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Abstract

The Bou Dahar Pb–Zn–Ba (± Sr) is hosted in the Lower and Middle Liassic carbonate platform in the oriental High Atlas of Morocco. The paragenetic sequence includes quartz–pyrite–melilite–sphalerite–galena–calcite–barite ± fluorite ± celestite. Fluid-inclusion studies were conducted on sphalerite (early mineralizing stage) and barite, and celestite (latter mineralizing stage). These studies reveal two end-member fluids, a hot (-143 °C) and saline fluid (-23 wt.% NaCl eq.) and a cooler (<50 °C) and diluted fluid (-5 wt.% NaCl eq.). Based on fluid-inclusion and C–O–S–Pb isotope studies, a conclusion is reached that the Bou Dahar ore deposits were formed by the mixing of two fluids—a diluted, SO4 4-rich fluid, and an δ18O-enriched basinal brine that carried Pb, Zn, and Ba. The sulfur required for the precipitation of sulfides was generated by the thermochemical sulfate reduction of dissolved sulfate (SO4 2-) of the Mesozoic seawater, and delivered to the site of ore deposition. The sulfur of sulfate minerals was derived directly from these dissolved SO4 2-. The Pb isotope compositions are homogenous with 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb ratios ranging from 18.124 to 18.183, 15.630 to 15.634, and 38.325 to 38.440 respectively. This Pb isotope composition is indicative of an upper crust and orogene reservoirs as the source of lead and other metals. The emplacement of mineralization occurred during the Eocene–Miocene Alpine orogeny, and tectonic burial and compression were the driving forces behind the circulation of the orogenic brines. These ore-forming fluids migrated, along thrusting regional E–W and NE–SW deep-seated faults, to the confined carbonate-Liassic reservoir.

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1. Introduction

The Bou Dahar Pb–Zn–Ba district, an ENE–WSW-trending plateau extending over about 40 km, is located in the oriental High Atlas Mountains of Morocco 150 km west from the city of Rich (Fig. 1). It is one of the most important districts in the oriental High Atlas, and is similar in economic value to the Touissit–Bou Beker district, located in the “la Chaîne-des-Horsts” Atlas belt in northeastern Morocco. The Bou Dahar ore deposits, with sulfide and non-sulfide ores, were discovered in 1911 and were exploited by the mining company of Guir (la Société Minière du Haut Guir) from 1924 to 1955. In 1955, the Mining and Metallurgical Company (Société Minière et métallurgique) of Pêharroya took over the exploitation of the district until 1958. Afterward, local artisanal miners have been permitted to exploit these mines with the assistance of The Central for Purchasing and Development of the Mining Region of Tafilalet and Figuig (la Centrale d’Achat et de Développement de la région minière de Tafilalet et de Figuig (CADETAF)). The total production is estimated at 400,000 tonnes of ore grading from 17% to 47% Zn and 40% to 70% Pb. The Zn is mainly extracted from the zinc oxides (calamine). The production of barite, mined mainly from Taboudaharte deposit, is estimated at 220,000 tonnes.

Based on mapping and broad mineralogical descriptions, some researchers proposed that the genesis of the Bou Dahar ore deposits was related to the mobilization of deep fluids of magmatic or brine during the post-Cretaceous tectonic phase that formed the Atlas mountains (Agard and Du Dresnay, 1965; Le Blanc, 1968; Bazin, 1968; Rddad et al., 1995). Bazin (1968) investigated the Tizi-n-Ferrest ore deposits, in particular the Karstic ore deposits hosted in Lower reef limestone, and proposed an epigenetic origin for some ores and syngenetic for others. Le Blanc (1968) proposed an epigenetic origin for the Bou Arhous Pb–Zn ores which are hosted in Lower and Middle Liassic limestone. Çaia (1968) investigated the Tirrhist Pb–Zn ore deposit, and proposed that the genesis of the mineralization was related to the post-Jurassic tectonic movement.

Later on, microthermometric data were obtained from sphalerite of Toutia, Conre Wast, Chitane, and Yacoub; barite of Taboudaharte; and from celestite of Rich-Khole (Rddad and Bouhlel, 1997; Rddad, 1998), and later from sphalerite and calcite (Adil et al., 2004). The microthermometric results revealed that the mixing of two different fluids was responsible for the mineralization (Rddad and Bouhlel, 1997; Rddad, 1998; Adil et al., 2004). Using Cl/Br halogen, Adil et al.
(2004) concluded that the mineralizing fluid acquired its high salinity mainly from evaporated seawater.

The sources and interrelationships of the ore-forming fluids, the sources and mode of migration of metals and sulfur, as well as the timing of ore deposition remain poorly constrained. The present paper aims at reaching a more comprehensive understanding of the physico-chemical nature and sources of the fluids involved in the genesis of the Bou Dahar Pb–Zn–Ba (±Sr) ore district. To that end, this work combines ore petrography, mineralogy, stable (S, C, O) and radiogenic (Pb) isotope studies, microthermometry of fluid inclusions data.

