



Petrology, Geochemistry (Ore Deposits)

## Mesozoic vein-type Pb–Zn mineralization in the Pyrenees: Lead isotopic and fluid inclusion evidence from the Les Argentières and Lacore deposits

Marguerite Munoz<sup>a,\*</sup>, Sandrine Baron<sup>b</sup>, Adrien Boucher<sup>a</sup>, Didier Béziat<sup>a</sup>, Stefano Salvi<sup>a</sup>

<sup>a</sup> Géosciences Environnement Toulouse (GET), Observatoire Midi Pyrénées, Université de Toulouse, CNRS, IRD, 31400 Toulouse, France

<sup>b</sup> Travaux et Recherches Archéologiques sur les Cultures, les Espaces et les Sociétés (TRACES), CNRS, Université de Toulouse Jean-Jaurès, 31058 Toulouse cedex 9, France

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### ABSTRACT

The Axial Zone of the Pyrenees contains numerous sedimentary-exhalative Pb–Zn deposits formed during the Early Palaeozoic, which have been the subject of several studies. In addition to these, base-metal vein-type mineralizations are also exposed within the Axial Zone metasediments. These deposits, however, have not been investigated in depth and the timing and geodynamic context of their formation has not been specifically addressed. The vein-type Pb–Zn deposits of Les Argentières and Lacore are located in Devonian terranes of the eastern Pyrenees, south of the Mesozoic Aulus basin. They are interpreted as having been emplaced under an extensional setting. They are characterized by silver-rich tetrahedrite that occurs with Pb–Zn sulphides deposited by low-temperature NaCl–CaCl<sub>2</sub> brines. Lead isotopic <sup>208</sup>Pb/<sup>204</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb ratios acquired on galena show more radiogenic values compared to those from the Palaeozoic sedimentary-exhalative mineralization, thus indicating younger ages. According to the model ages, the formation of the two deposits may be narrowed down to middle Late Triassic and Late Jurassic periods, respectively, which allows us to argue in favour of the role of pre-Alpine rifting phases in hydrothermal fluids circulation and mineralization deposition in a vein system bounding the Mesozoic Aulus basin.

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## 1. Introduction

Lead–zinc sulphide deposits are common in the Pyrenees. Most economic occurrences consist of stratiform mineralization contained within Lower Palaeozoic meta-sediments (Ordovician to Lower Devonian terranes) such as the Pierrefitte deposit (Bois et al., 1976; Nicol et al., 1997) and the Bentaillou deposit (Pouit, 1986) in French

Central Pyrenees, or the deposits of the Aran Valley (Cardellach et al., 1996) and the Benasque Pass (García-Sanseguno et al., 2014) on the Spanish side of the chain (Fig. 1). All of these deposits were classified as sedimentary-exhalative. Some of these deposits were subjected to an intense remobilization and recrystallization during the Variscan orogeny, particularly in the Spanish Pyrenees, as indicated by Cardellach et al. (1996). Lead isotopic data from the literature (Cardellach et al., 1996; García-Sanseguno et al., 2014; Marcoux et al., 1991) are in agreement with the formation of these deposits during the Palaeozoic. However, Cadarso (2000) indicates that several Pyrenean Pb–Zn sedimentary-exhalative-type deposits (Lamanère,

\* Corresponding author at: GET, 14, avenue Édouard-Belin, 31400 Toulouse, France.

E-mail address: [margot.munoz@get.obs-mip.fr](mailto:margot.munoz@get.obs-mip.fr) (M. Munoz).

Carboire, Pierrefitte) show evidence suggesting late-stage mineralization, related to an extensional tectonic event, probably after the Palaeozoic. Similarly, Subías et al. (1999) demonstrated the overlapping of ore forming events in the Yenefrito Pb–Zn mine (Central Spanish Pyrenees) with late vein-type Pb–Zn mineralization characterized by saline, low-temperature fluids. These authors proposed that the mineralized veins developed during extensional tectonics related to the early Alpine rifting. Similarly, Johnson et al. (1996), based on fluid geochemistry and field constraints, favour a Mesozoic extensional faulting framework for the Pb–Zn Cierco deposit formation in the central Spanish Pyrenees. Although geochronological data are not available, both Subías et al. (1999) and Johnson et al. (1996) suggested that this metallogenic model could be extrapolated to other mineralizations showing similar genetic processes.

The involvement of Mesozoic hydrothermalism in base-metal vein formation has already been illustrated in western Europe (e.g., Cathelineau et al., 2012) and needs to be more precisely addressed in the Pyrenees, where numerous albitite and talc mineralization occurrences formed by metasomatism of Palaeozoic formations of the Axial Zone, have been related to pre-Alpine rifting activity (Fallourd et al., 2014; Poujol et al., 2010). New data on the Trimouns talc deposit, which confirmed the Albian age of talc formation, have also evidenced earlier (Permo-Triassic and Jurassic) metasomatic events (Boutin et al., 2014) and point to the role of repeated hydrothermal fluid circulation during the Mesozoic.

This study focuses on the Pb–Zn deposits of Les Argentières and Lacore, located next to Aulus-les-Bains in the central Pyrenees. These Pb–Zn vein deposits display a geological setting and paragenetic characteristics that are clearly different from those of the Palaeozoic sedimentary-exhalative mineralizations known in the Axial Zone of the Pyrenees. Thanks to our new lead

isotopic and fluid inclusion data, we can demonstrate that Mesozoic hydrothermal fluids were at the origin of this mineralization, and propose a genetic model consistent with the geodynamic context of the Pyrenees during Mesozoic times.

## 2. Geological setting and deposit geology

### 2.1. Geology of Pyrenees

The Pyrenees are a polyorogenic mountain chain, where the actual structure is Alpine in age, superimposed on Palaeozoic terranes and Precambrian basement affected by the Variscan orogeny. Alpine deformation of the Palaeozoic series is mostly limited to thrusting and faulting. The Variscan orogeny in the Pyrenees took place during the Namuro–Westphalian (320–300 Ma), involved polyphased tectonics and was accompanied by calc-alkaline magmatism and a HT–LP metamorphism (Denèle et al., 2009; Laumonier et al., 2010).

