Non-sulfide Zn deposits in the Moroccan High Atlas

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Abstract. We have investigated six Zn non-sulfide ore deposits (also called "calamines") from the Moroccan High Atlas, in order to understand processes and timing of their formation. Structural field observations have revealed a genetic link between regional faulting and cavities filled by ores. Based on our mineralogical investigation, we propose the following stages: 1) formation of the protore sulfides, 2) early supergene weathering with formation of Zn-Pb-bearing carbonates and iron oxi-hydroxides and 3) late supergene weathering with deposition of Zn-carbonates and silicates. Direct replacement of primary sulfides is the dominant process. A complementary rock magnetism study shows similar horizontal magnetic fabrics for calamines and internal sediments. Isolated high temperature components are of primary origin and the paleomagnetic directions of calamines and internal sediments are compatible. The calculated poles are consistent with the last 30 Ma of the Apparent Polar Wander Path (APWP) of Africa. These promising results pave the way for an efficient method to constrain the age of Zn supergene deposits.

Keywords. Supergene deposits, Calamines, Moroccan High Atlas, Rock magnetism.

1 Introduction

Non-sulfide zinc ore deposits, also called "calamines" have been reconsidered, as metallurgical techniques have improved. Typical examples are found in Sardinia, in Belgium and in Iran (Hitzman et al. 2003). Hypogene and supergene deposits are distinguished and supergene deposits may be divided into three subtypes: 1) direct-replacement deposits, 2) wall-rock replacement deposits and 3) karst-fill deposits.

Reichert and Borg (2008) have pointed out the features that control the formation of such deposits. These include: 1) the morphology of the protore sulfide body, the structure of the host rocks and the pre-existing faults, 2) the nature of the host rock and its ability to interact with Zn-rich solutions, 3) the open or closed conditions of the karst, 4) the climatic factors and 5) the competition between regional uplift and erosion.

In Morocco, the High Atlas Mountains expose a great number of non-sulfide Zn ore deposits, whose origin is not well constrained by traditional models. This Tertiary intra-continental belt has recorded represents a natural laboratory to understand the link between tectonic, climatic and weathering processes.

This work presents new field and mineralogical observations from six ore deposits, and we propose a scenario for calamines formation. In parallel, rock magnetism studies revealed the rock fabric and allow us to timely constrain ore deposition.

2 Geological setting

2.1 The Moroccan High Atlas

The Moroccan High Atlas is composed of Mesozoic to Cenozoic sedimentary rocks (mainly carbonates) covering a Variscan basement (Fig. 1). A complex evolution with successive episodes of uplift related to intra-plate tectonics has been recorded (Frizon de Lamotte et al., 2000). This ENE-WSW trending fold belt displays narrow faulted anticlines and large synclines.

Mechanisms for belt formation are still debated. Thin-skinned tectonics, with a décollement zone located in the soft Triassic layers is generally opposed to thick-skinned tectonics, which emphasizes the role of Variscan structures and suggests deformation of the crust in depth.

2.2 Zn-Pb ore deposits

Zn-Pb ore deposits are numerous in northern Africa; they often represent stratabound lenses in the Jurassic carbonate series. In Morocco, two metallogenic periods can be distinguished. Lower Jurassic deposits are related to normal faulting associated with the opening of Tethys and Atlantic oceans. Middle Jurassic deposits may be of magmatic and hydrothermal origin, but several deposits seem to present similarities with MVT ore deposits.

3 Sampling and methodology

In this study, we have selected six ore deposits or prospects from the Moroccan High Atlas (Fig. 1): Aït Labbès, Beni Tajite, Bou Arhous, Tadaghast, Tizi n'Firest and Toulal. Samples have been collected from galleries or dumps. At Aït Labbès, Beni Tajite, Tadaghast and Toulal, we have collected 165 cores of limestone, flat lying internal sediments and calamines from 10 sites to perform rock magnetism studies.

