

LEAD-ZINC AND IRON MINERALIZATIONS IN THE URGONIAN OF THE BASQUE-CANTABRIAN BASIN



Open-pit of the Reocín mine (Torrelavega, Santander). The landslide affecting the left slope forced the exploitation to stop a few months before its planned closure in 2003.

The international relevance of the Urgonian (Aptian-Albian) carbonate facies of the Basque-Cantabrian Basin lies on its sedimentological, tectonic, paleogeographic, and particularly metallogenic significance. The extension and quality of the Urgonian exposures allow to establish sequences corresponding to the development of carbonate ramps and shelves, and to identify slope and basin facies transitions with unique examples. At the same time, it presents several examples of great interest for the study of synsedimentary tectonics. The existence and good preservation of sedimentary bodies and structures allows for detailed studies of basin evolution during the Aptian-Albian time interval, increasing the knowledge on mechanisms and chronology of the Biscay Bay opening. Due to its scientific and economic relevance, in this chapter we will also deal with the metallogenic processes associated with Urgonian basin evolution, and with the ore deposits present in the Urgonian sequences.

The Basque-Cantabrian Basin is located in the western end of the Pyrenees Mountain Range, surrounded and limited by Paleozoic massifs: Asturian Massif to the west, La Demanda Massif to the south, and Cinco Villas and Quinto Real massifs to the east. This inner plate basin formed during the Triassic related to the beginning of the opening of the North Atlantic and, as a consequence of the opening of the Biscay Bay, was bounded to the northwest and southeast by transform faults. Figure 1 shows the three domains considered by Barnolas and Pujalte (2004) within the basin shown schematically, and which approximately coincide with the North Iberian and European paleomargin segments, especially from the Middle Cretaceous, when these paleomargins were individualized.

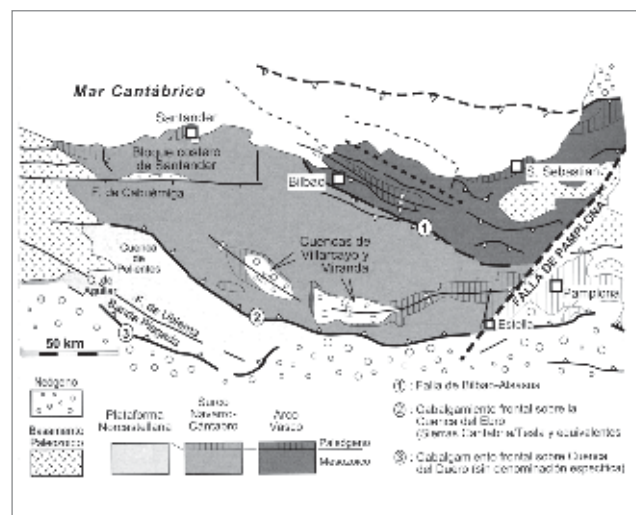
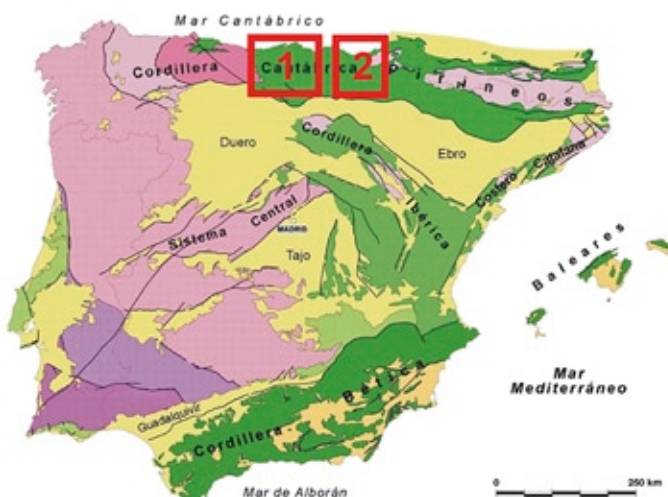
During the Upper Jurassic and Cretaceous, thick (15000 m) sedimentary piles were deposited with a high sedimentation rate linked to important extensional tectonic subsidence in the basin. These fault-