The Alpine Pyrenees, at the western end of the Alpine Belt, were formed due to the convergence of Iberia and Europe during the Late Cretaceous–Tertiary (Olivet, 1996). This collision generated compression that resulted in the framework of the Pyrenean range, divided into four longitudinal structural zones trending ESE–WNW and separated by major faults (Fig. 1). The Palaeozoic domain, the Axial Zone, is bounded by the North and South Pyrenean Zones, which are mainly composed of Mesozoic and Cenozoic sedimentary rocks. The Alpine compression produced the inversion of previous Mesozoic rifted basins. The Pyrenean rift started during the Triassic, synchronously with the opening of the Atlantic (Ziegler, 1988), and culminated with the opening of the Bay of Biscay, which connected with the Tethys Ocean during the Late Cretaceous (Vergés et al., 2002 and references therein).

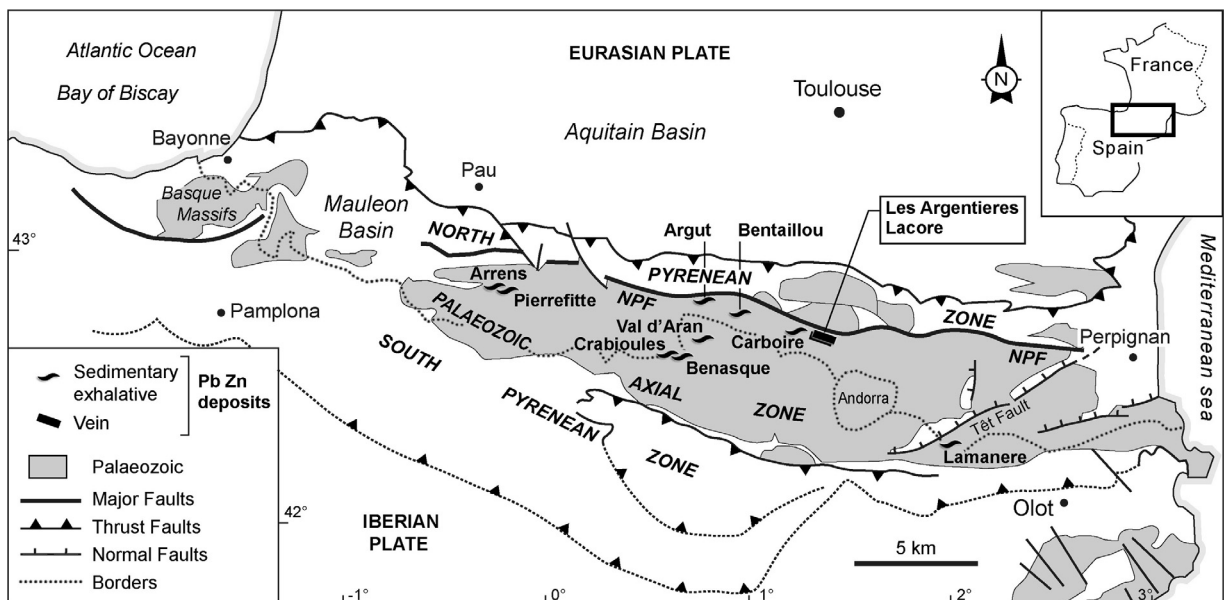


Fig. 1. Schematic structural map of the Pyrenees with the locations of the Pb–Zn deposits cited in the text.

## 2.2. Geology of the Aulus-les-Bains area

The Aulus-les-Bains area straddles the Axial Zone and the North Pyrenean Zone. The Axial Zone of the Pyrenees is mainly composed of low-grade Palaeozoic metasediments that comprise Cambrian, Silurian and Devonian units deformed during the Variscan orogeny. These form stacked thrusting layers, with a fan-shape geometry, that dip mainly to the south (Ternet et al., 1997) (Fig. 2).

The metasediments were intruded by the Bassies granitic pluton at  $312 \pm 2$  Ma (U–Pb on zircon), i.e. during the main plutonic event of the Variscan orogeny in the Pyrenees, essentially Carboniferous in age and syntectonic in nature (Paquette et al., 1997). The granite and the metasedimentary rocks were truncated by the North Pyrenean Fault, which brought into contact the Mesozoic succession of the North Pyrenean Zone with the northern edge of the Axial Zone. The Aulus Basin, now an inverted basin, is formed of verticalized Jurassic to Lower Cretaceous limestone, marble, dolomite and flysch, and hosts the well-known mantle-derived peridotite bodies of the Lherz pond (Lagabrielle and Bodinier, 2008). Some Triassic diapiric intrusions in Jurassic terranes are associated with ophites (Ternet et al., 1997).

These terranes have suffered the Pyrenean high-temperature–low-pressure mid-Cretaceous metamorphic

event, genetically related to crustal thinning and associated with alkaline magmatism, dated between 90.5 and 86.5 Ma (Montigny et al., 1986).

## 2.3. Geology of the deposits

In the Aulus-les-Bains area, some thirty Pb–Zn occurrences have been reported (Dubatik, 1981; Gramont, 1963), the majority of which are reported to consist of vein-type mineralization, mainly trending east–west, within Late-Silurian and Devonian calc-schist, limestone and dolomite. The deposits from the Aulus-les-Bains area produced 40 tons of Ag between the 13th and the 16th centuries (Dubois, 1999).

Les Argentières and Lacore vein deposits are located in the Axial Zone of the Central Pyrenees, 4 km ESE of the Aulus-les-Bains village, 200–300 m south of the North Pyrenean Fault and parallel to it in this area (Fig. 2). They are close to the Bassies granite, which has been intersected by the mining operations in Les Argentières deposit (Dubatik, 1981). Although both deposits are small in size, in situ observation and sampling is still feasible.

