Discussion of the chemical composition of the pelites. The chemical compositions of 18 representative samples of detrital rock units from the Baren area are given in Table 1. Most are pelites, some are sandstones (44 and 1) or calc-schists (68,

Table 2 - Analyses of chloritoid having extreme Fe, Mg and Mn contents

	1	2	3
SIO2	25.42	25.04	24.92
TIO2		.07	.04
CRO2		.11	.02
AL2O3	41.76	40.91	41.54
FEO	23.94	24.65	24.45
CAO	.06		
MNO		.15	.28
MGO	2.43	1.51	1.99
K2O	.03	.08	
H2O+	6.36	7.48	6.77
TOTAL	100.00	100.00	100.01
SI	2.099	2.056	2.058
AL IV	3.000	3.000	3.000
TI		.005	.005
CR		.007	
AL VI	1.065	.957	1.040
	1.065	.969	1.045
FE2+	1.652	1.691	1.686
CA			
MN	.005	.010	.020
MG	.298	.182	.243
K		.010	
	1.955	1.893	1.949
OH	3.502	4.092	3.729
	11.621	12.01	11.781
ATOM FE	84.7	89.8	86.5
% MG	15.3	9.7	12.5
MN		.05	1.0

(F. Saupé - Camebax microprobe, University of Nancy I)

1 - sample AB 62 (3)

2 - sample AB 62 (8)

3 - sample M5

Table 3 - Fe^{II} and calculated Fe^{III} contents of three chloritoid schists

	AB 61	AB 62	AB 93	ANAL. METHODS
FE2O3 T	8.51	9.23	8.75	AES
FEO	6.94	7.94	7.15	VOLUMETRY
FE2O3	1.41	1.16	1.44	BY DIFFERENCE

69 and 49). These two groups will not be discussed. Further, among the trace elements listed in Table 1, discussion will be confined to those which deviate strongly from the average values for black shales, as estimated by Vine and Tourtelot (1970). The latter values are given in brackets after the symbol of the different elements. The mineralogical expression of the various elements in the schists can be determined only by multivariate analysis, which requires a larger number of samples. It will be dealt with in a forthcoming paper covering the results obtained in all of the areas studied in the Pyrenees by our group.

Two important conclusions may be derived from the major-element chemistry: (1) all four diagrams underline the purely sedimentary origin of the

schists studied. Thus, the hypothesis of a volcano-clastic contribution to these sediments is clearly eliminated, as is a volcanogenetic interpretation of the ores; (2) the Silurian and Devonian pelites are strongly enriched in Al. A similar, although less pronounced (from 20 to 25% Al_2O_3), enrichment was observed in anchizonal schists of the same age at Almaden, Spain (Saupé, unpubl. data, 1966), and of other areas of the Pyrenees. The Lower Silurian (where it can be identified) and the chloritoid schists have the highest Al contents. Sample 14 has the highest figure found, 34.73% Al_2O_3, close to the theoretical content of kaolinite, 39.50%. This mineral must have been the dominant constituent of the initial sediment, which also explains the high TiO_2 and Cr contents of this sample. Two mechanisms can lead to such high amounts of kaolinite: (1) intense weathering under a tropical climate, followed by near-shore preferential deposition of kaolinite (because of its larger grain size compared to other phyllosilicates) or (2) diagenetic reactions of phyllosilicates with formation waters. Although they are not excluded in argillaceous sediments (Dunoyer de Segonzac, 1969), porous materials are privileged sites for these reactions (Millot, 1964). Therefore mechanism (1) is preferred.

Because the source area delivering the detrital material is still unknown, the palaeogeographic conclusions remain tentative, but the problem deserves attention on a larger scale (for example the regional distribution of primary kaolinite). The dominant alteration process giving rise to these materials is kaolinization. At present, the latter is active (1) mostly at latitudes near 20° and exceptionally up to 30°, that is, near the boundary between temperate and tropical climatic zones, (2) provided the yearly amount of rain exceeds 500 mm (Pedro, 1968). According to reconstructions of the Middle Silurian continents (e.g. Scotese et al., 1979) the area later forming the Pyrenees was situated at an approximate latitude of 35° S. This complies with the first condition of Pedro (1968). The second condition cannot yet be discussed. Further, black shale formation on extensive continental shelves is related by Berry and Wilde (1978) to interglacial high sea levels. Anoxic conditions develop by lack of deep circulation, as opposed to dense cold, oxygenated waters formed at high latitudes during glaciations and flowing to great depths in lower latitudes. Kaolinite weathering crusts formed in Eastern Siberia during the Wenlock period (Cherkasov, 1973; in Seslavinskiy, 1979), which at that time was at a latitude between 25° to 30° N (cf. Scotese et al., 1979).