2. Regional geologic setting and Zn–Pb ore deposits distribution

The Atlas Mountains extend from Morocco to Tunisia with significant lateral variations of altitudes. The Moroccan segment of the Atlas includes the Middle Atlas to the north and the High Atlas in central...
Morocco. The High Atlas is bounded by the Variscan Meseta and the High Plateau to the north, and the Precambrian Anti-Atlas massif with its Paleozoic cover to the south (Fig. 1). It consists of Mesozoic to Cenozoic sedimentary rocks covering a Precambrian to Paleozoic basement which was deformed by the Hercynian orogeny (Piqué and Michard, 1989). The Paleozoic succession, composed mainly of siliciclastic rocks, outcrops in Mouguer and Tamlet inliers. The regional Paleozoic section of the High Atlas consists of Cambro-Ordovician facies (schist and quartzite), and the Silurian facies (phhtanites, schist, and graptolites) (Du Dresnay, 1975).

The High Atlas region underwent the Triassic rifting which was related to the opening of the central Atlantic Ocean and the formation of the Tethys Ocean (Laville, 1988; Giese and Jacobsen, 1992). The Hercynian NE–SW-trending faults, entrenched in the Paleozoic basement, were reactivated (Laville, 1985) and led to the formation of the Triassic rift basins. These basins received detrital clastic rocks and evaporates interbedded with tholeiitic and doleritic flows (Du Dresnay, 1987; Thane et al., 1983). The Lower Liassic carbonate platform, overlapping the Triassic series, was developed and upgraded into marls alternating with turbiditic limestone (Du Dresnay, 1979). This change in sedimentation was related to the Middle Liassic–Middle Jurassic rifting (Warne, 1988). At the end of the Middle Jurassic, a regional uplift occurred (Saddiqi et al., 2009) and a marine regression led to the deposition of continental red beds (Jenny et al., 1981; Charrière et al., 2005).

Tectonic inversion due to the convergence between the African and European plates started toward the end of the Cretaceous period (Tapponier, 1977; Olivet, 1978). Successive compression events occurred during the Cenozoic and Quaternary (Laville et al., 1977; Laville, 1985). The first tectonic Atlantic event occurred during the Middle–Late Eocene, followed by a quiescent period during the Oligo–Miocene (Frizon de Lamotte et al., 2009). The second shortening Atlantic event, responsible for the uplift and the formation of the High Atlas, took place during the Late Miocene–Pliocene (Frizon de Lamotte et al., 2009). The tectonic model responsible for the formation of the Moroccan High Atlas is predominantly a thick-skinned model which involved the Hercynian faults, the Paleozoic basement structures, and the Mesozoic–Cretaceous cover (Teixell et al., 2003).

The Moroccan High Atlas Zn–Pb ore deposits constitute an important metallogenic province with several prospects and ore districts (Ovtracht, 1978). It is part of the Zn–Pb province of the circum-Mediterranean Sea and the Alpine Europe (e.g. Rouvier et al., 1985; Bouhlet, 2005). The ore deposits are located in the borders of the High Atlas and near the paleohighs (e.g., Mougueur, Bou Dahar). According to Mouguina (2004), the High Atlas ore deposits are distributed in two main stratigraphic levels as follows:

• The Lower Jurassic (Lias) — The ore deposits, hosted in the Lower Jurassic, are strata-bound. They consist of numerous lens-shaped Zn–Pb–Fe sulfide orebodies, and are considered to be syngenetetic origin (Agard and Du Dresnay, 1965; Emberger, 1965; Bazin, 1968; Aujaraj and Boulégue, 1999).

• The Middle Jurassic (Dogger) — The ore deposits, hosted in the Middle Jurassic, are carbonate-hosted Pb–Zn deposits related to the emplacement of magmas. The Pb–Zn ore is mainly disseminated in gabbro, with an early Cu–Ni mineralization (Chévermont, 1975) and a later Zn–Pb hydrothermal episode (Caia, 1968). On the basis of structural and mineralogical studies, Mouguina and Daoudi (2008) have proposed, however, that some of the Middle Jurassic Zn–Pb ore deposits of the High Atlas are similar to the ones described in the High plateau zone (e.g., Touissit and Mibladen) (Dagallier, 1977; Wadjimny, 1989; Bouabdellah et al., 2012), and probably also to the Eastern High Atlas Pb–Zn–Cu ore deposits described by Rajlich et al. (1983). For Touissit-Bou Beker, for example, the Pb–Zn mineralization was described as MVT ore deposits hosted in the Aalenian–Bajociian carbonate platform. According to Bouabdellah et al. (2012), metals in the ore-bearing fluids were sourced from the Visean rhyodacites and volcaniclastic rocks, and the ore emplacement took place during the Miocene Alpine orogeny.

