

# Geological features of the Zn-Pb prospect in the Bou-Izourane district (Morocco)

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The Zn-Pb mineralization in the Bou-Izourane district, located in the High Atlas Mountains of Morocco, contains estimated reserves of 40 200 tons of ore with an average grade of 20% Zn and 3.5% Pb. It is developed on N–S to NNW–SSE-trending faults that cut Liassic carbonate marl deposits. The paragenetic mineral sequence consists of galena, sphalerite and late-stage calcite. Oxidation phases of galena into cerussite and sphalerite into smithsonite are common in the Bou-Izourane ore, linked to the infiltration of meteoric waters and the oxidation of these sulphides. The Zn-Pb mineralization runs parallel to the fluorite veins associated with the igneous rocks of Tamazeght, but no petrographic or field relationship has been demonstrated between these two mineralizations (i.e., Zn-Pb and fluorite). The distribution of rare earth elements and yttrium (REY) in the Zn-Pb mineralization of Bou-Izourane shows a notable similarity with the Mississippi Valley Type (MVT) mineralization of the Central High Atlas of Morocco, although the concentrations more closely resemble those of REY in fluorite linked to the magmatic-hydrothermal activity of Tamazeght. However, the analysis of their distribution in post-fluorite calcite and post-Zn-Pb calcite reveals a strong concordance, suggesting that these two calcites are associated with the same phase and have a common origin. The classification of the Zn-Pb prospect in Bou-Izourane remains controversial, fluctuating between an MVT-type mineralization, similar to most Zn-Pb mineralizations in the Central High Atlas of Morocco, and a mineralization linked to the magmatic-hydrothermal activity of Tamazeght, which could provide heat and metallogenic material. Characterizing the Zn-Pb ore of Bou-Izourane is crucial for the future exploration of zinc and lead deposits in the High Atlas of Morocco and could advance the development of Zn-Pb mining in the region, from artisanal exploitation to professional mining.

Key words: Zn-Pb ore, fluorite, Tamazeght magmatic complex, Bou-Izourane, Moroccan High Atlas.

# INTRODUCTION

Morocco boasts a wealth of diverse mineral deposits and significant economic opportunities, making it a renowned destination for scientific exploration and research. The Zn-Pb deposits in the metallogenic provinces of the Moroccan High Atlas and eastern Morocco have attracted great geological and economic interest. Indeed, vein-type and stratabound ores (galena, sphalerite, barite, chalcopyrite and others) are currently exploited. The High Atlas ore (Zn-Pb) deposits were formed as a result of two major mineralizing events related to two stratigraphic levels (Mouguina, 2004; Rddad and Bouhlel, 2016; Rddad and Mouguina, 2021). The first event of Zn-Pb mineralization, hosted in the Lower Jurassic (Liassic), is related to the Triassic-Liassic thermal event that occurred during the opening of the Central Atlantic Ocean. This mineralization is represented by syngenetic Zn-Pb-Fe deposits in strata and/or lenses (Upper Moulouya mining district, Emberger, 1965; Tizi n'Firest, south border of the oriental High Atlas, Bazin, 1968; Tazekka ore deposit, eastern Morocco, Auajjar and Boulègue, 1999). The second episode involving Zn-Pb ore deposits in the Middle Jurassic (Dogger), is associated with the evolution of Jurassic magmatism along the palaeo-heights (ridges) of the central High Atlas. Not far from the Bou-Izourane district, at Ali Ou Daoud (Fig. 1), the Zn-Pb ore is mainly disseminated in the gabbro and is related to an early syngenetic Bajocian (Middle Jurassic) episode followed by a latest epigenetic hydrothermal episode (Mouguina, 2004). Structural and mineralogical studies allowed Mouguina (2004) and Mouguina and Daoudi (2008) to propose that some of the Middle Jurassic Zn-Pb deposits, such as those of Ali Ou Daoud and Tigrinine-Taabast, are similar to



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Fig. 1. Distribution of Zn-Pb ore deposits on the map of the central and eastern High Atlas of Morocco with the location of the ore district of Bou-Izourane Zn-Pb and the Tamazeght complex (redrawn and edited from the Moroccan Geological Map at a scale of 1/1000,000 and modified after Rddad and Mouguina, 2021)

the Mississippi Valley-type deposits described in the Eastern High Atlas (e.g., Bou Dahar; Adil et al., 2004; Bouabdellah et al., 2009; Rddad and Bouhlel, 2016) and the High Plateau zone (e.g., Touissit and Mibladen; Dagallier, 1977; Ovtracht, 1978; Wadjinny, 1989; Bouabdellah et al., 2012; Marcoux and Jébrak, 2021). A later ore-forming event, which occurred during the Eocene, is mainly characterized by fluorite ore deposits in veins and cavities (Achmani, 2017; Achmani et al., 2020, 2023). This event is related to the emplacement of the Eocene alkaline magmatism of Tamazeght. Other previous work has also reported the presence of sulphide minerals such as sphalerite, galena, pyrite and chalcopyrite in the Tamazeght pegmatites and nepheline syenites (Agard, 1960; Marks et al., 2008). In addition, Salvi et al. (2000) showed that nepheline crystals in the Tamazeght syenites contain fluid inclusions with sphalerite and galena daughter minerals, linked to hydrothermal-magmatic fluid circulation.