Two examples of bauxite (nos. 1 and 7 of Table 47, Tardy, 1969) plot in the $Si/3 - (Na + K) = f(Al - (Na + K))$ diagram (Fig. 5) with coordinates

(1080, 50) and (840, 113) that are in line with the clusters of the Lower and of the Upper Silurian formations, another hint towards a kaolinizing climate during the Middle Palaeozoic. Also noteworthy are the high TiO_2 contents (Table 1), related to the high kaolinite content of the initial sediment (A.C. report). The nature of this relationship is still unknown. Besides mere substitution, other possibilities exist: adsorption, micro-inclusions, etc.

The second most abundant mineral can only have been illite, as shown by the parallel nature of the Ba and Rb contents with those of K_2O. Orthoclase can be excluded, either detrital or authigenic, as seen from Figs. 4–7.

The contents of organic matter are high, not only in the Silurian schists, but also in the 'séries de transition I and II'. Most detrital rocks from Baren have normal Mn contents (Table 1). Mn is positively correlated with Ca, although the limestones (Table 4) do not have exceptional Mn values.

The Cr (100) and Cu (70) contents are highly variable, but do not diverge much from normal values. Cr is slightly in excess, and, like TiO_2, linked to kaolinite (A.C. report). Ba (300) is slightly enriched, less however than in the Devonian limestones (next §). Ni (50) has normal values, slightly higher in the Silurian and Devonian formations that in Ordovician. Sr (200) and V (150) are erratic, V being in excess. Rb (140 to 200, for common schists, Rösler and Lange, 1972) displays higher contents only in rocks initially rich in illite (A.C. report). U and Th (3.5 and 11, Rösler and Lange, 1972) are slightly enriched in Silurian materials, less than in similar rocks from Superbagnères (Brula, 1984).

Carbonate rocks (Table 4)

Ordovician. The 'calcaire rubané' contains from 13 to 31% CaO, that is a theoretical maximum of 23 to 56% calcite. Other minerals present are quartz, sericite, chlorite, organic matter, disseminated pyrite and sphalerite.

In the normal facies of the 'horizon troué' (70), detrital quartz, organic matter and biotite mark a foliation. As shown on Fig. 5, quartz is more abundant than biotite (Figs. 4, 6 and 7) (see § 1 for the continuous transition between this limestone and the schists).

Devonian. The 'calcaire massif' hosts Pb–Zn ores in its uppermost levels, similar to the 'CRGS'. The nature and proportions of the sheet silicates in samples 63 and 92 are similar to those of the horizon troué (figs. 4, 6 and 7), but quartz is less abundant.

Discussion of the chemical composition of the carbonate rocks. The carbonate rocks have low MgO contents; dolomite is almost completely absent. The elements which form sheet silicates (Fe, Al, K) show contents higher than the average in limestones. The K_2O/Al_2O_3 ratios of Table 2 vary between 0.09 and 0.24, which is less than the figure for this ratio in biotites (0.31 to 0.61), pointing to Al-rich sheet silicates such as kaolinite. TiO_2 is also above average (0.07%), because of its higher concentration in biotite and kaolinite.

Table 4 - Selected chemical analyses of Middle Palaeozoic limestones from the Baren area

	AB 70	AB 99	AB 63	AB 92	AB 100
	x̄	x̄	x̄	x̄	x̄
SIO2	28.64	22.26	14.32	9.22	10.49
AL2O3	3.73	8.68	3.69	3.26	1.71
FE2O3 T	1.64	1.73	1.51	0.74	3.15
MNO	0.15	0.14	0.09	0.08	0.21
MGO	0.58	0.23	0.55	0.66	0.57
CAO	35.16*	34.60*	41.91*	45.95*	46.07*
NA2O	0.04	0.19	0.07	0.13	
K2O	0.72	2.14	0.81	0.47	0.16
TIO2	0.19	0.58	0.25	0.15	0.13
P2O5	0.03	0.09	0.06		0.04
P.F.	28.61	28.90	35.22	38.17	37.20
TOTAL	99.49	99.54	98.48	98.83	99.73
CO2 M	27.69	27.09	34.41	38.00	37.26
C ORG	0.11	0.11	0.03	0.06	0.05
H2O T	1.20	1.75	1.26	3.92	0.93
S T	<0.02	<0.02	<0.02	<0.02	<0.01
BA	117	1297	610	263	1306
CR	50	90	72	57	70
CU	<10	<10	<10	<10	<10
NI	21	14	18	21	27
SR	316	225	458	394	419
V	64	136	94	34	117
RB	29	86	33	23	19
PB	17	35	22	17	238
ZN	41	25	12	7	107