These deposits were mined during different periods in the past, possibly since the Antiquity, as indicated by the toponymy of Les Argentières (Dubois, 1999). The Les Argentières and Lacore deposits were mainly mined for Pb and Ag, but they were prospected and mined again during the late 19th and early 20th centuries for Zn (Dubois, 1999). Mining works were described as galleries following a dense network of sulphide-mineralized quartz veins related to normal faulting activity, mainly trending east–west and dipping  $50\text{--}70^\circ\text{S}$  at Les Argentières and  $35\text{--}50^\circ\text{S}$  at Lacore (Gramont, 1963). The mineralization thickness was up to 5 m at Les Argentières and up to 1.3 m at Lacore. The extent of the mining workings slightly exceeded 100 metres in both cases (Gramont, 1963). Today, only a single excavation of several metres in all directions allows an easy access to the mineralized outcrops at Les Argentières. At Lacore, only a small vein outcrop at the entrance of the ancient gallery permitted to sample the mineralization.

Both the Les Argentières and Lacore ores are hosted within Lower Devonian dolomite. The latter occurs close to the faulted contact with Mid-Devonian calc-schists (Gramont, 1963). The Les Argentières veins display the typical “cockade” breccia texture, with silicified dolomite clasts and rare hydrothermally altered granite rimmed by pale brown siderite, brown sphalerite and galena, and cemented by quartz (Fig. 3a and b) with local centimetre-size euhedral clear quartz crystals, which occupy druzy cavities. At Lacore, sulphide mineralization is more massive, and is associated with quartz and scarce calcite.

## 3. Mineralogical and geochemical data

### 3.1. Sulphide paragenesis and composition

The sulphide paragenesis consists of sphalerite, galena and minor chalcopyrite, pyrite and a silver-bearing sulfosalt from the tetrahedrite series. Tetrahedrite generally appears as inclusions in galena that in some samples

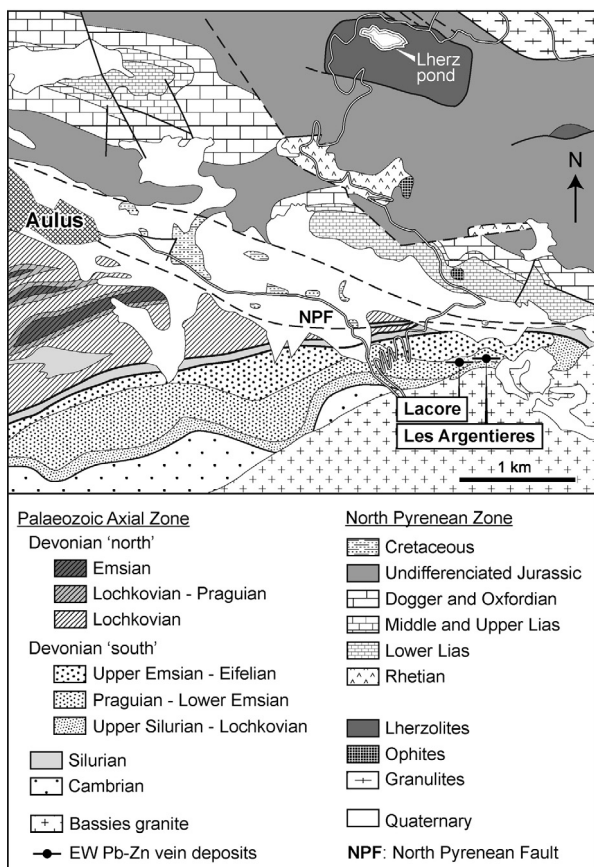


Fig. 2. Geological map of the Aulus-les-Bains area with the location of the Les Argentières and Lacore vein deposits (redrawn from Colchen et al., 1997).