controlled subsidence was particularly active during the Upper Jurassic-Lower Cretaceous, when the rifting and basin opening processes continued. The stratigraphic record from this period covers three big complexes (Rat, 1959): the Upper Jurassic-Barremian Wealdian Complex at the base (continental siliciclastic sediments); the Aptian-Middle-Upper Albian **Urgonian Complex** (shelf carbonates with rudists, and basin shales with siliciclastic interbeds); and the Upper Albian-Cenomanian Supra-Urgonian Complex (deep turbidites and fluvial siliciclastic sediments).

The Urgonian Complex reaches a thickness of 4000 m of marine sediments. It is limited at the base by siliciclastic formations of saline and fresh water environments, and at the top by a sandy complex. Its most characteristic facies is limestone with rudists, corals and orbitolinids. During the early Aptian (Bedoulian), there was a very significant change in basin paleogeography: the dominant siliciclastic sedimentation shifted to shallow marine sedimentation in a carbonate shelf with rudists, corals and orbitolinids (Gargasian or Upper Aptian), which was interrupted by erosion and episodes of terrigenous input (shale, marl and sandstone) located in depressions between the shelves or relative highs (García Mondéjar, 1990). This set is formed by a group of megacycles or sequences separated by discontinuities, whose synchronism allows to evaluate thickness variations and strong lateral facies changes. This process resulted from strong relative subsidence in relation to structuring of the basin in troughs and relative heights where carbonate shelves developed.

In general terms, the Aptian-Albian interval corresponds to an important rift stage, originated by the movements opening the Bay of Biscay (García-Mondéjar, 1989). This setting helped the rising of mineralizing fluids which metasomatized the Urgonian limestone.

Figure 1, left. 1) Cantabrian Area, with Reocín, Novales, Emilia mine, Udías, La Florida and Cabarga. 2) Basque Area with the mines of Gallarta, Turcios and Mutiola. To the right, Basque-Cantabrian Basin scheme (after Barnolas and Pujalte, 2004).



From the metallogenic point of view, the Basque-Cantabrian Basin is located in the North-Pyrenean Belt, one of the Zn-Pb belts limiting a unique metallic domain between Galicia and the Alps (Routhier, 1980). This singularity is shown within the basin by the existence of abundant Zn-Pb mineralizations presented in varied types, settings and morphologies: vein-like, replacements, associated to diapir margins, Mississippi Valley type, sedimentary exhalative (sedex), etc. Independently from the process and type of emplacement, the mineralizations are in all cases related to the shelf margin Urgonian limestones, where most of them are hosted.

The economical and historical importance of the iron mining district of Bilbao (and that of Peña Cabarga, Cantabria) must be emphasized. Abundant siderite mineralizations, with different types and morphologies (vein-like or replacing), are always found in the Urgonian limestone, dolomitized and silicified. Their exploitation produced more than 300 million tons of iron ore from the mid XIX century to the beginning of the XX century, and were the main source for the English iron and steel industry.

Both kinds of mineralization (Zn-Pb and Fe) are closely linked to the same sedimentary system and are related to a single metallogenic process, which belongs to a specific stage of the basin's evolution and of mineralizing fluids flow, which are channeled through the synsedimentary faults. Mineral concentrations were mainly caused by fracture and hydrothermal processes, synsedimentary as well as post-synsedimentary, causing stratabound and vein-like ore deposits by replacing the pre-existing carbonates and removing the previous mineral concentrations. In all cases, and later in time, surface weathering was responsible for the oxidation cap deposits (gossan), developing different minerals (goethite, limonite, hematite, etc.)