Analytical techniques - see table 1;

*Ca : AAS and totals recalculated

Among the trace elements (the estimated averages according to Rösler and Lange, 1972, are given in parentheses), Cr (11) and V (20) are abundant. The Rb (3) content is high, the K/Rb ratio varies between 70 and 200 and such low figures are characteristic of pelitic rocks and indicate that Rb is in detrital sheet silicates. This ratio varies between 120 and 320 for the samples of Table 1. Ni (20) and Cu (4) are normal. Ba is highly anomalous, especially in the Devonian limestones. The average of 10 ppm in limestones (Rösler and Lange, 1972, quoting Turekian) is underestimated and should be replaced by a value of 90 ppm (Puchelt, 1972) or 150 ppm (Graf, 1960). The Ba contents of the Devonian limestones of the Pyrenees are generally higher. Aye *et al.* (1981) noticed baryte or celsian frequently associated with the Devonian ores of the Pyrenees, but not with the Ordovician ores.

Conclusions

The different pelite units can be distinguished in the chemical–mineralogical diagrams (Figs. 4–7). These diagrams can therefore be used for stratigraphical correlations and can make up for the lack of fossils. In the diagrams presented here, the overlap between various stratigraphical units is limited and underlines the efficiency of the method.

The limestones of the sequence contain no dolomite, but detrital minerals are present in variable amounts. The initial clay sediments, transformed later into pelites, consisted of kaolinite, with quartz and illite. This trend was extreme during the Silurian, expressing a kaolinizing meteoric alteration of the source area, not contradicted by large-scale palaeogeographical reconstructions (Scotese et al., 1979). Indeed, the future Pyrenees were then located at an approximate latitude of 35° S, a latitude under which kaolinization can develop at present. No indications were found in the field for the supposed glacial episode at the Ordovician-Silurian boundary and, if present, it was probably very short. The Middle Palaeozoic pelites are purely sedimentary in the Baren area, and no volcanic or volcanoclastic contribution to these sediments could be detected.

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Appendix

Comment on the interpretation of major-element data by chemico-mineralogical diagrams

The simultaneous graphic representation of the contents of 10 major elements would require ten-dimensional space. It can be simplified by the use of planar projections with adequate parameters. These are chosen in such a way that the points representing the minerals to be discussed fall far apart in the diagram. Minerals to be eliminated from the discussion can be made to fall together or to disappear from the diagram. The representative point of a sample is the centre of gravity of the representative points of the minerals that form it, balanced by the abundance of the respective minerals. Furthermore, the position of the major rock groups in these diagrams is known by experience. This method allows one to:

(a) determine the initial mineralogical composition and the origin of the starting sediments. After metamorphism, the chemical data often remain the only witnesses of the original materials.

(b) compare rocks of different geographical origins and

of different metamorphic grade. A chemical identity is an indication, not a proof, for a similar origin; to be taken into consideration it should appear on all diagrams used. A difference in chemistry is a proof of different origins or evolutions and, similarly, isochemical metamorphism can be inferred from the method. Four diagrams were successively used to improve the deductions and to identify the various minerals (Puxeddu et al., 1984). The weight percent of oxides are first transformed into atom grams/100 g of rock and multiplied by 10^3 (= 'milliatoms') for ease of calculation, and the different parameters are calculated from the milliatoms.

This approach does not exclude a previous petrographic study and requires a subsequent cross-check.

* $Al/3 - K = f(Al/3 - Na)$ (Fig. 4) (de La Roche, 1968).

The three feldspars are at the apices of an equilateral triangle; quartz, carbonates and sulphides are located at the point of origin. Igneous and sedimentary rocks are distinguished at a glance, as well as the maturity of detrital rocks.

* $$Si/3 - (Na + K) = f(Al - (Na + K))$$
(Fig. 5) (Moine, 1974).

Quartz and sheet silicates are separated from each other and from a complex third group formed by the alkali feldspars and the most common carbonates and oxides. The major groups of detrital rocks are distinguished well in this diagram.

* $Na/Al = f(K/Al)$ (Fig. 6) (Moine, 1974).

Albite and orthoclase are opposite to each other and to the third pole representing anorthite and the sheet silicates. Quartz and the common oxides and sulphides are ignored.

* $$K/(Al - Na) = f[(Fe + Mg)/(Al - Na)]$$
(Fig. 7) (Moine et al., 1974).

Illite, chlorites and the pure-Al sheet silicates project onto three distinct points.

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