The present study of the Bou Dahar district provides a broader understanding of the origin of ore-forming fluids and the genesis of carbonate-hosted Pb–Zn–Ba ore deposits in the High Atlas metallogenic province.

3. Geology of Jebel Bou Dahar district

The Bou Dahar structure, rock ages and lithologies are presented in Fig. 2. The Bou Dahar is a flat anticline striking ENE–WSW. 40 km long and 15 km wide plateau which lies near the central part of the Eastern High Atlas (Fig. 1). It is located about 15 km to the west of the Paleozoic Tamlielt Massif. The Bou Dahar Jurassic plateau corresponds to a preserved Pliensbachian coral reef and carbonate platforms (Agard and Du Dresnay, 1965). While a Paleozoic paleorelief crops out in the folded central part of the Jebel Bou Dahar, the southern domain rather displays a tabular architecture that is marked by a rim of coral-rich limestone surrounding thin-bedded limestone originally formed in a lagoon (Agard and Du Dresnay, 1965).

The Paleozoic facies of Cambrian–Silurian age (Agard and Du Dresnay, 1965) outcrops in the core of the Bou Dahar fold, and is well exposed in the Sebbab Kebir area where it forms an E–W oriented outcrop that is 12 km long and about 2 km wide (Fig. 2a). It consists of thick folded series of schists alternating with quartzite, dipping 15° to 20° to the north. The Paleozoic was affected by numerous E–W- to NE–SW-trending faults. Locally, it was intruded by micragabbro dikes most likely of Triassic age.

The Triassic formation consists of deformed red beds and basaltic rocks where the evaporate component may have been dissolved at or near the surface. This formation is transgressive, in discordance D_0 over the Paleozoic basement (Fig. 2b). The Jurassic succession, which forms most of the Jebel Bou Dahar, was studied by Agard and Du Dresnay (1965), Crevello (1990), Campbell and Staffeau (1992), Rddad (1998), Della Porta et al. (2012) among others. The following six Jurassic units (from the base upwards) were distinguished (Fig. 2b and c):

- Unit 1 (10–50 m) — thick laminatedstromatolitic dolomite strata of Lower Sinemurian age, transgressive over the Triassic rocks.
- Unit 2 (~200 m) — oolitic limestone beds, locally silicified, of Middle–Late Sinemurian, intercalated with red marls. Units 1 and 2 form the Lower Liassic carbonate platform which hosts the stratabound Pb–Zn ore deposits.
- Unit 3 (10–50 m) — thin marlstone beds of Carixian age, overlapping the oolitic limestone.
- Unit 4 (~200 m) — massive bioclastic and reef limestone forming the Pliensbachian carbonate platform, locally silicified and dolomitized. This unit is the host of the vein-type Pb–Zn ore deposits.
- Unit 5 (~200 m) — Toarcian marls and Aalenian black mudstones that progressively onlap the Pliensbachian platform flanks, and overlie the top platform. This indicates the abrupt cessation of carbonate platform evolution at the Donerian–Toarcian transition (Du Dresnay, 1975; Crevello, 1990; Campbell and Staffeau, 1992). The Aalenian black mudstones locally filled synsedimentary fractures within the upper part of the Pliensbachian limestones (Rddad, 1998).
- Unit 6 (~500 m) — deep marine basin shales and marls with few thin beds of limestone of the Bajociian age (termed the Talsint Marls). They overlay the Toarcian and Aalenian shales and mudstones.

Units 1 and 2, which form the Lower Liassic carbonate, are composed of shallow marine-type carbonate that developed on an active marine
rift basin (Della Porta et al., 2012). During the Late Sinemurian, block-faulting activities uplifted the Paleozoic basement along Sebbab Kebir forming a paleohigh. The Bou Dahar platform evolved from a low-relief ramp to a high-relief ramp (Della Porta et al., 2012) on which the Middle Liassic carbonate (Unit 3) was developed. The block-faulting activities, caused by the overall E–W-trending normal faults, led to the differentiation of four distinct paleogeographic domains that are from north to south: (i) the Talsint basin; (ii) the Sebbab Kebir paleohigh; (iii) the Pliensbachian carbonate platform and (iv) the deep Beni Bassia basin.

The Domerian–Toarcian transition period was marked by a major extensional tectonic activity resulting from the reactivation of E–W and NE–SW striking faults. This activity segmented, fractured, and drowned the Bou Dahar carbonate platforms. These platforms were later sealed by the Toarcian and Aalenian shales and marlstones. At the margins of the Bou Dahar platform, the sedimentation consists of alternating beds of marls and argillaceous limestones, indicating a relatively deep marine environment maintained during the Bajocian (Du Dresnay, 1975).