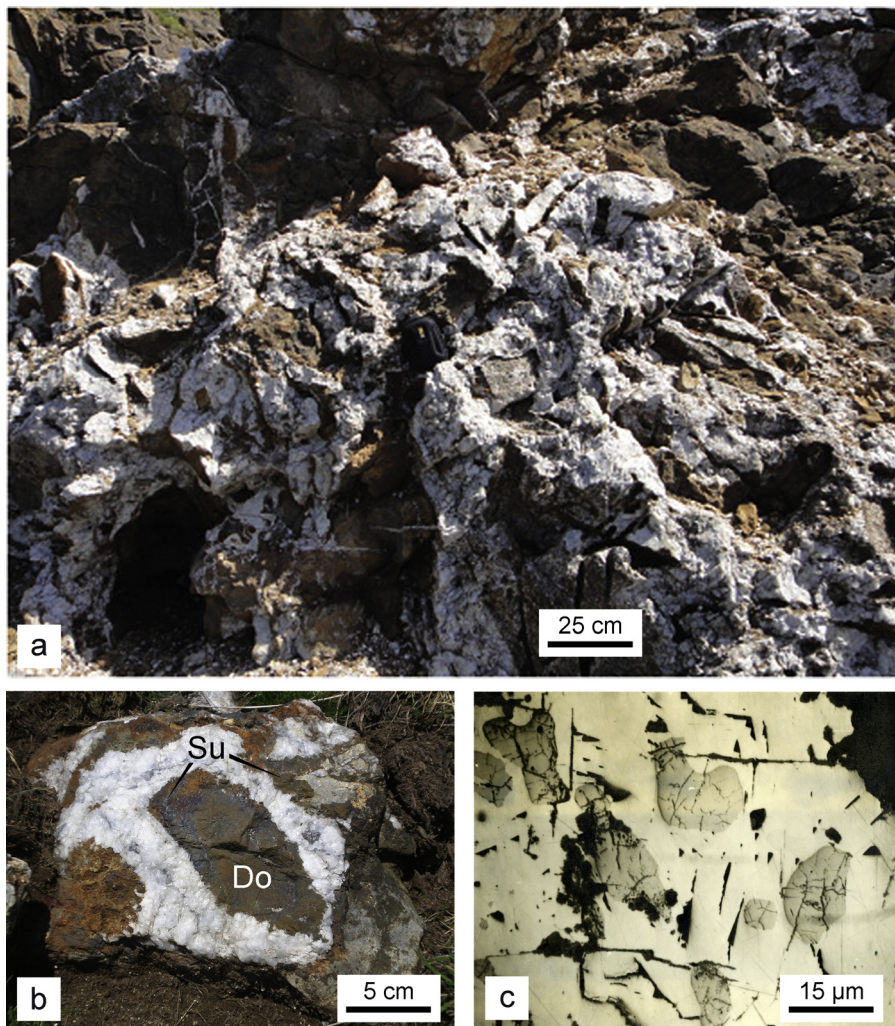


Fig. 3. (Colour online.) Images showing features of the mineralized veins at the Les Argentières deposit: a: outcrop photograph of a strongly brecciated vein; b: photograph of a sample with dolomitic clasts (Do) rimmed by sulphides (Su) and quartz; c: photomicrograph, taken in reflected light, of multiple inclusions of tetrahedrite (medium grey) in galena (light grey).

occupies up to 30% of the volume of the galena grains (Fig. 3c). Chemical analyses were carried out with a CAMECA SX 50 (Samx automation) Electron Probe Micro Analyzer equipped with three spectrometers (LiF, PET and TAP crystals). Analytical conditions used were 25 kV for the accelerating voltage and 20 nA for the beam current. Standard reference materials used for calibration were pure metals, synthetic minerals and natural minerals. In standard conditions, counting times of 10 s on the peak and 5 s on the background were applied. In order to improve the detection limit of silver in galena, counting times were increased in the sulphide program to 60 s on the peak and 15 s on the background. With these conditions, the detection limit for Ag was improved down to 0.06 wt%. The results are listed in Table 1.

The iron contents of sphalerite are low in both sites, with an average of 4.2 wt% Fe in Les Argentières and 1.1 wt% Fe in Lacore. The silver contents in galena are very similar for both sites, from 0.11 to 0.28 wt% Ag at Lacore, with a mean value of 0.18 wt% Ag (42 analyses), and from

0.11 to 0.26 wt% Ag at Les Argentières, with a mean value of 0.19 wt% Ag (8 analyses).

The compositions of tetrahedrite from the two deposits are presented with their structural formulae in Table 1. The silver contents are high, with a mean value of 21.7 wt% Ag for Les Argentières and 12.1 wt% Ag for Lacore. Plotted on a ternary Ag–Sb–Cu diagram (Fig. 4), tetrahedrite compositions from the Les Argentières and Lacore deposits fall within two distinct fields.

### 3.2. Lead isotopic data

Galena grains were separated by handpicking and dissolved according to the protocol described in Baron et al. (2006). Pb was separated from the other elements by ion exchange using AG1X8 resin (Strelow and Walt, 1981). After separation, the solution was evaporated at 60 °C and the residues were taken back in 1 mL of 0.3 N HNO<sub>3</sub> (Merck Suprapur quality). The lead isotopic compositions of the Les Argentières and Lacore mining areas were measured

**Table 1**  
Chemical composition of tetrahedrite from the Les Argentières and Lacore deposits.

Wt%							
Tetrahedrite	S	Fe	Cu	Zn	Ag	Sb	As
Les Argentières							
Min	23.3	4.77	21.5	1.09	21.3	26.5	1.33
Max	23.6	5.22	22.0	2.33	22.3	26.8	1.47
Mean (n = 8)	23.4	4.96	21.7	1.40	21.7	26.7	1.42
Lacore							
Min	23.3	2.06	27.1	3.80	6.65	24.5	0.81
Max	24.7	2.55	33.0	6.07	14.3	27.0	2.40
Mean (n = 54)	23.8	2.84	29.0	4.39	12.1	25.8	1.46
Structural formulae <sup>a</sup>							
Les Argentières	13	1.51–1.66	6.00–6.18	0.30–0.63	3.52–3.70	3.88–3.92	0.32–0.35
Lacore	13	0.65–0.79	7.38–8.90	0.98–1.61	1.04–2.37	3.50–3.95	0.19–0.54

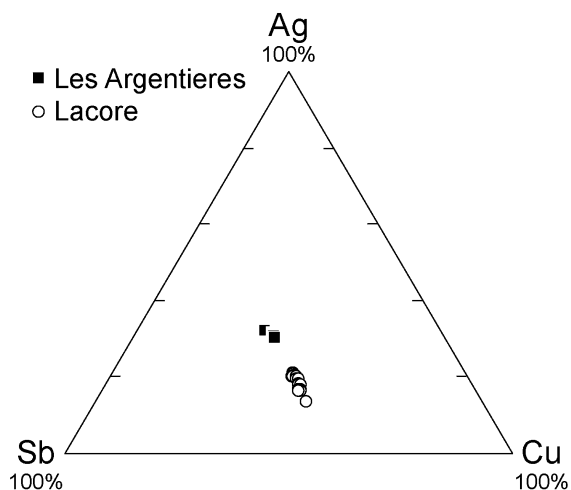
<sup>a</sup> The structural formulae were calculated on the basis of thirteen sulphur anions leading to a of general simplified formula: (Cu, Ag, Fe, Zn)<sub>12</sub>(Sb,As)<sub>4</sub>S<sub>13</sub>.

with a MC–ICP–MS device (Neptune VG Instruments) following the procedure reported by [Baron et al. \(2006\)](#). Repeated measurements of the NIST NBS 981 Pb reference material yielded reproducibility (2 standard deviations) of better than 130 ppm for all the reported Pb isotopic ratios ([Table 2](#)). Repeated measurements on the three triplicates of three samples allowed us to estimate a total external uncertainty better than 300 ppm (2 standard deviations) for each reported Pb isotopic ratio ([Table 2](#)).