The metallic mineralizations of the Basque-Cantabrian basin are linked to Urgonian carbonate rocks of Aptian (Bedoulian and Gargasian) as well as Albian ages. The geographical distribution of the main mineral concentrations shows a preferential east-west zonation. In western Cantabria (Reocín), the Zn (Pb) prevails; west of Vizcaya there are many Zn-Pb and Fe mineralizations, in the Bilbao sector the mineralization is almost exclusively of Fe, and Zn-Pb again crop out south of Guipuzcoa. Timing of mineral emplacement varies, from simultaneous to subsequent to the sedimentation, and resulted from metasomatic replacement by hydrothermal fluids (magmatic or diagenetic). Pre-Urgonian siliciclastic deposits have been identified to be the metal source, and even in metamorphic and igneous domains due to the circulation of fluids through deep faults (García-Mondéjar *et al.*, 2004).

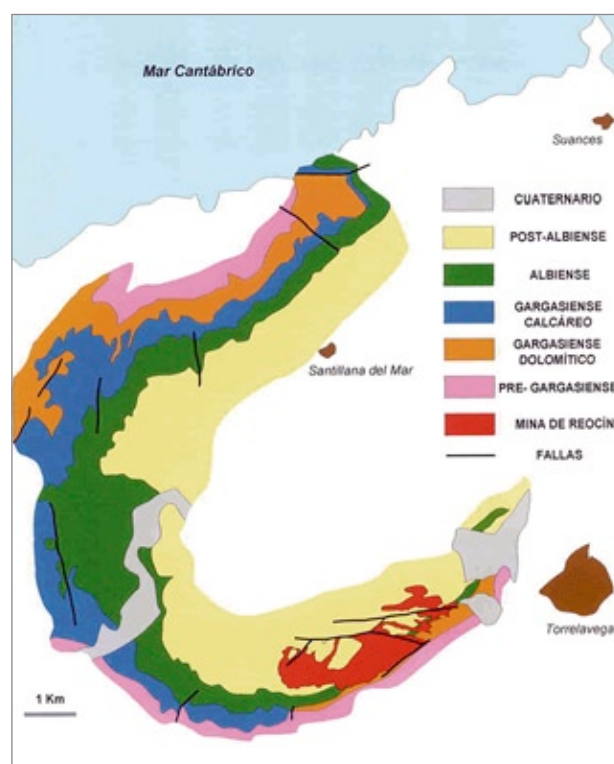
Some mines stand out in this geological framework as sites of geological and mining heritage due to their metallogenic, economic and historical interest. Some of them must be highlighted: Reocín, Novales, Udías, La Florida and Cabárceno, in Cantabria; and the

mining districts of Gallarta (Vizcaya) and of Mutiloa (Guipuzcoa), in the Basque Country.

A wide syncline structure stands out in the western end of the Basque-Cantabrian Basin: the Santillana-San Román syncline, striking NE-SW. Along its borders are several zinc-lead deposits within Urgonian dolostones and related to faults. The **Reocín deposit** (Figure 2) is located on the southeast flank, near the periclinal end of the syncline, towards Torrelavega (Cantabria). This is a stratabound ore deposit 3300 m long and 800 m wide, formed by different mineralized and overlapped bodies with variable richness, locally reaching thicknesses up to 100 m included in barren intermediate zones (Barrendera zone). All the mineralizations are hosted in the Urgonian limestone rocks, which are heavily dolomitized in this area. This is a world class deposit, concentrating more than 4 million tons of Zn and near 1 million tons of lead, which has been exploited since the mid XIX century to the present day.

The geometry of the mineralized bodies is highly variable, conditioned by synsedimentary faults contributing as paths for the circulation of dolomitizing and mineralizing fluids, which formed deposits along bedding planes and fractures. Based on the different facies where it is hosted, and on the thicknesses of the mineralized bodies, two areas can be distinguished within the ore deposit: Central-Western (South layer, North layer and Third layer), and Western (Barrendera), separated by La Visera fault (Figure 3), which is very important as it conditioned fluid circulation and mineralizations towards the south.