The Bou-Izourane Zn-Pb mineralization is developed in the sedimentary cover along generally N-S to NNW-SSE-oriented fractures. This district has been exploited since the 1980s by local artisanal miners for sulphide and non-sulphide ores. The Bou-Izourane district, currently exploited by the "Global Mine" company, is one of the most important fluorite producers in Morocco. Fluorite reserves amount to ~300 kilotons and the Zn-Pb ore has estimated reserves of 40,200 tons, with 15-28% Zn and 2-5% Pb. Several extensive studies are currently focused on the fluorite mineralization in the Bou-Izourane area. By contrast, the Zn-Pb mineralization in the same area has received less attention due to the company's focus on fluorite exploration. However, since global demand for these metals is enormous, there may be increased interest at Bou-Izourane in the future. With no geological study of the Zn-Pb mineralization in the Bou-Izourane district, the present paper is the first such study of Zn-Pb mineralization at Bou-Izourane. Its presence in the core of the Central High Atlas Mountains and in proximity to the Tamazeght magmatic complex (svenitic-peqmatitic-carbonatitic) and also in the vicinity of fluorite mineralization (Achmani, 2017; Achmani et al., 2020, 2023) raises questions about the geological characteristics of these Zn-Pb concentrations. Based on mapping, petrographic, geochemical - including rare earth elements in galena and calcite - and micro-thermometric data, we explore the geological features of the Zn-Pb ore in the Bou-Izourane district. This contribution also seeks to address the following questions: 1 - is there a relationship between the concentration of Zn-Pb and the Tamazeght magmatic complex, and/or with the fluorite mineralization?; 2 - is the Bou-Izourane Zn-Pb mineralization similar to that already exploited in the Central High Atlas of Morocco (e.g., the Tigrinine-Taabast mining district)? Furthermore, the comparison of the Zn-Pb mineralization in the Bou-Izourane district with other Zn-Pb deposits in the Central High Atlas of Morocco (e.g., Tigrinine-Taabast) will help understand the processes involved in this mineralization.

### GEOLOGIC SETTING

#### REGIONAL GEOLOGIC SETTING

In the eastern part of the Central High Atlas, which encompasses our study area, the mountain range comprises synclinal megastructures with broad, flat bottoms, as well as anticlinal megastructures that are sharp and narrow. Some synclines have a lozenge geometry. They generally show marlycalcareous outcrops of the Dogger overlain by red detrital deposits of the Bathonian-Callovian to Lower Cretaceous (Fadile, 1987; Laville and Piqué, 1992; Ibouh, 1995). The main orientation of the anticlines in the region is ENE–WSW to E–W, and they occasionally display "S" or "Z" shaped undulations (Ibouh et al., 2001). The anticlinal structures in places lack hinges and possess a core occupied by a mega-breccia with clasts of different compositions, such as

- Triassic basalts and/or Jurassic magmatic rocks;
- Jurassic limestone fragments;
- Triassic clays.

Moreover, the Central High Atlas shows a succession of folds in the Mesozoic sedimentary cover in the form of large synclines alternating with sharp anticlines. The cores of the folds, commonly bounded by faults, reveals either Triassic rocks only, or volcanic rocks of Jurassic age, or Variscan basement which outcrops in some places (Brede and Heinitz, 1986; Heitzmann, 1987; Benammi, 2002; Teixell et al., 2003; Ibouh, 2004; Ait Addi and Chafiki, 2013; Torres-López et al., 2018). A synthesis of the lithostratigraphy of the High Atlas Mountains and the main regional tectonic events is summarized in Figure 2A.

### PRE-RIFT PHASE

In the south of the High Atlas Mountains, the Anti-Atlas exposes rocks of Precambrian to Paleozoic age of the West African craton. The Pan-African orogeny and Variscan deformation influenced the Upper Proterozoic rocks. The dislocation of



Fig. 2A – synthetic column of the central and eastern High Atlas Mountains, showing the main tectonic events and detachment levels (El Harfi et al., 2006); B – synthetic stratigraphic column of the Bou-Izourane district (Achmani, 2017; this study)

Pangea by post-convergent extension, forming Late Triassic and Early Jurassic syn-rift basins, led to large-scale reactivation of previous Hercynian-Alleghanian thrusts in the Late Paleozoic (Laville et al., 2004; El Harfi et al., 2006; Fig. 2A).

#### SYN-RIFT PHASE

The High Atlas domain experienced extension and rifting during most of the Mesozoic. At first, in the Triassic, this extension is resulted in red beds and tholeiitic basalts. Later, during the Jurassic, it is expressed by the deposition of carbonates and marine shales, overlain by continental red beds (Michard, 1976). The geodynamic development of Morocco, in particular the "Atlas Fault", is strongly linked to the Atlantic rifting in the west, and to the creation of the Tethys in the north, during the Cretaceous. A transfer fault basin model (Laville and Piqué, 1992) and an extensional basin model ("Atlas Rift"; Jacobshagen et al., 1988) can both be used to explain the extensional architecture of the Atlas basins in the Jurassic. The Triassic structures are guided by the normal fault reactivation of the Variscan structures trending E/NE and SE (Mattauer et al., 1977; Laville et al., 1977; Laville, 1977, 1978; Laville and Piqué, 1991, 1992; Aït Brahim et al., 2002), inducing general NNW-SSE to NW-SE extension. Intra-basinal faults, oriented NNE-SSW to NE-SW, are considered as dip-slip extensional faults (Mattauer et al., 1977; Laville and Petit, 1984; Beauchamp, 1988).

#### POST-RIFT PHASE

Large parts of North Africa were flooded by shallow seas adjacent to the Atlantic and Tethys oceans in the late Jurassic and Cretaceous. The post-rift sedimentary rocks of the Atlas Mountains consist of shallow transgressive continental, carbonate and marine clastic sedimentary rocks ranging in age from the Lower Cenomanian to the Eocene. The geotectonic development of the High and Middle Atlas changed considerably during the Late Eocene. The earlier rift grabens (or half-grabens) underwent compressional/transpressional deformation, resulting in considerable uplift, as shown by the presence of Atlas pebbles in the foreland basins along the southern and northern margins of the High Atlas (El Harfi et al., 2001, 2006). During the Eocene, the N-S compression recorded in Morocco and which affected the whole of the Western Mediterranean (Tapponnier, 1977) was due to relative displacement between North Africa and Europe (Olivet et al., 1984). The gradual closure of the Tethys eventually led to continent-continent collision (Ricou, 1994), during which the Tamazeght complex (Tamazert) was established in the N-S compressive phase.