The Jurassic tectonic activities caused three disconformities in the Jurassic succession (Fig. 2b) (Agard and Du Dresnay, 1965). The first disconformity (D1) along with the local conglomeratic layers developed between unit 1 and unit 2. The second (D2) and third (D3) disconformities developed at the boundary between unit 2 and unit 3, and between unit 4 and unit 5 respectively.

The Alpine orogeny of the late Cretaceous–Miocene caused the inversion of the E–W- to NE–SW-trending faults, and the uplift of the present day Bou Dahar plateau.

4. Mineralization and paragenetic sequence

The Bou Dahar district contains more than thirty Pb–Zn ore deposits and numerous small showings hosted in the Liassic limestone (Fig. 2a). The ore deposits are concentrated along the rims of the Bou Dahar plateau, and also around the Sebbab–Kebir Paleozoic paleohigh. Currently, thirty deposits are mined for sulfides and non-sulfide Pb–Zn ores. Most of them are located in the western area of the plateau (Fig. 2).
The description of the orebodies led to the distinction between low-grade, strata-bound and massive, high-grade, vein-type ores (Agard and Du Dresnay, 1965; Rddad, 1998). Most of the ore zones followed E–W to NE–SW trends parallel to the structural trend of the Bou Dahar anticline. Mineralization is hosted in two stratigraphic units: the Lower Liassic (Sinemurian) oolitic limestone, and the Middle Liassic (Pliensbachian) bioclastic and reef limestone.

The Sinemurian-hosted ore forms discontinuous, strata-bound, lens-shaped orebodies 20 to 30 m thick (Agard and Du Dresnay, 1965). The ores cemented fractured and brecciated limestone strata, and formed ENE–SSW-trending mineralized zones parallel to the regional faults. Two mineralization styles with similar paragenetic sequences are identified: (i) irregular disseminations of small galena crystals (~0.2 cm) (Fig. 3a) and euhedral sphalerite crystals (up to 15 mm), and (ii) stockwork type in a thin and dense fissures network. Both sulfides replace bioclasts, pellets, and oolites (Fig. 4a).

The Pliensbachian-hosted mineralization forms numerous parallel veins (Fig. 4b) within E–W- to ENE–WSW-trending faults (e.g., Toutia, Chitane, Yacoub, and Taboudaharte deposits). Fault intersections were the site of wide dissolution and ore emplacement, and thus represent zones of economic interest. The veins’ dimensions are variable from one ore deposit to another, but the average dimensions are 300 m-length and 1 m-width. The total length of the known veins is estimated at 130 km (Agard and Du Dresnay, 1965). The sulfides, non-sulfide Pb–Zn ores, and barite are exploited over a depth extending from 30 to 170 m. Locally, the veins intrude the Aalenian black mudstone filling synsedimentary faults that crosscut the Pliensbachian limestone (e.g. Corne Wast deposit).

Fig. 3. Some underground views and some hand samples from the Bou Dahar ore district. a: Disseminated galena (Gn) in the oolitic limestone. Inset shows limestone hand samples with galena crystals disseminations in limestone (Sebbab). b: Vein filled with massive galena (Gn) embedded within calamine masses (cal) hosted in limestone (Lim), (Chitane). c: Massive sphalerite (Sp) hosted in limestone (Corne Wast). d: Green-colored sphalerite crystals (Sp) cemented by galena (Gn), then by barite (Brt) (Yacoub). e: Galena cemented by sparry ore calcite (Cte1) (Yacoub). f: Honey red and green sphalerite (Sp) cemented by post-ore calcite (Cte2) (Toutia).
The macroscopic and microscopic mineral assemblage is simple and includes pyrite, melnikovite, sphalerite, galena with tetraedrite inclusions, barite, and subordinate celestite. Upon examining the underground, a vertical ore zoning is noticed, with sulfides occupying the deeper zones while the sulfate minerals occupy the shallow zones.

Minor pyrite aggregations occur in both the strata-bound and the vein-type ores as subhedral and euhedral crystals, and have a fine-to moderately coarse-grained texture. Pyrite is associated with galena and sphalerite and occurs locally as inclusions in sphalerite and galena (Fig. 4b). Some iron sulfide occurs as colloform textures typical of the melnikovite associated with pyrite, or as inclusions in both sphalerite and galena (e.g., Yacoub). Translucent honey- to dark green-colored, cm-sized, sphalerite crystals occur as massive patches within the vein (e.g., Chitane), and as fracture-fillings in the limestone host rock (Fig. 3c). They are also disseminated within the bioclastic limestone. Sphalerite crystals are often cemented by galena (e.g., Toutia, Corne Wast, Chitane), or by galena and barite successively (Figs. 3d and 4b) (Yacoub). Relics of sphalerite can be found within calamine. Galena occurs as euhedral, coarse-grained, fracture-controlled, massive patches in veins (Fig. 3b) and in dissolution cavities (e.g., Yacoub, Ksar Moghal).