Figure 2. *Southwest periclinal end of the Santillana syncline: geological location of Reocín mine (AZSA).*



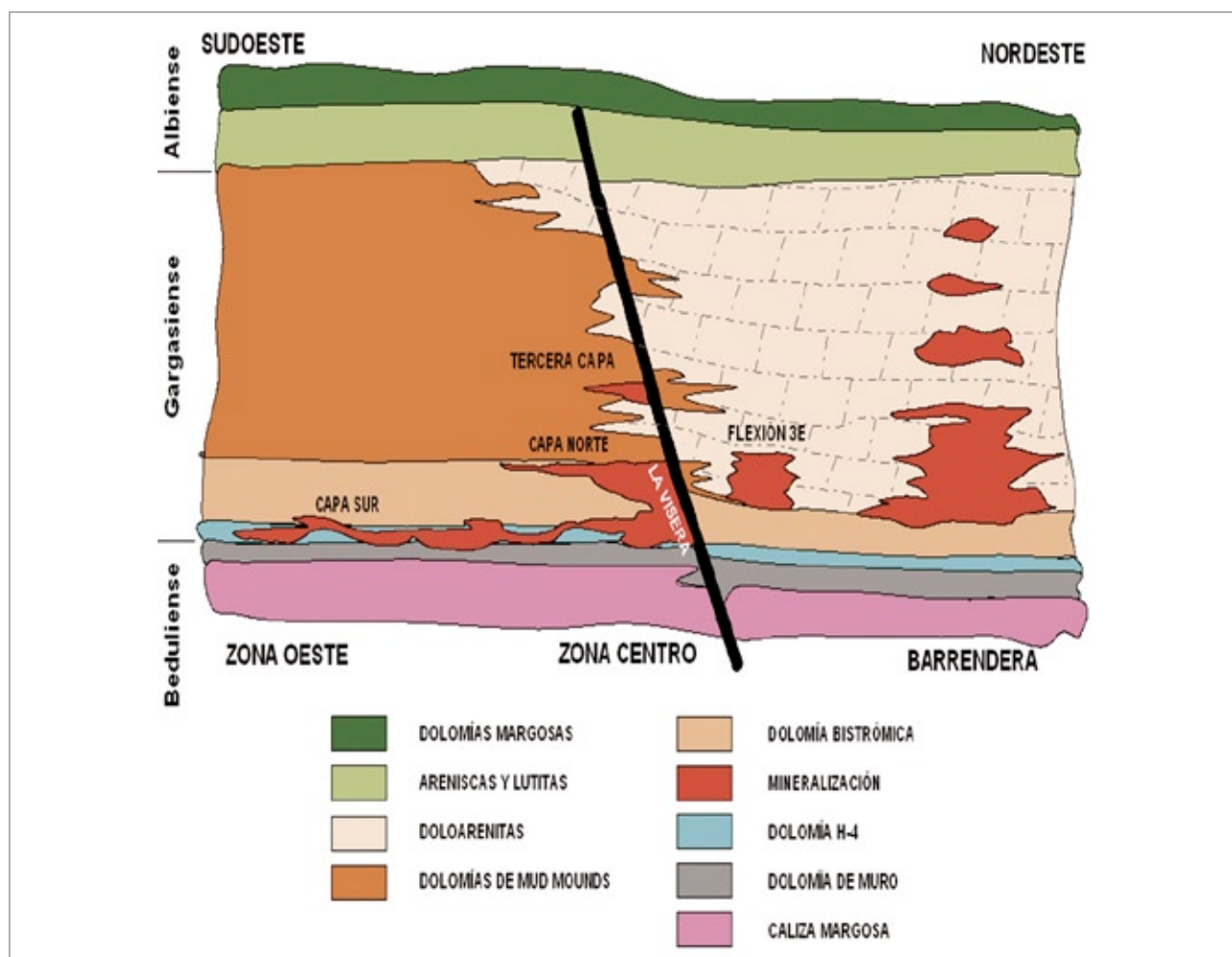


Figure 3. Geological cross-section of Reocín mine, with the location of mineral deposits.