#### HIGH ATLAS UPLIFT

The uplift of the Moroccan High Atlas Range began in the Late Eocene with a rapid transition from marine to continental conglomerate deposition, followed by a quiescent phase in the Oligocene and Early Miocene due to reduced horizontal orogenic forces along the African/European plate boundary. The Early-Middle Miocene interval, characterized by a first phase of lithospheric thinning plus a shortening component, led to the establishment of tectonically- and gravity-driven transport of rock masses along the High Atlas. This was followed by large-scale subsidence, caused by a decrease in the intensity of lithospheric thinning. The shortening resumed throughout the Pliocene-Quaternary leading to the formation of the present orogen, with a second lithospheric thinning episode (Frizon de Lamotte et al., 2000, 2009; Leprêtre et al., 2015; Skikra et al., 2021).

# GEOLOGY AND LITHOSTRATIGRAPHY OF THE BOU-IZOURANE DISTRICT

The ore's host rock consists of folded Mesozoic rocks, part of a succession of folds in the Mesozoic sedimentary cover of the Central High Atlas. These are broad synclines alternating with sharp anticlines, the cores of which are commonly bounded by faults, revealing the Triassic alone or Jurassic-age volcanic rocks and/or locally the Variscan basement (Brede and Heinitz, 1986; Heitzmann, 1987; Teixell et al., 2003). The study area map illustrates the oldest Liassic units (Sinemurian) overlain by Pliensbachian, Toarcian, Aalenian, Bajocian, and Bathonian strata, whose dip varies depending on the location (Fig. 3). The entire succession is intruded by the Tamazeght magmatic complex rocks of Eocene age (44 ±4 Ma - Tisserant et al., 1976, 35 ±3 Ma - Klein and Harmand, 1985, and ranging between 47 ±1 Ma and 35 ±3 Ma - Achmani, 2023; Fig. 3A). These terrains are affected by the play of several faults that may be inherited from the Variscan Orogeny and that probably reactivated during the Alpine phase.

To gain insight into the spatial distribution and lithostratigraphy of the geological units, we constructed a lithostratigraphic log for the Bou-Izourane district (Fig. 2B).

### LOWER SINEMURIAN

This succession comprises massive dolomitic limestones occupying the core of the Jbel Bou-Izourane Anticline. The extent of the outcrop varies depending on the location. The rock has a brown patina and a fresh dark grey fracture. Due to the abundance of vacuoles and karstic pockets, it has high porosity. Microscopically, it is an oolitic limestone formed in a shallow and turbulent marine environment. The ooids have a nucleus and cortex and are cemented by microsparite.

#### UPPER SINEMURIAN

This unit consists of alternating bedded limestone and marl. The limestone beds have decimetric thicknesses (20–40 cm) and become thicker in the east. They have a light grey patina and a blackish colour on fresh surfaces. Its base is marked by flint nodules. The marls have a greenish patina, and the marl layers are millimetric, becoming increasingly thick towards the top of the formation (Achmani, 2017).

# PLIENSBACHIAN

This consists of light grey limestones rich in ammonites and belemnites. These limestones, which bear a sandstone-like appearance, form beds 25 to 30 cm thick and alternate with green marls.

#### TOARCIAN

The Toarcian strata are characterized by an increase in the thickness of the marl intervals (50 cm to 1 m). The marls are friable, flaky, greenish to greyish in colour and rich in ammonites, with thinner beds of of dark yellow limestone 5 to 10 cm thick. The



Fig. 3A – simplified structural map of northern Morocco with the geographic context and geological map of the Eocene Tamazeght magmatic complex (Agard, 1973; Kchit, 1990; Salvi et al., 2000; Schilling et al., 2009; Marks et al., 2009; Bouabdellah et al., 2010; Achmani et al., 2023) indicating the position of the area investigated (red rectangle); B – geological map showing details of the study area with Zn-Pb mineralization in the Bou-Izourane district, High Atlas, Morocco

unit thickens from west to east. Toarcian deposition started with marls (with the limestone beds containing ammonites) and ended with thick carbonate intervals indicating a shallow marine environment.

#### AALENIAN

The marly-limestone facies of the upper Toarcian is overlain by greyish lithic limestones in thin beds (15 to 30 cm) with *C. ancellophycus* of Aalenian age and marly joints. The passage from Toarcian to Aalenian is gradational, generally going from marls, with small beds of limestone, to alternating marls and limestones of the Upper Toarcian, to smooth limestones with marly joints.

### **BAJOCIAN-BATHONIAN**

This succession begins with a poorly sorted conglomerate facies that outcrops in the northeastern part of the Bou-Izourane Anticline at its base. It is overlain by biodetrital limestones, followed by green marls covering a large part of the study area. The whole forms a broad flat bottom of the syncline, in turn locally overlain by Quaternary deposits.

### QUATERNARY

The Quaternary, in the form of alluvial terraces, consists of sandstone and clay at the base, overlain by scree and gravel. The Quaternary deposits generally overlie, with angular unconformity, various older rocks of the study area, most commonly Bajocian-Bathonian marls.

# ORE DEPOSIT GEOLOGY

The vein-type Zn-Pb mineralization, with a thickness of ~1 to 2 metres and a length of 400 metres, hosted in Jurassic strata of Jbel Bou-Izourane, is primarily exploited for Zn-Pb ore. The vein is oriented N–S to NNW–SSE and cross-cuts Liassic carbonate marl deposits (Pliensbachian and Toarcian; Figs. 3B and 4). The ore-bearing faults have a similar N–S to NNW orientation as those in the Tamazeght igneous complex (Fig. 3). The sulphide mineralization at the Bou-Izourane prospect underwent heavy supergene oxidizing processes, occurring as both sulphide and oxidized sulphide (non-sulphide) ores (Fig. 5). The sulphide ore is mainly characterized by galena occurring in: massive (Fig. 5A–C), vein (Fig. 5D, E), and dissemi-