The lead isotopic data acquired on galena from the Les Argentières and Lacore deposits ([Table 2](#)) display some discrepancies between the two sites. <sup>208</sup>Pb/<sup>204</sup>Pb values range from 38.56 to 38.57 and from 38.71 to 38.73 for Les Argentières and Lacore, respectively, and <sup>206</sup>Pb/<sup>204</sup>Pb values range from 18.36 to 18.38 and from 18.49 to 18.50, for Les Argentières and Lacore, respectively.

### 3.3. Study of the fluid inclusions

Fluid inclusions were investigated in transparent quartz associated with the sulphide paragenesis from



**Fig. 4.** A ternary Ag–Sb–Cu diagram (wt%) showing the composition of tetrahedrite from the Les Argentières and Lacore deposits.

the Les Argentières and Lacore mineralizations. Petrographic studies were carried out on 150- $\mu$ m-thick doubly-polished sections using the criteria of [Roedder \(1984\)](#) and [Goldstein and Reynolds \(1994\)](#). Microthermometric measurements were performed at the GET laboratory, following the procedures of [Roedder \(1984\)](#) and [Shepherd et al. \(1985\)](#), using a Linkam THMGS 600 heating–freezing stage mounted on a BX-51 Olympus microscope. The stage was calibrated using synthetic pure-H<sub>2</sub>O inclusions (0 and +374.1 °C) supplied by SynFlinch and natural fluid inclusions from Campeirio (Ticino, Switzerland) containing pure CO<sub>2</sub> (–56.6 °C). The measurements below 0 °C are accurate to  $\pm 0.1$  °C, whereas at the highest temperature measured, they are accurate to  $\pm 1$  °C. Cryogenic experiments were carried out before heating to reduce the risk of decrepitating the inclusions. Salinity (expressed as wt.% equivalent NaCl) and bulk composition were calculated using the spreadsheet of [Steele-MacInnis et al. \(2011\)](#).

Primary inclusions were recognized along growth zones in quartz. They are generally rectangular to ellipsoidal in shape and measure less than 5  $\mu$ m in diameter, with a few exceptions that reach 15  $\mu$ m in diameter. Only one type of fluid inclusion was observed in all the samples studied. These fluid inclusions contain a liquid and a vapour phase with a low vapour-to-liquid ratio ranging, at room temperature, from less than 5 to 15 vol.%. In samples from both deposits, the fluid inclusions froze below –70 °C and displayed a brownish colour on freezing. For all fluid inclusions, the first melting of ice was observed at temperatures as low as –50 °C, i.e., well below the eutectic temperature of the binary H<sub>2</sub>O–NaCl system, indicative of the presence in the fluid of CaCl<sub>2</sub> and possibly MgCl<sub>2</sub> in addition to NaCl ([Crawford, 1981](#)). In samples from Les Argentières, final ice melting took place between –34.8 °C and –26.5 °C (mean of –31.4 °C). In some inclusions, hydrohalite was identified, which melted between –23.7 °C and –18.5 °C. Bulk salinity values calculated from these data range between 25.6 and 28.2 wt% NaCl eq. (mean of 26.8 wt% NaCl eq.) with NaCl/CaCl<sub>2</sub> ratios from 0.2 to 0.5 ([Fig. 5](#)). In the fluid inclusions from Lacore samples,

**Table 2**  
Lead isotopic data for the Les Argentières and Lacore deposits.

	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
NIST SRM 981 Pb					
Certified values <sup>a</sup>	2.16768 ± 23	1.09310 ± 07	36.722 ± 08	15.4980 ± 25	16.9408 ± 21
This study: Session July 2014	2.16747	1.09309	36.719	15.4984	16.9411
2 sd ( $n = 87$ ) <sup>b</sup>	0.00008	0.00003	0.003	0.0010	0.0010
RSD ppm	37	27	76	64	61
This study: Session December 2014	2.16744	1.09309	36.719	15.4987	16.9414
2 sd ( $n = 36$ ) <sup>b</sup>	0.00026	0.00012	0.003	0.0011	0.0021
RSD ppm	120	106	89	70	127
Galena Ores					
Les Argentières deposit					
1	2.09853	1.17162	38.570	15.6876	18.3796
2	2.09842	1.17168	38.570	15.6869	18.3802
3	2.09952	1.17064	38.557	15.6875	18.3644
Total external uncertainties <sup>c</sup> 2 sd	0.00020	0.00020	0.010	0.0010	0.0061
Lacore deposit					
4	2.09339	1.17818	38.707	15.6939	18.4902
5	2.09294	1.17891	38.723	15.6940	18.5018
6	2.09334	1.17840	38.712	15.6935	18.4930
7	2.09323	1.17852	38.716	15.6940	18.4957
8	2.09305	1.17885	38.725	15.6949	18.5018
9	2.09319	1.17870	38.723	15.6948	18.4994
Total external uncertainties <sup>c</sup> 2 sd	0.00020	0.00020	0.010	0.0010	0.0061

<sup>a</sup> Referenced values by double Spike TIMS (Thirlwall, 2002).

<sup>b</sup> 2 sd from the mean ( $n = 87$  represents 3 days of analytical session).

<sup>c</sup> Twice the standard deviation from the mean of three triplicates.

hydrohalite melting temperatures ranged from  $-25.7$  to  $-23.9$  °C while ice melted between  $-26.0$  °C and  $-15.8$  °C (mean of  $-20.1$  °C). The calculated bulk salinities range between 18.8 and 25.1 wt% NaCl eq., with NaCl/CaCl<sub>2</sub> ratios from 0.5–0.9 (Fig. 5). Homogenization temperatures range from 108 °C to 139 °C (mode of 129 °C) for the Les Argentières samples and from 118 °C to 179 °C (mode of 144 °C) for the Lacore samples.