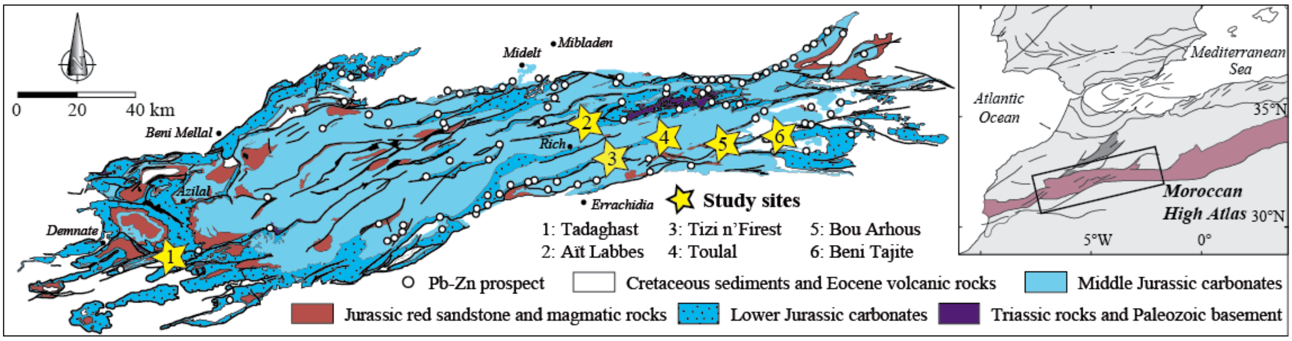

Figure 1. Map of the Moroccan High Atlas and location of the six studied ore deposits.

Mineralogy was investigated by using petrographic microscopy, secondary electron microscopy, Raman spectroscopy and X-ray diffraction at ISTO and CBM, Orléans. To get quantitative compositions, we have used the Cameca SX50 electron microprobe at BRGM.

Thermomagnetic measurements for determining the Curie points and isothermal remanent magnetization (IRM) acquisition have provided constraints for the magnetic mineralogy. The anisotropy of the magnetic susceptibility (AMS) was measured by using an AGICO KLY3S kappabridge susceptometer. Stepwise thermal demagnetizations were performed with a laboratory-built furnace and magnetic remanence was measured with an AGICO JR-5A automatic spinner magnetometer.

4 Results

4.1 Macroscopic observations

The Toulal prospect is located in the periclinal termination of an ENE-WSW trending narrow anticline. The northern and southern limbs display Pliensbachian thin-bedded limestone, while the Upper Sinemurian para-reef massive black limestone forms the fold hinge. White massive calcite (early calcite) occurs in the extrados fractures of the fold. Syn-compressive faults are documented by cataclasite and breccia. Calamine veins are mainly located in the cataclastic zone that cuts the Upper Sinemurian black limestone. Red and grey calamines occur within veins that form N70°E striking steeply dipping boudins and crosscut the extrados fractures. Preserved sulfides (galena and sphalerite) are enclosed in the red calamine. Internal sediments such as marl or calcareous shale are with horizontal bedding.

The Bou Arhous Ore Deposit is a part of an ENE-WSW trending anticline. Folding is associated with faulting along a major top-to-the-south thrust, which exposes crushed Triassic clayey material. The entire mineralization is located in the footwall of this fault and ore, hosted in Sinemurian black limestone, is distributed in E-W trending veins that parallel the anticline axis. The veins form a complex karst network, but often display a vertical zonation related to the oxidation process, with sulfide preserved in the deeper levels. Calamine is red or white (black in case of willemite). Internal sediments with horizontal bedding fill the karstic cavities. These sediments are generally barren but may sometimes have high Zn content and contain fragments of calamine.

The Tadaghast Ore Deposit is situated in the southern shallow-dipping limb of an open anticline. Liassic formations include Pliensbachian beige marl and limestone, and Sinemurian black para-reef limestone with intra-formational breccia and evidence of intense karstification. Internal sediments, with horizontal bedding, fill the grikes. N-S trending fractures are filled by massive white calcite, and these fractures may be reactivated to form a breccia containing fragments of the black limestone cemented by drusy or collomorphic calcite. This calcite is observed in the subsidiary E-W trending fractures. In depth, mineralization seems to be distributed according to three structural directions. N-S trending fractures are filled by calamine but also present breccia and white massive calcite. E-W trending fractures include banded and/or vacuolar red calamine. The horizons are concordant to the bedding of Sinemurian black limestone and display sulfide lenses partly replaced by red and white calamine.