Fig. 4A, B – Zn-Pb-Ca vein intersecting the Liassic marly limestone in the Bou-Izourane district with a hand specimen of ore (Zn-Pb); C – simplified block diagram of Zn-Pb ore in the Bou-Izourane district

Galena - Gn, smithsonite - Sm, late calcite - Ca



Fig. 5. Specimens of galena-smithsonite-late calcite mineralization in the Bou-Izourane district

A-C – late calcite (Ca) includes galena (Gn) and smithsonite (Sm) fragments; D, E – galena (Gn) veins cut the host rock; F – massive galena (Gn) fragments in calcite (Ca); G – vuggy smithsonite (Sm); H, I – relationship between vuggy smithsonite (Sm) and disseminated galena (Gn); the entire mineralization (Cal + Gn) is enclosed in late-stage calcite (Ca)

nated forms (Fig. 5H, I). The non-sulphide ore, yellow and brown in colour, is mainly represented by vuggy smithsonite (derived from dissolution-replacement of coarse-grained sphalerite) (Fig. 5G–I). Late white calcite cements the sulphide (galena and sphalerite) ore following fracturing (Fig. 5A–C, E, F, I).

# MATERIALS AND METHODS

Systematic sampling was carried out for a detailed petrographic study on thin-sections (30 m thick slices of rock, polished on both sides and attached to a glass slide with epoxy resin) and on samples embedded in resin and then polished, for optical microscopy, cathodoluminescence microscopy (CL), and scanning electron microscopy (SEM) at the Geosciences Paris-Saclay laboratory, following a methodology to characterize the Zn-Pb mineralization of Bou-Izourane (Fig. 6). CL observations were performed on an *Olympus BX41* microscope coupled to *Cathodyne* cold cathode catholuminescence (NewTec) equipment operating at 12–14 kV and 140–250 µA and a *QicamFast* 1394 digital camera. SEM images were produced at an accelerating voltage of 15 keV and semi-quantitative elemental compositions were measured by energy-dispersive spectrometry

(EDS) at an accelerating voltage of 15 keV and an accumulation time of 30 s. Two samples of calcite associated with Zn-Pb mineralization from the Bou-Izourane district were selected for microthermometric analysis of fluid inclusions. Homogenization (Th) and water ice melting (Tm) temperatures of two-phase aqueous inclusions were acquired using a LINKAM MDS600 cooling and heating stage, mounted on a Leica microscope and equipped with a Lumenera Infinity 3 camera, at the Geosciences Paris-Saclay laboratory. Each liquid inclusion was measured twice, and any data that could not be replicated was excluded. Several fluid inclusions from the same plane that exhibited varying liquid-to-vapour ratios were excluded, as they were considered evidence of post-trapping distortion (Goldstein and Reynolds, 1994). 1.0 and 0.1°C, respectively, are the measurement uncertainties for Th and Tm. For a detailed analysis of the galena and calcite samples in the Bou-Izourane district, we separated and collected them individually, using manual sampling techniques under binocular microscopy. The hand-selected materials were then ground to a size of 200 mesh (0.074 mm), and a 0.25 g sample fraction was heated in HNO<sub>3</sub>, HClO<sub>4</sub> and HF until dry. After dissolving the residue in HCl, Bureau Veritas Minerals (Exploration Geochemistry, Canada) conducted trace element and rare earth element analysis using inductively coupled plasma mass spectrometry (ICP-MS) following method MA250.



Fig. 6. Methodology flowchart of petrology, fluid inclusion and geochemical study of Zn-Pb mineralization in the Bou-Izourane district

# RESULTS

### PETROGRAPHIC FEATURES OF Zn-Pb ORE

The Zn-Pb deposits hosted in the Jurassic carbonates of the Central High Atlas (Fig. 1) have a primary paragenetic sequence, excluding alteration minerals (cerussite, smithsonite, covellite, and hematite), that can be summarized as: galenasphalerite ± pyrite-calcite. These deposits are considered to be of MVT (Mouguina, 2004; Mouguina and Daoudi, 2008; Bouabdellah et al., 2012; Rddad et al., 2018; Rddad, 2021; Marcoux and Jébrak, 2021; Rddad and Mouguina, 2021).

The mineral association within the vein ore at Bou-Izourane mainly consists of galena, sphalerite, smithsonite (sphalerite oxide), cerussite (galena oxide) and calcite, with galena and smithsonite being the most abundant minerals (Fig. 7). Galena appears as centimetric crystals that are either automorphic or sub-automorphic (Fig. 7A, B). Sphalerite, which is mainly represented by small unoxidized fragments, can be observed in yellow under natural light (Fig. 7C) and in dark brown under reflected light (Fig. 7D). Calcite-filled fractures intersect both galena and sphalerite (Fig. 7A-D). Frequently, fragments of galena and sphalerite are found encased in calcite (Fig. 7G). They substitute for sulphide minerals, in particular sphalerite and galena. Smithsonite replaces almost all the sphalerite (Fig. 7E-H). It has a vuggy texture and occurs in large areas measuring from millimetres to centimetres. However, cerussite is only developed on the edges of the galena (Fig. 7A, B). The phase of calcite precipitation in fractures is intimately associated with the oxidation of galena to cerussite and sphalerite to smithsonite (Fig. 7B, E-H). The petrographic SEM/EDS analysis of the Bou-Izourane prospect ore reveals the presence of smithsonite, as a common phase of the supergene mineralization (Fig. 8A). Cerussite, less abundant, develops only on the edges of galena (Fig. 8B). Similarly, dolomite fragments from the host rock have been identified trapped in the Zn-Pb mineralization and late calcite (Fig. 9A-C). In addition, the textural and micro-petrographic relationships between minerals in the assemble are observed in different forms:

- smithsonite resulting from the oxidation of sphalerite surrounds the galena veinlets (Fig. 9C, D);
- galena is also disseminated in smithsonite (Fig. 9D, E).