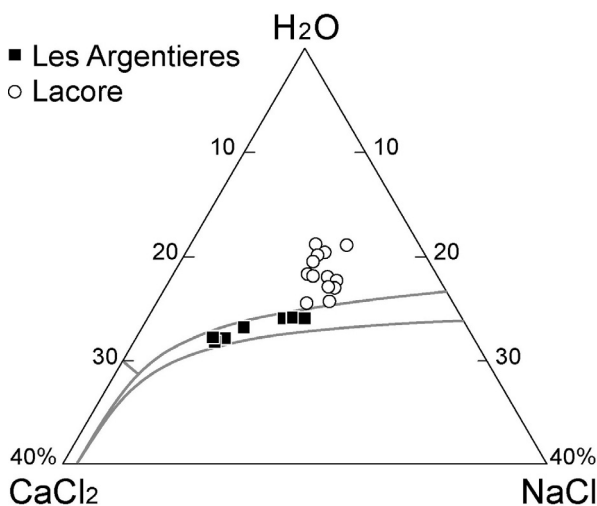


Fig. 5. A plot of the ternary H<sub>2</sub>O–NaCl–CaCl<sub>2</sub> system showing fluid inclusion compositions for the Les Argentières and Lacore samples, calculated from microthermometric measurements, using the Microsoft Excel spreadsheet of Steele-MacInnis et al. (2011).

## 4. Discussion

### 4.1. Pb–Zn type deposits from the Axial Zone of the Pyrenees

#### 4.1.1. Pb–Zn sedimentary-exhalative deposits

In the Pyrenean Axial Zone, there are many occurrences of Pb–Zn mineralizations hosted in Ordovician to Devonian sedimentary and volcano-sedimentary layers; they are considered sedimentary-exhalative and were formed during the Early Palaeozoic rifting periods (Cardellach et al., 1996; Pouit, 1978, 1986; Pouit and Bois, 1986). These deposits have several characteristics in common, such as a stratiform character and a tectonically unstable depositional environment, and are hosted in a sedimentary hydrothermal gangue that can be related to syn-sedimentary faulting and to a more-or-less distal volcanism. Mineralogically, they are characterized by the predominance of sphalerite over galena and by relatively low amounts of chalcopyrite and iron sulphides (which consist mostly of pyrite and pyrrhotite). Another common feature is the occurrence of exsolutions of chalcopyrite and pyrrhotite in sphalerite, and a medium-to-high iron content (5–12 wt%) in the latter. These deposits also have low Ag contents (averaging a few tens of g/t in the ore) and commonly contain Ni- and Co-bearing minerals (García-Sansegundo et al., 2014; Oudin et al., 1988). In addition, a lateral zoning of Zn–Pb–Ba was described in one case (Arrens deposit, Pouit and Bois, 1986). Lead isotopic data obtained by Marcoux et al. (1991), Cardellach et al. (1996) and García-Sansegundo et al. (2014) on several of these deposits cluster between 17.999 and 18.101 for  $^{206}\text{Pb}/^{204}\text{Pb}$  and between 15.656 and 15.704 for  $^{207}\text{Pb}/^{204}\text{Pb}$  (Table 3).



**Table 3**

Compilation of published lead isotopic data for Pyrenean Pb–Zn sedimentary-exhalative deposits.

Palaeozoic deposits	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	References
La Manère	18.052	15.663	38.150	Marcoux et al., 1991
Carboire	17.999	15.662	38.209	Marcoux et al., 1991
Pierrefitte	18.046	15.671	38.189	Marcoux et al., 1991
Pierrefitte	18.101	15.704	38.332	Marcoux et al., 1991
Pierrefitte	18.091	15.688	38.277	Marcoux et al., 1991
Pierrefitte	18.097	15.678	38.280	Marcoux et al., 1991
Argut	18.031	15.668	38.172	Marcoux et al., 1991
Argut	18.022	15.658	38.145	Marcoux et al., 1991
Bentaillou	18.042	15.684	38.206	Marcoux et al., 1991
Crabioules	18.091	15.700	38.323	Marcoux et al., 1991
Arrens	18.095	15.702	38.312	Marcoux et al., 1991
Gèdre	18.153	15.711	38.357	Marcoux et al., 1991
Chèze École	18.160	15.687	38.360	Marcoux et al., 1991
Chèze École	18.163	15.685	38.351	Marcoux et al., 1991
Nerbiou	18.109	15.701	38.330	Marcoux et al., 1991
Nerbiou	18.106	15.698	38.320	Marcoux et al., 1991
Taichougnes	18.023	15.664	38.217	Marcoux et al., 1991
Aran Valley, Margdalida	18.021	15.656	38.157	Cardellach et al., 1996
Aran Valley, Font dels Lladres	18.064	15.696	38.288	Cardellach et al., 1996
Aran Valley, Liat	18.042	15.671	38.213	Cardellach et al., 1996
Aran Valley, Liat	18.054	15.671	38.213	Cardellach et al., 1996
Aran Valley, Victoria	18.080	15.676	38.226	Cardellach et al., 1996
Aran Valley, Mauricio	18.045	15.670	38.198	Cardellach et al., 1996
Aran Valley, Mauricio	18.045	15.670	38.198	Cardellach et al., 1996
Benasque Pass	18.087	15.690	38.299	García-Sanseguno et al., 2014
Benasque Pass	18.094	15.692	38.321	García-Sanseguno et al., 2014

#### 4.1.2. Pb–Zn vein deposits

The geology of the Les Argentières and Lacore deposits is drastically different from their sedimentary-exhalative counterparts described above, although they are hosted by the same Palaeozoic metasediments. The ore bodies consist of sets of quartz veins developed in Devonian dolomite and crosscutting the Hercynian Bassies granite. These high-level vein systems have a main east–west trend, parallel to the southern edge of the Aulus basin. The veins formed in a normal faulting environment, and commonly contain brecciated clasts of the host rock and display open-space filling textures. Their mineralogy is also quite different from that of the sedimentary-exhalative ores, particularly in terms of tetrahedrite and sphalerite compositions, which at Les Argentières and Lacore are richer in silver and poorer in iron, respectively. Another difference is the lead isotopic composition; the ore at Les Argentières and Lacore is significantly more radiogenic than for the sedimentary-exhalative deposits (Cardellach et al., 1996; García-Sanseguno et al., 2014; Marcoux et al., 1991). However, a plot of Pb isotopic data for all deposits in the Axial Zone (the sedimentary-exhalative deposits and Les Argentières and Lacore deposits) forms a linear trend that suggests a common source of lead extracted at different times (Fig. 6). Hence, the Les Argentières and Lacore deposits may be considered significantly younger than the sedimentary-exhalative deposits.