In the west central area of the deposit, upon the "roof dolostone" (uppermost Bedoulian) is a dolomitic level (H-4), followed by a biostromal dolostone (biostromes are reefs with bedded geometry) and a thick interval of massive dolostone, corresponding to carbonated mud-mounds. The most important mineralized level in Reocín, for its extension and grades (>25% Zn), is the so-called "Southern Layer", mostly hosted in the dolomite H-4, and even replacing it locally. The dominant mineral is sphalerite. The so-called "North Layer", with somewhat lower grades and smaller in size, is hosted along the surface limiting the biostromal dolostone and the mud-mounds. The "Third Layer" appears some meters higher than the previous, within the mud-mound facies, and is related to the mineralizing role of La Visera fault. All along this structure, the mineral replaces most of the biostromal dolostone.

In the eastern zone (Barrendera) north of La Visera fault, the mud-mound dolostones change facies laterally to dolarenites (dolomitized calcarenites). A series of isolated mineral bodies (Flexure 3E) or superimposed bodies (Barrendera) are hosted within them, which have a lens geometry exceeding 50 m thicknesses in some cases. In both cases, the average grade is lower than 7% Zn, although it may be higher locally.

The origin of the Reocín deposit is related to dolomitization processes (replacing calcite by dolomite) of the Aptian (Bedoulian and Gargasian), Albian and Lower Cenomanian carbonates, and which spatially affect the Reocín area. Banded, coloform and botryoidal sphalerite (with associated galena) and ankeritic or ferrous dolostone (Figure 4) can be recognized upon the light-colored hosting dolostone.

The mineralogy in Reocín is not very diverse, mainly made of sphalerite (ZnFeS) and its polymorph wurtzite, and galena (PbS) scattered among the sphalerite and the dolomite. Other primary minerals present here are the marcasite, pyrite and melnikovite (FeS_2). Dolomite ($\text{CaMg}(\text{CO}_3)_2$) and calcite (CaCO_3) appear as a companion to the ore. The following minerals are found in the open pit showing supergenic alteration: smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5((\text{OH})_3\text{CO}_3)_2$), goethite (FeOOH), hemimorphite ($\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2\text{H}_2\text{O}$), etc.

Present knowledge confirms the hydrothermal character of the deposit, originated by the escape of rising fluids leaching the existing metals in pre-Urgonian sediments (black slates) and depositing them while circulating through the Gargasian carbonates, along syndimentary faults. The moment of origin of the deposit is controversial, although the dolomitization-

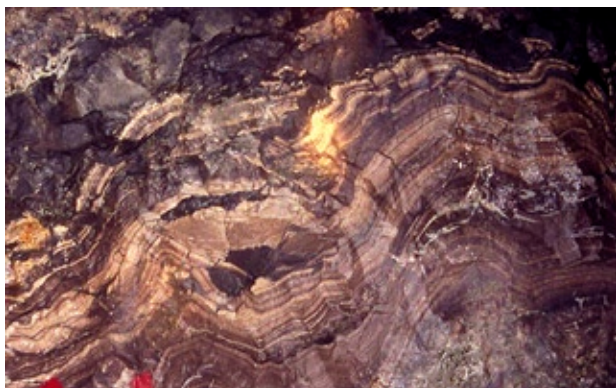


Figure 4, above. *Mineral deposits of sphalerite and galena in ankeritic dolostone, "Capa Sur" (Reocín).*

Figure 5, below. *Mine shaft at San José, Novales (Cantabria). Photograph by J. Locutura.*

mineralization relationships point to a late diagenetic (epigenetic) model of the Mississippi Valley type, with features typical of a hydrothermal karstic deposit.