Late-stage calcite seals the fractures and cements the sulphides (Figs. 7 and 9G). Smithsonite almost completely replaces sphalerite, with some relics observed in the centre of the smithsonite (Fig. 9F, G). However, the alteration of galena is less advanced, and its oxidation to cerussite is limited to its peripheries (Fig. 9H, I). The oxidation of galena to cerussite and sphalerite to smithsonite is closely related to the calcite precipitation in the fractures (Fig. 9G–I). Additionally, iron oxides are developed on dolomite fragments and late calcite (Fig. 9B).

### FLUID INCLUSION PETROGRAPHY AND MICROTHERMOMETRY

Study of fluid inclusions in the late calcite samples revealed the presence of primary inclusions in the thick sections (200 m thick slices of rock, polished on both sides and attached to a glass slide with epoxy resin, can be detached from their support with acetone as a stand-alone sample for fluid inclusion analysis). However, due to the advanced oxidation of sphalerite to smithsonite, identification of fluid inclusions and micrometric analyses proved to be very difficult for sphalerite. Classical criteria have been used to distinguish primary and secondary inclusions based on the morphology of the cavities, their position on the growth planes, and the nature of the phases trapped at room temperature (Roedder, 1979, 1984; Van den Kerkhof, 1988; Van den Kerkhof and Hein, 2001). The fluid inclusions in the calcite are aqueous two-phase (liquid + vapour) with the liquid phase dominant (liquid >50%) and sizes ranging from 5 to 30 µm (Fig. 10A, B). The summary results of the microthermometric study of the homogenization temperatures (Th) as well as the temperatures of the last melting of the ice (Tm) and the corresponding salinities, measured on primary two-phase inclu-





**A**, **B** – galena (Gn) oxidized to cerussite (Cer) intersected by calcite (Ca) veinlets in reflected light and plane-polarized light; **C**, **D** – sphalerite (Sp) oxidized to smithsonite (Sm) intersected by calcite (Ca) veinlets in reflected light and plane-polarized light; **E**, **F** – calcite (Ca) intersects sphalerite (Sp) oxidized to smithsonite (Sm) and associated galena (Gn) in reflected light and plane-polarized light; **G**, **H** – cathodoluminescence microphotography shows calcite (Ca) packing fragments of sphalerite (Sp) oxidized to smithsonite (Sm) and associated with galena (Gn)

sions trapped in the crystals of the calcite, are shown in Table 1. Salinities were calculated using the *HokieFlincs\_H2O-NaCl Microsoft Excel* spreadsheet (Steele-MacInnis et al., 2012). The homogenization temperatures of the primary calcite fluid inclusions show a unimodal distribution, with temperatures ranging from 70 to 120°C and a mean homogenization temperature value of 94  $\pm$ 8°C (n = 26) (Fig. 11). The salinities vary between 0.35 and 0.79 wt.% equiv. NaCl.



Fig. 8A – SEM images and EDS spectrum of sphalerite (Sp) and smithsonite (Sm) from sphalerite oxidation; B – SEM images and EDS spectrum of galena (Gn) and cerussite (Cer) from galena oxidation

# RARE EARTH ELEMENT GEOCHEMISTRY

The rare earths element composition can offer insights into the physical and chemical conditions that were present as the Zn-Pb mineralization form. Rare earth and yttrium (REY) analyses were carried out on galena and calcite to better understand the source of the mineralizing fluids, the geochemical conditions and the processes that led to the formation of the leadzinc mineralization at Bou-Izourane (Table 2). A comparison of the distribution of rare earths and yttrium in the Bou-Izourane mineralization with others in the central High Atlas of Morocco (e.g., Tigrinine-Taabast) has been very helpful. The calcite shows high REY concentrations with total REY varying between 37.3 and 115.2 ppm, compared to their low concentrations in galena (5.8–9.7 ppm). However, the post-fluorite calcite of meteoric hydrothermal origin [isotopic composition  $\delta^{18}$ O (-5.5 to -1.6‰ V-SMOW); Achmani et al., 2023], that precipitated in the fractures intersecting the fluorite, displays average REY concentrations of ~50 ppm.

# DISCUSSION

#### PARAGENETIC SEQUENCE

The Bou-Izourane ore district contains two types of mineralization: the first, located in the core of Jbel Bou-Izourane, is characterized by fluorite structures (Achmani, 2017; Achmani et al., 2020); the second, detected on the outskirts of Jbel Bou-Izourane, is characterized by Zn-Pb mineralization. Although both types of mineralization are located in a common area separated by 600 m, no apparent field or petrographic relationship has been demonstrated between the fluorite and the Zn-Pb mineralization up to now. The macroscopic and microscopic observations of the Zn-Pb ore have led to the identification of different mineral phases; these represent a mineralogical assemblage consisting mainly of sphalerite and galena (Figs. 7 and 9). The small sphalerite crystals are yellowish-brown in colour. Additionally, subordinate oxidized mineral assemblages consist-



Fig. 9. SEM petrographic microphotographs show the different mineralogical species of the Zn-Pb mineralization in the Bou-Izourane district

For other explanations see text



Fig. 10. Photomicrographs of isolated primary fluid inclusions hosted in the late calcite of the Zn-Pb district of Bou-Izourane

# Table 1

Mineral	Inclusion type	No.	Th [°C]	Tm <sub>ice</sub> [°C]	Salinity [wt.% equiv. NaCl]	Salinity Te .% equiv. NaCl] [°C]						
Post-Zn-Pb calcite	L+V	26	Range	Mean	Range	Mean	Range	Mean	Range			
			[70 to 119]	94	[-0.45 to -0.2]	-0.31	[0.35 to 0.8]	0.5	[-45 to -38]			





Fig. 11. Frequency histogram of homogenization temperatures for primary inclusions in post-Zn-Pb calcite of the Bou-Izourane district

ing of smithsonite and cerussite developed as a result of oxidation of the sulphide minerals. Such supergene mineral formation may be related to sulphide oxidation by meteoric waters (Sw d and Duczmal-Czernikiewicz, 2019), during the last 20 My (Choulet et al., 2014). The close association of calcite with smithsonite and cerussite at Bou-Izourane (Figs. 7B, E, H and 9G, I), suggests that this calcite precipitated during the sulphide oxidation that occurred in the last 20 My. The paragenetic sequence of the Bou-Izourane Zn-Pb ore, excluding for alteration minerals, can be summarized as follows: galena, sphalerite and late calcite. The non-sulphide mineral assemblage is mainly represented by smithsonite and cerussite, which result from the oxidation of sphalerite and galena, respectively, as well as iron oxides (Fig. 12).