#### 4.2. Model ages of Pb–Zn vein deposits

The Pb isotopic data from all Pb–Zn deposits discussed above plot above the theoretical growth curve of Stacey and Kramers (1975), which was obtained using a mean

crust value for  $\mu_2$  (9.74) (Fig. 6b). However, all values fit this curve (Fig. 6b) if a consistently higher  $\mu_2$  value is used (i.e. 10.10). In this case, though, galenas from the syn-sedimentary-exhalative deposits give model ages that are older than those of their host rock (Late Ordovician to Middle Devonian) (Fig. 6b), which invalidates this model. On the other hand, using the two-stage crustal-Pb evolution curve of Ludwig et al. (1989), which was established with a  $\mu_2$  value of 9.80, the ages obtained for galenas from the syn-sedimentary ores, 370–470 Ma, are consistent with the ages of the host rock. It was Michard-Vitrac et al. (1981) who first illustrated that Pb isotopic compositions of K-feldspars from Variscan granitic rocks correlated well with crustal domains in Western Europe. This finding was subsequently confirmed by several authors (e.g., Brévarc et al., 1982; Köppel, 1984; Sinclair et al., 1993; Vollmer, 1985), who recognized southwestern Europe as a geological province characterized by  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios significantly higher than those predicted by the crustal-Pb evolution model of Stacey and Kramers (1975), but that fitted well the two-stage Pb evolution model of Ludwig et al. (1989). This lead isotopic province includes the Central and Eastern Pyrenees, where the two vein deposits studied in this contribution are located. Modelling our data with the growth curve of Ludwig et al. (1989) results in a Mesozoic model age for both deposits, which can be estimated graphically at 231–242 Ma for the Les Argentières deposit and 155–164 Ma for the Lacore deposit (Fig. 6a).

#### 4.3. Genetic considerations and geodynamic context

The fluid inclusion data indicate that the deposition of the ore took place in the presence of a high-salinity

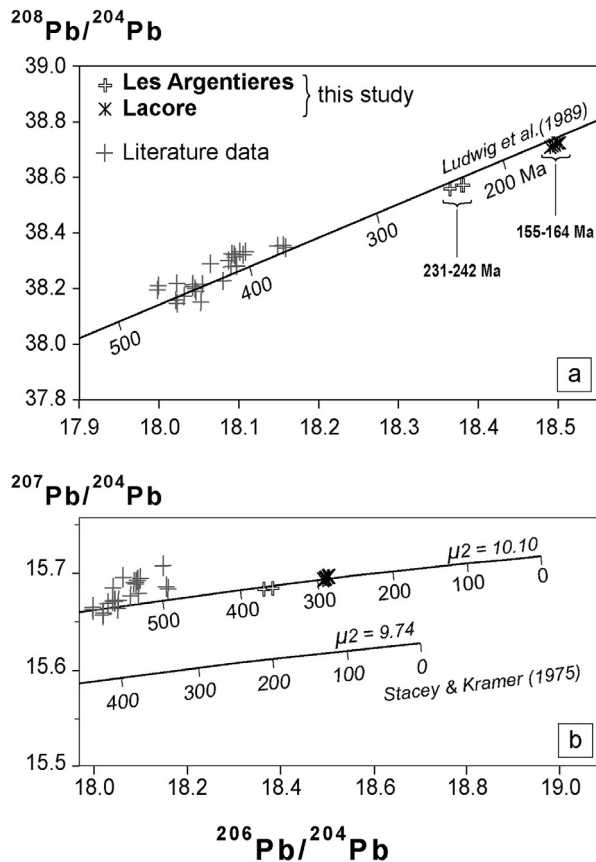


Fig. 6. Lead isotopic composition of Pb–Zn mineralizations from the Axial Zone of the Pyrenees: Les Argentières and Lacore data are from this study, the rest of the data are from Cardellach et al. (1996), García-Sansegundo et al. (2014), and Marcoux et al. (1991). Lead-growth evolution curves are from a) Ludwig et al. (1989) and b) Stacey and Kramers (1975). For the isotopic data from this study, the total external uncertainties (2sd) are smaller than symbol sizes.

CaCl<sub>2</sub>-rich fluid, at relatively low-temperatures. The pressure corrections of the homogenization temperatures are probably not very important, given the occurrence of druzey cavities and geodes in the veins; thus trapping conditions were probably in the whereabouts of 200 °C. It is possible that these temperature are only low-end estimates, as it has been recently shown that the homogenization temperatures of fluid inclusions trapped in the ore minerals (e.g., sphalerite) are systematically higher than those in the quartz host (Kouzmanov et al., 2014). The presence of carbonates in the veins suggests that the fluid's pH was probably near neutral to slightly acidic. At these conditions and such elevated chloride activities, it is most likely that metal-chloride complexes were the dominant species responsible for transporting Pb and Zn to Les Argentières and Lacore (e.g., Sverjensky, 1987). There is no evidence for a specific depositional mechanism such as boiling or mixing with another fluid, thus, given that the deposit is characterized by an extensional vein system favouring a rapid ascent of hydrothermal fluids at low depth, we

are tempted to consider that the cooling of the fluid may have been the main precipitation factor. In addition, this temperature range coincides with the temperature range at which the solubility of Zn and Pb sulphides decreases drastically in cooling in such high salinity brines (Barrett and Anderson, 1988). Another efficient mechanism for metal precipitation is a decrease in  $f_{O_2}$  and a consequent increase in the activity of reduced sulphur (e.g., Leach et al., 2005, and references therein). However, the redox conditions of the fluid cannot be estimated at present.