The Beni Tajite Ore Deposit is a part of a WSW-ENE range including preserved Pliensbachian coral reef. The ore body mainly occurs within E-W trending veins or NW-SE trending fractures. Sulfides are frequent at depth, as disseminations within limestone, or in association with rhombohedral white calcite. The latter may represent the original karst hosting the sulfides prior to weathering. In the shallow levels, the banded red calamine is distributed according to a complex vein network, whereas the white calamine includes botryoidal masses of hemimorphite or bands of white hydrozincite, which impregnates the wall of the veins.

The Aït Labbès Ore Deposit is located in a narrow anticline cut by an ENE-WSW trending fault. The bedding of the limestone is steep and the fold hinge has been eroded. The ore body occurs within ENE-WSW vertical veins that parallel the bedding of the Sinemurian black para-reef limestone. The calamine veins show a boudin-like distribution along this fault. Isolated masses of sulfides are preserved within the red calamine composed of smithsonite and clays. Large euhedral crystals of beige calcite, predating the calamine lodes, fill fractures in the host limestone. Conversely, white or translucent banded calcite postdates the Zn-rich veins. Internal sediments with horizontal bedding are barren.

The Tizi n'Firest Ore Deposit is part of an anticlinal ridge, whose axis parallels an E-W trending thrust. Folding has exhumed Triassic marl and basalt, as well as Sinemurian massive limestone hosting the ore. The ore body represents a vast cavity that dips to the north at 70°.

Calamine veins striking parallel to the E-W major thrust form numerous digitations, which are partly filled by clays with horizontal stratification. Clays may contain residual galena associated with euhedral crystals of white calcite and concretions of banded smithsonite.

4.2 Microscopic observations

Based on previous investigation in the six studied ore deposits, we have established the following paragenetic successions: 1) limestone, 2) protore sulfides, 3) red or black calamine and 4) grey or white calamine.

The host rocks always correspond to massive limestone with coral fossils. Dolomite was only identified in Toulal within fractures. Quartz needles often occurred and are preserved during weathering.

A protore composed of primary sulfides and massive white calcite is common to the six deposits. Protore sulfides are galena, sphalerite and pyrite, with relative proportions. Sphalerite shows correlated variations in Cd and Fe content, while the Bi content of galena may reach 7600 ppm. The initial amount of sulfides can be different between ore deposits and relative proportions may vary with supergene oxidation. Massive white calcite cleaving into rhombs is often deformed, identically to galena.

For each ore deposit, pyrite has been pseudomorphed by iron oxi-hydroxides, with hematite surrounded by goethite. Such replacement textures are typical of supergene oxidation in neutralizing carbonates. At Toulal, lepidocrocite was identified (Fig. 2) and may have been formed after maturing of a ferric gel (Kosakevitch, 1983), frequently observed in the pseudomorphs. Galena is frequently replaced by botryoidal cerussite, and anglesite has only been observed close to dissolved pyrite (Fig. 2). Direct replacement of sphalerite by smithsonite is rarely observed. Smithsonite and cerussite are associated with secondary sulfides (covellite, galena and greenockite).

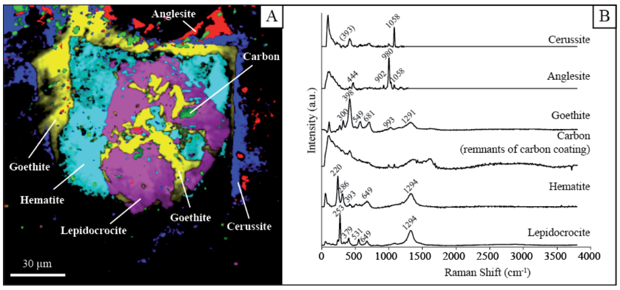

Figure 2. Raman composition map (A) and associated Raman spectra (B) of the iron oxi-hydroxides pseudomorph after pyrite (Toulal ore deposit).