# GEOCHEMICAL CONSTRAINTS

The Central High Atlas is known for its hydrothermal-magmatic activity that occurred after the Triassic-Jurassic rifting

Table 2

Mineral	Gal	ena	Post-Zn-Pb calcite								Post-fluorite calcite				
Element [ppm]	Gn-1	Gn-2	Ca-Gn-1	Ca-Gn-2	Ca-Gn-3	Ca-Gn-4	Ca-Gn-5	Ca-Gn-6	Ca-Gn-7	Ca-F-1	Ca-F-2	Ca-F-3	Ca-F-4	Ca-F-5	
La	0.7	0.5	3.53	2.27	13.66	12.66	2.62	13.66	8.32	8	3.96	5.6	6.1	3.67	
Ce	0.6	0.55	6.7	5.37	31.4	30.4	5.2	31.4	18	12.9	10	9.9	7.51	5.7	
Pr	0.3	0.4	1.08	0.73	3.7	2.7	0.75	3.7	1.23	1.79	1.23	1.13	1.99	1.14	
Nd	1.8	2.8	5.4	2.98	16.4	15.4	3.8	16.4	4.38	7.66	5.3	6.5	8	3.2	
Sm	0.5	1.5	1.37	0.85	4.12	3.11	1.3	4.12	1.23	1.76	1.1	0.98	1.94	0.88	
Eu	0.1	0.19	0.8	0.5	0.93	0.55	0.31	1.2	0.5	0.362	0.296	0.261	0.4	0.213	
Gd	0.5	1.1	2.13	1.23	4.3	3.3	2.5	4.3	2.61	2.17	1.15	1.22	2	1.16	
Tb	0.08	0.1	0.355	0.22	0.67	0.33	0.44	0.67	0.427	0.37	0.222	0.179	0.34	0.272	
Dy	0.4	0.8	2.22	1.4	4.12	3.12	1.2	4.12	3.84	2.85	1.35	1.37	2.25	1.65	
Y	0.5	1.1	22.9	20	34.6	25	36.9	30.7	68.7	32.4	14.6	11.8	18.9	21.7	
Ho	0.08	0.16	0.39	0.29	0.8	0.4	0.5	0.8	0.65	0.377	0.213	0.2	0.24	0.24	
Er	0.1	0.21	1.52	0.771	1.91	0.91	0.83	1.91	2.18	1.07	0.58	0.342	0.88	0.79	
Tm	0.02	0.04	0.145	0.1	0.262	0.2	0.12	0.262	0.261	0.17	0.091	0.069	0.131	0.066	
Yb	0.08	0.21	0.94	0.58	1.69	0.69	0.96	1.69	1.21	1.34	0.7	0.39	1	0.4	
Lu	0.03	0.04	0.125	0.06	0.229	0.256	0.151	0.229	0.167	0.188	0.106	0.089	0.177	0.055	
Pb	866000	866000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
S	134000	134000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
ΣREE	5.29	8.6	26.705	17.351	84.191	74.026	20.681	84.461	45.005	41.01	26.298	28.23	32.958	19.436	

ICP-MS concentrations of rare earths and yttrium of calcite and galena from the Bou-Izourane district.



Fig. 12. Mineral paragenetic sequence in the Bou-Izourane Zn-Pb ore district

(Laville, 1985). This resulted in an exceptionally high geothermal gradient, which reached up to 60°C/km away from the Jurassic intrusions (Zayane, 1992). The homogenization temperatures reach up to 290°C in areas of mineralization located near the Jurassic igneous intrusions in the Central High Atlas (Mouguina, 2004). The Pb-Zn ores (karst cavities and veins) in the Central High Atlas (CHA) of Morocco, are distributed in three geographic areas (Rddad and Mouguina, 2021; Fig 1):

- northern frontier zone (Aoudine, Sidi Belghite);
- central zone (Ali Ou Daoud, Tazoult, Wawrirout);
- southern/western frontier zone (Tadagaste, Bou Dahar, Tigrinine-Taabast, Imi N'Tazaght, Isk N'Ait Mraou).

The isotope geochemistry studies conducted by Rddad and Mouguina (2021) on the Pb-Zn deposits of the Moroccan Central High Atlas (CHA) showed that the sulphur is derived from Triassic-Jurassic sulphates and/or from coeval pore water sulphates. The sulphur isotopic compositions ( $\delta^{34}S = -18.6$  to 22.2‰) exhibit regional zoning, with isotopically heavy  $\delta^{34}$ S (14.3‰) in the central zone, negative  $\delta^{34}$ S values (–16.9‰) at the northern frontier and -9.1‰ at the western frontier (i.e., Tadagaste), to intermediate  $\delta^{34}$ S values (4.4‰) at the southern frontier (Fig. 1). This zonation reflects different mechanisms of sulphate reduction, including bacterial sulphate reduction (BSR) at low temperatures, which produces negative  $\delta^{34}$  S values, and thermochemical sulphate reduction (TSR) at high temperatures, which produces positive  $\delta^{34}$ S values (Rddad and Mouguina, 2021). The intermediate sulphur isotopic composition in the southern and western zone of the CHA reflects the mixing of the sulphur derived from TSR and bacteriogenic sulphur (BSR). The Pb isotopic compositions are fairly homogeneous among the CHA deposits (<sup>206</sup>Pb/<sup>204</sup>Pb = 18.151 to 18.709, <sup>207</sup>Pb/<sup>204</sup>Pb = 15.631 to 15.668, <sup>208</sup>Pb/<sup>204</sup>Pb = 38.433 to 38.808), and suggest that Paleozoic rocks are the primary source of lead and other metals (Rddad and Mouguina, 2021). The Bou-Izourane district (Jbel Bou-Izourane), located 35 km south of Midelt city, can be added to the deposits located in the northern part (northern frontier zone) of the Moroccan Central High Atlas (Fig. 1).