In the absence of stable isotopic data, the source of the fluid and metals for the Les Argentières and Lacore hydrothermal system remains uncertain. The low-temperature and the high Ca content of the fluid exclude magmatic sources, which in most cases produce high-temperature, Na–K–Fe-rich fluids, as it is the case for porphyry-forming brines (e.g., Bodnar et al., 2014). The low-temperature high-salinity CaCl<sub>2</sub>-rich fluid found in the fluid inclusions has strong resemblance with fluids interpreted in the literature as representing basinal brines, formed either by interaction of meteoric waters with Triassic evaporites, by evaporation of seawater, or deriving from deep density-stratified basinal waters (Yardley and Bodnar, 2014, and references herein).

The lead isotopic data indicate that vein formation at Les Argentières and Lacore took place during the Middle Triassic and the Late Jurassic, respectively, which coincides with the rifting period that prevailed during the breakup of the Pangea and the opening of the Alpine Tethys and Atlantic Ocean (Ziegler, 1988). This was accompanied by an elevated heat production and extensional faulting activity at the margins of rift basins. Hence, during the Mesozoic, two aborted rifts occurred in the Pyrenees (Vergés and García Senz, 2001). The first rift was initiated synchronously with the opening of the North Atlantic at about 250 Ma (Ziegler, 1990), took place during the Middle–Upper Triassic, and caused extensional basin sedimentation associated with doleritic sills (ophites) of tholeiitic composition (Béziat et al., 1991). The second rift took place during the Jurassic, coinciding with the northward propagation of the Atlantic oceanic basin (James et al., 1996; Lemoine, 1983; Vergés and García Senz, 2001).

The Les Argentières and Lacore deposits are located very close to the North Pyrenean Fault, which bounds the Mesozoic extensional Aulus basin to the south. In this context, the mineralized veins might be considered as part of the normal faults that bound the Aulus basin, through which metal-bearing fluids could have been easily expelled. Similarly, Johnson et al. (1996) proposed that the mineralization of the Cierco deposit in the central Pyrenees took place from brines circulating along an extensional fault system postdating the Triassic series, at the margin of a subsiding marine basin during the breakup of Pangea. A similar genetic model, relating a hydrothermal system to syn-sedimentary tectonics, had also been proposed for base-metal vein deposits in Western Europe, regardless as to whether these were emplaced in Mesozoic rocks or in the Palaeozoic



basement (Boiron et al., 2010; Muchez et al., 2005). In France, this is the case for the Les Malines deposit, situated in the southeastern Hercynian Massif Central at the margin of the eastern basin, the biggest economic concentration of Zn in France with 2 Mt extracted, considered as having been deposited around 150 Ma (Le Guen et al., 1991; Sinclair et al., 1993). Another example is the Saint-Salvy deposit, the second largest Zn deposit in France (450,000 tons of Zn extracted), also in the Massif Central, at the margin of the Aquitaine Basin (Muñoz et al., 1994). In Spain, this model has been applied by Velasco et al. (1996) for mineralization in the Basque-Cantabrian region (northern Spain), where a rift basin formed during pre-Alpine times. The Pb–Zn vein deposits, described as a subordinate type of the sedimentary-exhalative mineralization that occurs in the basin, are associated with normal faults related to extensional tectonics before the onset of the Alpine orogeny, which formed channels that favoured the circulation of basinal brines.

Moreover, if we consider that the Mesozoic geodynamic context of the Peri-Tethyan Platform originated what Salas et al. (2001) described as a “network of rifted basins” in southern and northern Europe, this model might also apply to numerous deposits in these regions. It is worth noting that Cathelineau et al. (2012) dated a major Late Jurassic fluid/heat/mass transfer event inducing F–Ba (Pb–Zn) mineralization in western France and, after an overview of U–F–Ba–Pb–Zn deposits of comparable ages at the scale of Europe, proposed that the role of major rifting in distant zones needed to be reconsidered.

Knowing that a rifting context is a favourable environment for sedimentary-exhalative mineralization (Leach et al., 2005; Wilkinson, 2014), one may question the possibility that such a type of Pb–Zn deposits could occur within the sediments of the Pyrenean Mesozoic rift basins. It is conspicuous that in the Pyrenees *sensu stricto* no sedimentary-exhalative deposits have been reported in relation to the pre-Alpine rifting. However, in the Basque-Cantabrian basin, to the southwest of the Pyrenees, stratabound Pb–Zn mineralization in Albian–Aptian sediments has been described by Velasco et al. (1996) as sedimentary-exhalative.

## 5. Conclusion

The Les Argentières and Lacore Pb–Zn vein deposits are located in Devonian terranes of the Axial Zone of the Pyrenees. The deposits were formed in a normal fault system that bounds the Aulus Mesozoic rift basin. The metals are believed to have precipitated from a low-temperature high-salinity NaCl–CaCl<sub>2</sub>-rich fluid with very similar characteristics to basinal brines, which are commonly interpreted as having a strong base-metal scavenging efficiency. The mineralizations give lead isotopic signatures consistent with Mesozoic ages, which can be narrowed down to Middle–Late Triassic and Late Jurassic times, when two aborted rifts occurred in the Pyrenees. These data allow us to argue in favour of the role of an extensional setting during pre-Alpine rifting

triggering hydrothermal fluid circulation, and of ore deposition in the syn-sedimentary fault system at the margin of the Aulus basin. A reappraisal of the origin of other Pb–Zn vein deposits in the Pyrenees, together with a more thorough geochemical characterization of fluid and metal sources, would provide precious clues allowing one to strengthen this premise. In light of these findings, the Mesozoic sediments of the Pyrenean rift basins could prove to be a suitable target for getting further insights into sedimentary-exhalative mineralization in the chain.

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