In the wall rocks, galena occurs as disseminated, fine- (100 μm) to coarse-grained (up to 4 cm) euhedral crystals, and as stockwork-type mineralization. Disseminated galena forms numerous large swarms which is guided by fissures parallel to the regional ENE–WSW-trending faults. Galena and minor sphalerite replace the limestone without any dissolution or recrystallization of the host limestone. At the microscale level, polished and thin sections show galena replacing oolites, bioclasts, and calcitic cement. Micro-inclusions (50 μm) of tetraedrite are embedded in or coated by galena (e.g., Tighanimine ore deposit). Locally, chalcopyrite forms rare aggregates within the veins (Agard and Du Dresnay, 1965).

Barite postdates sphalerite and galena, and fills either E–W veins (Taboudaharte) or dissolution cavities (Yacoub) (Fig. 3d). Minor celestite is observed at Rich-Khole, and occurs as prismatic and fibro-radial crystals at the center of the vein, and a massive band at the border. At the base of the massive celestite is a ferruginous strip that is rich in fine-grained quartz. Ore calcite occurs as coarse-grained crystals, and is usually associated with galena and sphalerite (Fig. 3e). It also forms agglomerations in the host rock and fills dissolution cavities. Late calcite (post-ore calcite) seals the small fractures that affect sphalerite (Fig. 3f).

The wall–rock alteration, associated with the various styles of mineralization, consists mainly of silicification (Fig. 4d), and occurs as needle bipyramidal quartz crystals crosscutting oolites, bioclasts, and sparry cement. Quartz is often engulfed or corroded by the sulfide minerals (Fig. 4d), and represents the pre-ore stage of the mineralizing system. Beside silicification, Agard and Du Dresnay (1965) observed rare dolomite replacing the host limestone.

A large portion of the exploited ores corresponds to the non-sulfide secondary Pb–Zn mineralization studied in detail by Choulet et al. (2014). These supergene minerals formed as a result of the oxidation of sulfides by meteoric water during the last 20 Ma (Choulet et al., 2014). The first abundant oxide assemblage, consisting of calamine (Fig. 3b), developed at the expense of sphalerite. The calamine includes banded smithsonite, white hydrozincite, collomorph hemimorphite, and red clays. The second but minor oxide assemblage consists of a mixture of cerussite, covellite, and iron oxides.

The paragenetic sequence is independent of the ore style and of the host rock age, and consists of four mineralizing stages/events summarized in Table 1. Stage 1 is the sulfide event and consists of pyrite–galena–sphalerite–ore calcite (calcite-1) succession. Stage 2 is the sulfate event and consists of barite and celestite. Stage 3 corresponds to the post-ore calcite (calcite-2) that fills small fractures crosscutting sulfide ores and limestone host rocks. Stage 4 corresponds to the oxidation stage of the sulfide ores.

5. Fluid inclusions

Samples were prepared as standard 200 to 500 μm-thick, doubly-polished wafers. The microthermometric measurements were carried out at the Department of Earth Sciences, Faculty of Sciences of Tunis, using a Linkam THM600 freezing-heating stage on a Leitz microscope. The system was calibrated using pure CO2 fluid inclusion (−56.6 °C), the freezing point of H2O (0 °C), and melting points of Merck standards. The precision was ±0.5 °C. Fluid salinity was calculated as weight percent NaCl equivalent (wt.% NaCl eq.) using the equation of Bodnar (1993).
5.1. Petrography

The fluid inclusions are rounded, elongated, and rarely irregular in shape, and have an average size of 30 μm. Fluid inclusion assemblages of Goldstein and Reynolds (1994) and genetic classification as primary, secondary or pseudosecondary of Roedder (1984) were used to classify fluid inclusions. Fluid inclusions that are clustered or isolated are considered primary. Fluid inclusions that are aligned and occur as planar trails are considered secondary.

Sphalerite shows primary and secondary fluid-inclusion assemblages. The primary fluid inclusions (L + V) are aqueous, two-phase inclusions, with a liquid/vapor ratio of ~85%, and are either isolated or clustered (Fig. 5a). The secondary fluid inclusions (L + V) are aqueous, two-phase inclusions which occur as trails. These secondary fluid inclusions are suspected to have undergone necking-down phenomena. They have a narrow salinity range and a wide range of temperature. Therefore, they are not considered in this study.

Barite and celestite contain liquid, one-phase, primary fluid inclusions that are clustered or isolated (Fig. 5b). Because barite and celestite are susceptible to stretching and/or leakage (Ulrich and Bodnar, 1988), fluid inclusions that are hosted in these sulfate minerals and that show necking-down or FIs with inconsistent microthermometric data, are not considered in this study.