In addition to its geographic location in the northern frontier zone (near the Aoudine and Sidi Belghite deposits, in particular; Fig. 1), the REY patterns of Bou-Izourane galena, normalized to chondrite (Sun and McDonough, 1989), show an almost parallel distribution to those of the Tigrinine-Taabast sulphides (Rddad, 2021; Fig. 13). The distribution of REY in the sulphides of the Bou-Izourane and Tigrinine-Taabast districts is characterized by significant negative Y and Ce anomalies. Therefore, the low REE values and negative Ce anomalies are considered typical of a deposit strongly related to hydrothermal fluids (Jach and Dudek, 2005; Josso et al., 2017; Ehya and Marbouti, 2021), and the presence of sulphates increases the solubility of Y (Guan et al., 2022).

Based on many similarities between the Zn-Pb ores of Bou-Izourane and others in the Moroccan Central High Atlas (e.g., Tigrinine-Taabast), we can suggest the possibility of a common source of lead and sulphur. These similarities include their occurrence in the same geological and chronological context within the Liassic strata of the Moroccan Central High Atlas, as well as their petrographic characteristics and REY patterns. Therefore, the main source of lead (Pb) and other metals for the Bou-Izourane Zn-Pb ore would be related to Paleozoic basement rocks, as is the case for all deposits in the Central High Atlas metallogenic province (i.e. Tigrinine-Taabast, Aoudine, Sidi Belghite, Ali Ou Daoud, Tazoult, Wawrirout, Tadagaste, Bou Dahar, Imi N'Tazaght, Isk N'Ait Mraou; Rddad and Mouguina, 2021). However, the source of sulphur will be related to Triassic-Jurassic sulphates and/or coeval pore water sulphates reduced by bacteriogenic activity (BSR), as is the case for the northern frontier zone (i.e., Aoudine, Sidi Belghite; Rddad and Mouguina, 2021). Therefore, the formation of the Zn-Pb ore in the Bou-Izourane prospect can be attributed to the same process that produced all the Mississippi Valley type Pb-Zn deposits in the Central High Atlas. These are thought to be related to the mixing of a metalliferous fluid from Paleozoic rocks and a colder, sulphur-rich fluid from Triassic-Jurassic sulphates and/or coeval pore water sulphates (Rddad and Mouguina, 2021). Furthermore, the slight enrichment in rare earths and yttrium in the Bou-Izourane galena is typical of sulphides found in magmatic deposits (Ohmoto and Goldhaber, 1997). Several studies (e.g., Agard, 1960; Salvi et al., 2000; Marks et al., 2008), have reported the presence of sulphide minerals (sphalerite, galena pyrite and chalcopyrite) in pegmatites and nepheline syenites of the Tamazeght magmatic complex. The presence of sulphide mineral traces within the Tamazeght rocks, in the same geographical area of the Bou-Izourane Zn-Pb mineralization (Fig. 4), suggests that similar hydrothermal-magmatic fluids played a role in the REY enrichment of the Bou-Izourane galena. The origin of some fluorites from the Tamazeght complex and the Bou-Izourane region has been linked to the contribution of fluids from the magmatic hydrothermal activity of Tamazeght. Furthermore, the post-mineralization calcite from Bou-Izourane is characterized by low-salinity fluid inclusions (0.5 wt.% equiv. NaCl) and homogenization temperatures ~94°C. These values are closely comparable to those of the post-mineralization calcite from the Tigrinine-Taabast district (Th ~96°C, salinity ~0.3 wt.% equiv. NaCl.) (Rddad, 2021; Fig. 14). There is a perfect fit between the REY patterns with positive Y anomalies of fluorite and post-fluorite calcite, and post-Zn-Pb calcite (Fig. 13). Based on data published previously (Achmani et al., 2020, 2023), the post-Zn-Pb calcite may be related to the same genesis process as the fluorite and post-fluorite calcite in the Bou-Izourane district.

# GENESIS OF THE Zn-Pb ORE MINERALIZATION

The Pb-Zn deposits in the Moroccan High Atlas are located near Jurassic igneous intrusions (e.g., Tirrhist, Tigrinine-Taabast, Ali Ou Daoud). The Bou-Izourane Zn-Pb mineraliza-





Bou-Izourane fluorite is from Achmani et al. (2020); galena and sphalerite of Tigrinine-Taabast is from Rddad (2021)



### Fig. 14. Homogenization temperature (Th) versus salinity diagram of primary fluid inclusions of post-ore calcite crystals from the Bou-Izourane district

Post-ore calcite of Tigrinine-Taabast is from Rddad (2021)

tion is developed in a N–S to NNW–SSE-trending subvertical fault in the Liassic carbonate marls, the same fault direction as hostingthe fluorite mineralization in the area (Achmani, 2017; Achmani et al., 2023). This direction is almost parallel to the direction of the regional faults inherited from the Triassic-Jurassic rifting phase. Furthermore, the ore formed after the Jurassic rifting, during which significant hydrothermal-magmatic activity occurred in the Central High Atas (Laville, 1985). In addition, NE–SW and NNW–SSE trending faults filled with similar mineral assemblages (e.g., Tigrinine-Taabast) were reactivated and formed in response to the Eocene-Miocene Alpine orogeny. In general, the role played by orogeny in large-scale fluid movement is widely recognized (Bradley and Leach, 2003; Leach et al., 2010; El Basbas et al., 2020). In particular, the Alpine orogeny produced two important mechanisms of fluid flow:

compressional forces (tectonic "compression" model) and topographic gradient, both of which have been proposed as major causes in various regions of MVT deposits (Garven and Freeze, 1984; Garven, 1985; Oliver, 1986). These activities resulted in the remobilization and circulation of large volumes of fluids from the high pressure zones to the basin boundaries. Fluid inclusions in the nepheline of the Tamazeght syenites contain galena and sphalerite daughter minerals (Salvi et al., 2000), and disseminated traces of these minerals in syenitic rocks suggest the presence of mineralizing fluids associated with hydrothermal-magmatic activity at Tamazeght. These fluids probably contributed to the formation of galena and sphalerite. Similarly, in the Central High Atlas, Mouquina (2004) demonstrated that Pb-Zn deposits in the Tirrhist and Tazoult districts (SE-NW oriented veins) near the Jurassic igneous intrusions (Fig. 1) show a significant abundance of rare earth elements. The mineralization have been interpreted as being of magmatic origin, where the magma served a dual role as a source of metals and heat (Mouguina, 2004). Elsewhere, in China for example, the Chuduogu deposit (Pb-Zn-Cu) has been related to regional magmatic hydrothermal fluids linked to the magmatic activity of a syenite porphyry. According to Sun et al. (2019), this magmatic activity served as both a heat source and the primary supplier of metallogenic material (Pb-Zn-Cu) for the Chuduoqu deposit.

The Bou-Izourane ore intersects Liassic carbonate marls (Pliensbachian, Toarcian), indicating that the ore must have formed after the Toarcian. The presence of oxidized sphalerite (smithsonite) at Bou-Izourane is related to the infiltration of meteoric waters and the subsequent oxidation of sulpphides during the last 20 My (Choulet et al., 2014). The last hydrothermal event is recorded in calcite-bearing fluid inclusions. Calcite precipitated from heated meteoric water (Th ~94°C, salinity ~0.5 wt.% equiv. NaCl). The tight association of this calcite with smithsonite and cerussite suggests that this calcite precipitated during the oxidation of sulphides that occurred during the last 20 My.

The synthesis of all the field data and petrographic analysis results shows that the Bou-Izourane mining district appeared in the Toarcian–Early Miocene, before the late oxidation of sulphides that occurred ~20 Ma. However, if we consider the intervention of mineralizing fluids related to the hydrothermal magmatic activity of Tamazeght during the

Eocene in the formation of the rare earth enriched Zn-Pb mineralization of Bou-Izourane, the timing of the genesis of this mineralization can be restricted to the Middle Eocene to Early Miocene interval. The similarity of geological features (i.e., occurrence in the same geological and chronological context in the Liassic succession of the Central High Atlas of Morocco, paragenetic sequence and REY patterns) between the Zn-Pb mineralization in the Bou-Izourane district and those of Central High Atlas (e.g., Tigrinine-Taabast, Sidi Belghite), suggest that the genesis of the Bou-Izourane Zn-Pb mineralization is largely related to the same process of circulation and migration of deep-seated fluids originating from the Paleozoic basement. They would have leached metals and evolved into Zn-Pb rich fluids. The mixing of these fluids with sulphur-rich fluids at shallow levels would have caused the precipitation of sulphidebearing ores (such as sphalerite and galena), similar to what occurred in the Tigrinine-Taabast and Sidi Belghite districts. In particular, the contribution of fluids related to the hydrothermal-magmatic activity of Tamazeght in the Bou-Izourane area, although in small quantities, is a particularity of our study area. Thus, the hydrothermal-magmatic activity of Tamazeght may have involved magmatic fluids that may have played a role in the genesis of lead-zinc mineralization at Bou-Izourane, and/or provided a heat source and driving factor for the percolation of fluids through the rocks and deposition of sulphide-bearing ores.

# CONCLUSIONS

Several important conclusions can be drawn from the geological, mineralogical and geochemical data provided in this study. In addition to the fluorite deposits, the Bou-Izourane district is characterized by Zn-Pb concentrations. These are structurally controlled by N–S to NNW–SSE-trending faults, the mineralization, in the form of veins, cuts through Liassic sedimentary rocks (limestones and marls). Brittle tectonics played an important role in the development of these metalliferous concentrations by creating pathways for mineralizing fluids and trapping them in mechanical discontinuities within the calcareous marly host rock. The paragenetic sequence of minerals at Bou-Izourane consists of galena, sphalerite and late calcite. The locally exploitable Zn-Pb mineralization could have regional economic importance, since the N–S to NNW–SSE fractures affect the entire sedimentary succession of the Bou-Izourane district. The presence of dolomite fragments in the Zn-Pb and calcite mineralization suggests a previous dolomitization phase. This dolomitization, associated with local fractures and faults, may have increased the permeability of the carbonate rocks and, consequently, enhanced the local flow of fluids. The oxidation phases of galena into cerussite and sphalerite into smithsonite are related to the late infiltration of meteoric waters and the oxidation of these sulphides. The similar geological characteristics of the Zn-Pb mineralization in the Bou-Izourane district to those of the Central High Atlas (e.g., Tigrinine-Taabast, Sidi Belghite) suggest that the regional precipitation of such mineralization may be related to a mixture of metalliferous fluids from Paleozoic rocks and shallow sulphur--rich fluids of dissolved sulphates from the Triassic-Jurassic and/or sulphates from coeval sea water pore fluids. However, we note that the galena is slightly enriched in REY compared to most of the other deposits of the Central High Atlas, with an expression of mineralization F-Zn-Pb concentrations that occurred during a limited interval in time and space in the Bou--Izourane district. This raises the possibility of the intervention of fluids, related to the hydrothermo-magmatic activity of Tamazeght, as a probable heat source and also as a "probable" supplier of metallogenic material such as Zn-Pb. Therefore, this study will have particular relevance to other exploration work that is underway in Bou-Izourane. However, future research should be conducted on S and Pb isotopic analyses in sulphides to test the extent of hydrothermal-magmatic fluid involvement in Tamazeght, as well as to constrain the probable sources of lead and zinc in the Bou-Izourane district.

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