Red calamine often shows high Fe content and is composed of iron oxi-hydroxides and smithsonite concretions therefore. Atypically, black calamine including willemite occurs at Bou Arhous, but never coexists with the red calamine. Several infrequent minerals, such as decloizite or psilomelane form thin encrustations closely associated with iron oxides.

Grey or white calamine develops after the red type, or is precipitated in karst cavities. It is characterized by the absence of iron oxi-hydroxides and includes hemimorphite and translucent smithsonite. The association of hydrozincite with red or grey calamine is not obvious. At Toulal or Bou Arhous, hydrozincite is contemporaneous to the formation of iron oxi-hydroxides, which impregnate the white patches of hydrozincite. Conversely, hydrozincite clearly postdates the red calamine of Beni Tajite ore deposit. However, the simplistic succession smithsonite I-hydrozincite-hemimorphite±smithsonite II remains a constant for each ore deposit. A late generation of drusy translucent calcite cements the calamine breccia or fills the karst cavities.

Internal sedimentation and recycling of calamine is a continuous process during the development of the karst. At Tadaghast, sedimentary reworking of quartz needles in the fractures of the sphalerite lodes predates the concretions of smithsonite. Conversely, in other deposits, internal sediments often fill post-red calamine cavities. The occurrence of clayey materials like sauconite, however, remains a constant.

4.3 Rock magnetism

IRM and X-ray diffraction analyses have revealed magnetite as the main magnetic carrier, and subsidiary high coercive minerals like goethite and hematite. Host limestone, calamines and internal sediments with horizontal bedding present similar mineralogical assemblage, and only the relative proportions may vary.

AMS directions of calamines and internal sediments are often consistent, while AMS data from limestone are too weak to be used. The magnetic foliation is horizontal, even if sedimentary reworking or differences in the supergene evolution may have disturbed the AMS signal (e.g. at Aït Labbès and at Tadaghast). The magnetic lineation is usually horizontal and parallel to the direction of the calamine veins. The attitude of the AMS parameters (P_J and T) suggests that deformation is lacking and supports the formation of magnetic fabric from sedimentary dynamics within the veins.

Directions of the high temperature component (HTC) were isolated for samples collected at Toulal, Aït Labbès and Tadaghast. For the two first localities, the reverse and normal directions of this HTC of both calamines and internal sediments are antipodal and similar within error. We therefore calculated an average paleomagnetic direction for each locality. HTC directions of calamines from Tadaghast are scattered, while the average HTC direction of internal sediments is isolated from others.

5 Formation of non-sulfide ore deposits

We have distinguished three types of ores (protore, red-black calamine, grey-white calamine), corresponding to the successive stages of ore deposition: 1) pre-oxidation stage, 2) supergene stage I and 3) supergene stage II.

5.1 Pre-oxidation stage

For each ore deposit, there is a strong lithological control of the protore deposition, which only occurs within Upper Sinemurian and Pliensbachian limestone formed in a reef environment. Deposition of primary sulfides closely follows the limestone sedimentation. The concordant sulfides lenses are closely associated with white massive calcite; both experienced post-deposition deformation. Silicification revealed by quartz needles and limited dolomitisation occurred before weathering.

5.2 Supergene stage I

Compression related to the Atlasic events contributes to tilting of the strata. This has facilitated the percolation of mildly acid meteoric water and dissolution of the host limestone giving rise to the karst. O_2 also reacts with pyrite to form iron oxi-hydroxide. In consequence, the pH decreases, although acidity is buffered by the dissolution of the host limestone. Oxidation also affects the other sulfides. Lead and zinc ions are released in the solution and may form smithsonite, cerussite and anglesite of the red calamine. Supergene secondary sulfides are frequent and their precipitation may be explained by short intervals of reducing conditions caused by local variations of the level of the water table due to seasonal or tectonic effects. Willemite occurring at Bou Arhous is traditionally interpreted as being of hydrothermal origin, but may be formed under low water activities, alkaline pH, oxidizing conditions, high silica activities and low P_{CO2} conditions.