5.2. Microthermometric results

A summary of the microthermometric data derived from the study of 225 primary fluid inclusions hosted in sphalerite, barite, and celestite is presented in Table 2.

Primary fluid inclusions in sphalerite have eutectic temperature (T_e) in the range of −74.2 and −39.3 °C, far below the eutectic of NaCl–H_2O system (−21.2 °C). This indicates the presence of other salts beside NaCl, such as CaCl_2 (T_e = −52 °C), MgCl_2 (T_e = −35 °C), and LiCl (T_e = −75 to −78 °C) (e.g., Roedder, 1984; Crawford, 1981; Dubois and Magnac, 1997; Davis et al., 1990). Final ice melting temperature (T_m(ice)) values range between −30.6 and −11.5 °C, corresponding to a salinity range of 15.6 to 29.7 wt.% NaCl eq. (average = 23 ± 0.5 wt.% NaCl eq.) (Fig. 6). Homogenization temperature (T_h) values vary from 106 to 180 °C (143 °C) (Fig. 7). These microthermometric values fall within the range of those measured by Adil et al. (2004).

Thermometric measurements on ore calcite were performed by Adil et al. (2004). The eutectic temperatures of the primary fluid inclusions range from −80 to −45 °C, indicating the presence of other solutes in the fluid. Ice melting temperatures vary between −29 and −12 °C, which yields salinity values in the range of 15 to 29 wt.% NaCl eq. Homogenization temperatures range from 60 to 150 °C.

Barite and celestite show only aqueous, single-phase, primary fluid inclusions. Eutectic temperatures vary from −52 to −40 °C (average = −46 °C), and from −31 to −24.8 °C (average = −27.9 °C) for barite and celestite respectively. This indicates the presence of other solutes in the fluid such as Ca^{2+} and Mg^{2+}. The T_m(ice) values range from −17.7 to −9.7 °C (average = −13.7 °C) for barite, and −4.5 to −1.9 °C (average = −3.2 °C) for celestite. These values yield a salinity range of 13.7 to 19.6 wt.% NaCl eq. (average = 17 ± 0.5 wt.% NaCl eq.), and of 3.2 to 7.2 wt.% NaCl eq. (average = 5 ± 0.5 wt.% NaCl eq.) for barite and celestite respectively (Fig. 6). These single-phase fluid inclusions in both barite and celestite were entrapped at a temperature lower than 50 °C (T_h = −40 °C).

5.3. Pressure corrections

Pressure corrections are minimal given the fact that the Bou Dahar MVT ore deposit would form at pressures lower than 1 kbar (Roedder, 1984). However, if a maximum cover of about 1 km is assumed, the pressure corrections to the observed temperatures would be approximately 30 °C (Farrington, 1952; Nwachukwu, 1975) at the time of ore formation.

6. Stable (C, O, S) and lead isotopes

6.1. Sampling and analytical procedures

Thirty ore samples were collected from the vein type and dissolution-cavities type, both hosted in the Pliensbachian limestone (Table 3), spanning the early- and late-stage mineralizing events. Samples were taken from 0 m to 170 m underground mining levels of the Toutia, Corne Wast, Yacoub, Chitane, Taboudaharte, and Rich-Khole (Fig. 2a).

Mineral separates, for stable and radiogenic isotopes, were carefully crushed and handpicked under a binocular microscope. Carbon, oxygen,
and sulfur isotopes were performed at the Stable Isotope Ratio Mass Spectrometry facility at the Department of Geological Sciences and Engineering, University of Nevada. Lead isotope analyses were made on Nu Plasma MC–ICP–MS at the Ecole Normale Supérieure in Lyon, France.

For carbon and oxygen isotopes, five samples of Pliensbachian host limestone, four samples of calcite, associated with the sulfide stage, from Toutia, Corne Wast, and Yacoub, and one sample of post-ore calcite from Toutia were analyzed. Oxygen isotopes were also measured for four barite samples from Yacoub and Taboudaharte, and for two celestite samples of Rich-Khole.

The C–O isotopic analyses were carried out using a Micromass MultiProd preparation device interfaced to a dual inlet Micromass Isoprobe stable isotope ratio mass spectrometer, using the phosphoric acid reaction method of McCrea (1950), except that the reaction was performed at 90 °C. The carbon isotopic compositions are reported in delta notation (δ13C) relative to VPDB, and the oxygen isotopic compositions are reported in delta notation (δ18O) relative to VPDB and VSMOW. Precision of the analyses is better than ±0.2‰.