The Reocín deposit began to be mined in the mid XIX century, although there are evidences for the development of the oxidation area since Roman times. Miners began the extraction of "calamines" (oxides, hydroxides and carbonates of Zn, Pb and Fe), and at

the beginning of the XX century, as the exploitation got deeper, the sulphides started appearing, forcing a change in the calcination treatment and the installation of the first European plant of sulphide flotation (1922). Between 1943 and 1965, mining work focused in the interior, but a collapse caused the re-activation of open pit mining (El Zanjón open pit). Since 1976, a mixed system was developed with both open pit mining and interior works (Santa Amelia well and Jorge Valdés ramp). Peak production was reached between 1990-95. The exhaustion of the deposit and the lack of new reserves caused the closure of Reocín in 2003.

Near Reocín there are several similar, but less important, mineral deposits. The **Novales deposit**, near the town with the same name, presents a paragenesis similar to Reocín with regard to primary minerals (sphalerite, galena and pyrite), as well as iron oxides and "calamines" in the oxidation gossans. The mineral is scattered in cavities related to faults, and was developed at the **San José** (Figure 5), **Aumento**, **Porvenir**, **Andrea**, **Codornos** and **Eucaliptal** mines, among others, until their complete exhaustion. Near Novales (Caborredondo), there is another small development, **Emilia mine**, with a mineralization similar to Novales.

The **Udías deposit** (Hermosa and Enriqueta mines in **Sel del Haya**, Figure 6) was, together with the exposure in Comillas, the first to be developed (mid XIX century) until its closure in 1930. It consisted of both interior and open pit mining works. This mine is connected with the Novales mine through a vast karstic conduit (cave). Sulphides in this deposit (sphalerite and galena) are scarce, and the ore corresponds to "calamines" (hemimorphite, smithsonite, etc.). Apart from the Hermosa and Enriqueta mines, in Sel del Haya, the deposit was developed in other mines such as **San Bartolomé**, **Pepita**, **La Cabaña**, etc.

The **deposit of La Florida** is located in Sierra de Armero, south of San Vicente de la Barquera. It is a deposit associated to fractures and within a karstic system thoroughly developed upon the Gargasian dolostones. The mineral paragenesis is mostly sphalerite and galena, but in this case they have barite (BaSO_4) as associated mineral, something not common in deposits like Reocín. Although its first development took place in Roman times, modern works began in 1855, lasting until its closure in 1979. This was a very important deposit, as indicated by the remains of several mining developments (Lecuerre, La Isidra, Cereceo, etc.)

Mining works in the area cut "soplaos" (blowings) at different depths. This is the name miners gave to the advance works when they cut karstic channels resulting in strong winds. Currently, there is a big underground maze with tens of kilometres of mining galleries intersecting karstic galleries and caverns, which at the time made easier the transit of the mining works. The best example is set by "**Cueva del Soplaio**", a cavity accessible from several of the Lacuerre mine mouths



Figure 6, above. Cog of the well at Sel del Haya, Udías (Cantabria). Photograph by J. Locutura.



Figure 7. Cueva del Soplao, La Florida (Cantabria).

(western end of La Florida deposit). It is an amazing sight to observe big surfaces covered in aragonite, false roofs, gours, stalactites and stalagmites (Figure 7). After being declared as a Natural Monument, it has been adapted for its use as tourist resource.

Iron mining was the oldest and most common one in Cantabria, as shown by the abundant remains of exploitations. They are mainly located in the eastern margin or Castro Urdiales zone (Lusa, Mioño, Ontón, etc.) and in the central zone (**Peña Cabarga or Cabárceno, Mercadal, and Camargo**). The deposits in the eastern zone (Castro Urdiales) are similar to those in the Biscay Mining Basin, and the mineral paragenesis consists of siderite (FeCO_3), hematites (Fe_2O_3), goethite (FeOOH) in nodules called "chirita", limonite ($\text{FeO} \cdot \text{OH} \cdot \text{NH}_2\text{O}$) and pyrite (FeS).