5.2 Supergene stage II

This stage is dominated by "grey to white calamine" and occurs after the partial to total consumption of pyrite due to oxidation. Consequently, the pH conditions become neutral to slightly alkaline. Smithsonite continues to precipitate causing a drop of P_{CO2}, which facilitates replacement of smithsonite by hydrozincite. In the case of solutions saturated with silica, hemimorphite is stable under pH below 7-8, but small variations of P_{CO2}, pH or [Zn] may rapidly change the equilibrium of the system, resulting in hemimorphite-hydrozincite assemblages. Much of the internal sediments were deposited lately in cavities of the gangue and of the calamine as well. Sauconite mainly composes the infilling material, although its origin is still unclear. It may be formed by interaction of Zn-rich solutions with barren clays observed in limestone interlayers.

6 Timing of calamines formation

Since paleomagnetic directions of internal sediments and calamines are consistent, an average direction has been calculated for Toulal and Aït Labbès ore deposits. Based on the AMS horizontal fabrics and the occurrence of antipodal polarities, we conclude that magnetization is primary and its acquisition is coeval with ore and sediment deposition. Therefore, the age of calamines may be estimated by comparing the paleopoles from Toulal and Aït Labbès to the apparent pole wander path of Africa (APWP; Besse and Courtillot, 2002; Fig. 3).

For Toulal, the age is statistically bracketed between 30 and 10 Ma. For Aït Labbès, the range of 60-10 Ma may be reduced to 40-10 Ma, since field observations have shown that ore deposits postdate the major tectonic event related to the Atlasic compression. It is worth noting that no orogenic rotation has been recorded by the samples. Statistical constraints could be improved after increasing the number of sample, but the limited absolute motion of Africa during the last 40 m.y. hinder better resolution for characterizing age deposition.

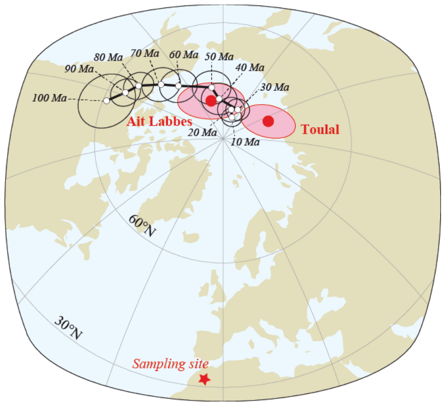

Figure 3. Equal-area projection of Toulal and Aït Labbès paleopoles and of the last 100 m.y. of Africa APWP.

6 Conclusion

Field observation and mineralogical investigation have revealed a two-stage supergene evolution controlled by both climate and tectonics. Calamines have mainly been formed by replacement of sulfide lenses or by minor precipitation and internal sedimentation in karst cavities. The AMS study brings crucial information on the structure of calamines and of the internal sediments, and thus reveals the dynamics within the karst. Age deduced from paleomagnetism is consistent with field interpretation. Dating ore deposition is therefore possible and could be cautiously applied to other targets where no field constraints are available.

Acknowledgements

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References

Besse J, Courtillot V (2002) Apparent and true polar wander and the geometry of the geomagnetic field over the last 200 Myr. J Geophys Res. doi:10.1029/2000JB000050.

Frizon de Lamotte D, Saint Bezar B, Bracene E et al. (2000) The two main steps of the Atlas building and geodynamics of the western Mediterranean. Tectonics 19:740-61

Hitzman MW, Reynolds NA, Sangster DF, et al (2003) Classification, Genesis, and Exploration Guides for Nonsulfide Zinc Deposits. Econ Geol 98:685-714

Kosakevitch A (1983) Etude morphogénétique des textures de remplacement et de remplissage dans les chapeaux de fer. BRGM Report No.: 83SGN936MGA.

Reichert J, Borg G (2008) Numerical simulation and a geochemical model of supergene carbonate-hosted non-sulphide zinc deposits. Ore Geol Rev 33:134-51