Sulfur isotopes were carried out on six sphalerite and eight galena samples from Toutia, Corne Wast, Chitane, and Yacoub. Sulfur isotope measurements were also performed on four barite samples from Yacoub, two barite samples of Taboudaharte, and two celestite samples of Rich-Khole. Sulfur isotope analyses were performed using a Eurovector elemental analyzer interfaced to a Micromass Isoprobe stable isotope ratio mass spectrometer, after the methods of Giesemann et al. (1994) and Grassineau et al. (2001). Vanadium oxide (V2O5) was added to sulfate samples as a combustion aid. S-isotopic compositions in sulfide and sulfate minerals are expressed as δ34S values relative to the VCDT standard, and O isotopic compositions in sulfates are expressed as δ18O values relative to the VPDB and VSMOW standard. Reproducibility was ±0.2‰ for sulfur, and ±0.5‰ for oxygen.

Lead isotope measurements were performed on four galena samples from Toutia, Chitane, Corne Wast and Yacoub. Every two samples were bracketed using SRM–981. Samples and Standards were corrected for mass fractionation using Thallium and an exponential law (Albarède et al., 2004). The Pb isotope ratios were normalized to the bracketing values of SRM–981. The 2σ errors on the TI-corrected NIST 981 values, measured during the period the samples were run, were 0.0017‰, 0.014‰, and 0.045‰ for 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb respectively.

6.2. Results

6.2.1. Carbon and oxygen isotopes

The C–O isotopic composition of carbonates and O isotopic composition of sulfates are listed in Table 4 and Fig. 8. The host Liassic (Pliensbachian) limestones have δ13C values ranging from 0.5 to 2.9‰ (mean = 1.7‰) (Fig. 8) that are within the range typical of marine Jurassic limestone (Veizer and Hoefs, 1976; Land, 1980). The δ13C values of the ore-calcite, associated with the sulfide mineralization, fluctuate between 1.6 and 2.5‰, and that of the post-ore calcite is 0.0‰ (Fig. 8). The δ18O values for the ore-calcite range from 18.4 to 21.6‰ (mean = 20‰), and are lower than those of the host limestone (Fig. 8). The post-ore calcite has a δ18O value of 15.4‰ (Fig. 8). The δ18O values of barite and celestite range from 16.1 to 18.2‰, and 16.1 to 17.9‰ respectively (Table 4).

6.2.2. Sulfur isotopes

Sulfur isotope compositions of sphalerite, galena, barite, and celestite are reported in Table 5 and Fig. 9. The δ34S values for galena and sphalerite range from −4.0 to 6.8‰ (mean = 1.4‰), and from 0.7 to 5.0‰ (mean = 2.9‰), respectively. The range of the isotopic compositions of sulfates is relatively small when compared to that of most sediment-hosted deposits. The δ34S values of sulfate minerals reveal a relatively small variation of 17.2 to 20.4‰ (mean = 18.8‰) for barite, and of 15.4 to 18.5‰ (mean = 16.5‰) for celestite (Table 5 and Fig. 9).

The δ34S values show the following trend: δ34S_Sulfates < δ34S_Sulfates. When comparing the δ34S values of the sulfide minerals, the trend δ34S_Gal < δ34S_Sph is observed for Toutia and Corne Wast ore deposits while the opposite trend δ34S_Sph < δ34S_Gal is observed for Chitane and Yacoub ore deposits. A hand specimen with the paragenetic sequence

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**Table 2**

Microthermometric data of the primary fluid inclusions in the Bou Dahar ore district.

<table>
<thead>
<tr>
<th>Location</th>
<th>Host mineral</th>
<th>Stage</th>
<th>Inclusion type</th>
<th>Num</th>
<th>T_melt (°C)</th>
<th>Salinity (wt.% NaCl eq.)</th>
<th>T hom (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Toutia</td>
<td>Sphalerite</td>
<td>Stage 1</td>
<td>L + V</td>
<td>45</td>
<td>−25.2 to −15.2</td>
<td>−20.7</td>
<td>19.0–26.2</td>
</tr>
<tr>
<td>Corne Wast</td>
<td>Sphalerite</td>
<td>Stage 1</td>
<td>L + V</td>
<td>30</td>
<td>−23.0 to −20.2</td>
<td>−21.7</td>
<td>22.8–24.7</td>
</tr>
<tr>
<td>Chitane</td>
<td>Sphalerite</td>
<td>Stage 1</td>
<td>L + V</td>
<td>29</td>
<td>−25.8 to −18.2</td>
<td>−21.6</td>
<td>21.4–26.5</td>
</tr>
<tr>
<td>Yacoub</td>
<td>Sphalerite</td>
<td>Stage 1</td>
<td>L + V</td>
<td>56</td>
<td>−30.6 to −11.5</td>
<td>−20.5</td>
<td>15.5–29.7</td>
</tr>
<tr>
<td>Taboudaharte</td>
<td>Barite</td>
<td>Stage 2</td>
<td>L</td>
<td>44</td>
<td>−17.7 to −9.7</td>
<td>−13.0</td>
<td>13.7–19.6</td>
</tr>
<tr>
<td>Rich-Khole</td>
<td>Celestite</td>
<td>Stage 2</td>
<td>L</td>
<td>21</td>
<td>−4.5 to −1.9</td>
<td>−3.3</td>
<td>3.2–7.2</td>
</tr>
</tbody>
</table>

---

**Fig. 6** Frequency of ice melting temperatures derived from microthermometric studies of the primary fluid inclusions in sphalerite, barite, and celestite from the Bou Dahar district.