The **mining exploitation of Peña Cabarga** (Cabárceno) stands out in the central area. This mine benefited from iron oxides and hydroxides filling the karstic cavities, coming from oxidation and hydration of the iron sulphides (pyrite and marcasite) within the Urgonian dolostones. Cabárceno is the best example, because as the iron ore was developed, the column shapes from the karst were almost cleaned. The result is a ruin-like landscape of great beauty which nowadays is used as a recreation area and a zoo park (Figure 8). The prevailing mineralogy, of a secondary origin, is made up by iron oxides and hydroxides, with high rates of sulphur, pyrite, manganese, phosphorus and arsenopyrite (FeAsS). The minerals developed were hematite, limonite, goethite, pyrite and pyrolusite (MnO_2).

The Basque Country was one of the areas with the biggest concentration of iron ore mines. The first works are from Roman times, and they reached a peak in the mid XIX century until the end of the XX century. Important iron deposits linked to Urgonian carbonates are those corresponding to the so-called "Mining Zone" (Gallarta, Ortuella, Muskiz, Sopuerta, Triano-Matamoros, Baracaldo, etc.), those in the northern and southern flanks of the Bilbao anticline (Basauri, Bilbao, Castrejana, Alén, etc.), and those in Guipúzcoa (Legazpia, Mutiloa and Zerain).

The best example of geological and mining heritage of the Basque Country, based on its importance and current preservation state, is the **Gallarta deposit**, developed in the Bodovalle mine and the Concha II open pit (Figure 9) located in the towns of Abanto, Ciervaza and Ortuella.

The deposit is mostly stratiform (hosted in Urgonian reef limestone) and resulted from replacement of calcium carbonate by iron carbonate (siderite) accompanied by dolomite and ankerite (Figure 10), and with calcite, quartz, pyrite and chlorite as accessory minerals. In some cases, there are vein-like geometries hosted in pre-Urgonian, Urgonian and post-Urgonian rocks, with siderite also being the main mineral.

The outcrops are weathered at surface into "oxidation gossans" with secondary deposits of goethite, hematite and limonite. Another very common deposit derived from the previous is the so-called "chirtera", consisting in the accumulation of iron oxide fragments (goethite, quartz and argillaceous minerals)



Figure 8, above. *Panoramic view of Los Frailes, Cabárceno (Cantabria). Karstic landscape modified by mining.*

Figure 9, below left. *Concha II open pit (Gallarta, Basque Country).*

Figure 10, below right. *Replacing of the calcium carbonate by iron carbonate (siderite), dolomite and ankerite. Bodovalle Mines (Gallarta, Vizcaya).*

eroded and transported into karstic cavities within the host rock.

Whereas the debate about the genesis of these deposits is still alive, the last data seem to confirm that they belong to a "Mississippi Valley" genetic model, with metal mobilization and transportation in hot brines during the late diagenetic stages, through syndimentary fractures until they precipitated in the Urganian limestones.

In the Basque Country there are also abundant sites with lead-zinc deposits, also hosted in Urganian rocks

and with similar features, where the galena-sphalerite mineral paragenesis is always present, together with siderite, dolomite, barite and fluorite. These are vein-like mineral deposits controlled by syndimentary fractures, and in occasions they are hosted in sedimentary bodies (stratiform) of the Infra-Urganian to Supra-Urganian Complexes.

In the towns of Trucios and Artzentales, there are remains of underground and open pit mining developments. As in the rest of the Basque-Cantabrian basin, the most intense mining activity took place from the XIX century to the mid XX century. In all cases, the

deposit consists of galena and sphalerite, with calcite, quartz and dolomite as secondary minerals. The **Mine of Siete Puertas (Trucios)** is a good example where it is still possible to see this minerals in interior works, with stratiform disseminated galena and sphalerite in silicified limestones, and where dolomitization and/or silicification processes were prior to or simultaneous with the mineralization.

In Mutiloa (Guipúzcoa) there are abundant ancient iron mines (carbonate and iron oxides) with mining remains going back to the Middle Ages. The **Troya Mine (Mutiloa)** was discovered in 1973 and developed from 1986. It is a stratabound ore deposit of lead and zinc sulphides, hosted in the Urganian complex related to an important synsedimentary fault (Troya fault). The prevailing sulphide is iron pyrite, with both sphalerite bandings and uneven concentrations of galena and markasite. An old mine gallery (Zerain) was rehabilitated for visits, as well some calcination ovens (kilns).

REFERENCES

- ASTURIANA DE ZINC S.A . Memorias de la Empresa.
- BOIXEREU, E. (2000). Contribución al conocimiento de la historia de la minería del hierro en Vizcaya (1818-1993). *Boletín Geológico y Minero*. 111-2 y 3, 119-130.
- CASTRO, A., CALVO, M., GARCÍA, G. and ALONSO, A. (2003). "Reocín (1856-2003)". *Rev. Min. Yac. España, Bocamina*, 8. 15-67.
- GARCÍA-CORTÉS, A., RÁBANO, I., LOCUTURA, J., BELLIDO, F., FERNÁNDEZ-GIANOTTI, J., MARTÍN-SERRANO, A., QUESADA, C., BARNOLAS, A. and DURÁN, J. J. (2000). Contextos geológicos españoles de relevancia internacional: establecimiento, descripción y justificación según la metodología del proyecto Global Geosites de la IUGS. *Boletín Geológico y Minero*. 111-6, 5-38. Madrid.
- GARCÍA-CORTÉS, A., RÁBANO, I., LOCUTURA, J., BELLIDO, F., FERNÁNDEZ-GIANOTTI, J., MARTÍN-SERRANO, A., QUESADA, C., BARNOLAS, A. and DURÁN, J.J. (2001). First Spanish contribution to the Geosites Project: list of the geological frameworks established by consensus. *Episodes*, 24 (2), 79-92.
- GARCÍA MONDÉJAR, J. (1990). The Aptian-Albian carbonate episode of the Basque-Cantabrian (northern Spain): general characteristics, controls and evolution. *I.A.S. Spec. Pub.*, 9, 257-290.
- GARCÍA MONDÉJAR, J., AGUIRREZABALA, I., ARANBURU, A., FERNÁNDEZ-MENDIOLA, P., GÓMEZ PÉREZ, I., LÓPEZ-HORGUE, M. and ROSALES, I. (1996). Albian-Aptian Tectonic Pattern of the Basque-Cantabrian Basin (northern Spain). *Geological Journal*, 31, 13-45.
- FERNÁNDEZ-ÁLVAREZ, G. and FERNÁNDEZ-MAROTO, G. (2002). Minerales de Cantabria. In: *Nuche del Rivero, R. (Ed.). Patrimonio Geológico de Asturias, Cantabria y País Vasco*. ENRESA. 330-355.
- RAT, P. (1959). Les pays crétacés Basco-Cantabriques, Espagne. *Publications de l'Université de Dijon*, 18, 1-525.
- REAL COMPAÑÍA ASTURIANA DE MINAS (1970). *Minas de Reocín*, Memoria, 33 p.
- SEEBOLD, I. et al (1992). Yacimientos estratoligados de blenda, galena y marcasita en dolomías. Mina de Reocín (Cantabria). *Recursos minerales de España*, CSIC. 947-967.
- VAZQUEZ GUZMAN, F. (1983). Depósitos minerales de España. *IGME*, 34-38.