**Fig. 7** Frequency of homogenization temperature derived from microthermometric studies of the primary fluid inclusions in sphalerite from the Bou Dahar district.
of ZnS → PbS → BaSO₄ from Yacoub has the following isotopic composition trend of δ³⁴S: ZnS < PbS < BaSO₄ (Fig. 10).

6.2.3. Lead isotopes
The Pb isotope compositions of galena samples (n = 5) from Bou Dahar are presented in Table 6 and plotted in the ⁲⁰⁶Pb/²⁰⁴Pb vs. ⁲⁰⁷Pb/²⁰⁴Pb (thorogenic diagram) and ⁲⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁸Pb/²⁰⁴Pb (uranogenic diagram) (Fig. 11). The Pb isotopic compositions of galena from the Touissit–Bou Bekr MVT district (Bouabdellah et al., 2012) are also plotted for comparison.

The Pb isotope compositions of the Bou Dahar district ores are homogenous with ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios ranging respectively from 18.124 to 18.13, 15.630 to 15.634, and 38.440 to 38.440. The parameters μ (²⁰₈Pb/²⁰₄Pb) and κ (²³²Th/²³⁸U), and model age (T) values are calculated using the equations of Albarède et al. (2004). The μ and κ values are homogenous and range from 9.79 to 9.80 and from 4.08 to 4.12 respectively. The calculated model age (T) is bracketed between 431 and 470 Ma.

7. Discussion

7.1. Nature of the ore fluids
The homogenization-salinity diagram (Fig. 12) reveals two distinct fluid end members trapped in sphalerite and sulfate minerals. The first fluid, trapped in sphalerite, is characterized by high salinity (~23 ± 0.5 wt.% NaCl eq.) and moderate temperature (average ~ 143 °C). This fluid corresponds to the sulfide-stage event. It is a NaCl–KCl–CaCl₂ ± LiCl brine as inferred from measured eutectic temperatures (T<sub>e average</sub> ~ −60 °C). The second end member fluid, observed in aqueous, one-phase, celestite fluid inclusions, has low salinity (average ~ 5 ± 0.5 wt.% NaCl eq.) and low temperature (~50 °C). The temperature and salinity obtained from fluid inclusions at Bou Dahar fall within the range of most MVT ore-forming fluids (salinity = 15–30 wt.% NaCl eq. temperature = 75 °C–200 °C) (Basuki and Spooner, 2004; Leach et al., 2005).

The temperature values recorded in fluid inclusions at Bou Dahar exceed values expected for geologically reasonable thermal gradients and estimated stratigraphic burial temperatures. Therefore, these temperatures can be explained by either: (i) an unusually high geothermal gradient, (ii) advective heat transport from deeper parts of the basin as observed for many other MVT ore districts (e.g., Touissit–Bou Bekr, Bouabdellah et al., 1996; Ozark MVT province, Leach et al., 2010), or

Table 6

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample</th>
<th>Lithology</th>
<th>δ¹⁸O (‰, VSMOW)</th>
<th>δ¹³C (‰, VPDB)</th>
<th>δ¹⁸O (‰, VSMOW)</th>
<th>δ¹³C (‰, VPDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOH</td>
<td>Yacoub</td>
<td>Barite</td>
<td>−12.6</td>
<td>−15.4</td>
<td>−14.1</td>
<td>18.2</td>
</tr>
<tr>
<td>YB3a</td>
<td>Yacoub</td>
<td>Barite</td>
<td>−14.3</td>
<td>18.2</td>
<td>−14.3</td>
<td>18.2</td>
</tr>
<tr>
<td>TaB1</td>
<td>Tabouedharte</td>
<td>Barite</td>
<td>−14.3</td>
<td>18.2</td>
<td>−14.3</td>
<td>18.2</td>
</tr>
<tr>
<td>RCG1</td>
<td>Yacoub</td>
<td>Celestine</td>
<td>−14.3</td>
<td>18.2</td>
<td>−14.3</td>
<td>18.2</td>
</tr>
<tr>
<td>RCo2</td>
<td>Yacoub</td>
<td>Barite</td>
<td>−12.6</td>
<td>17.9</td>
<td>−14.3</td>
<td>18.2</td>
</tr>
</tbody>
</table>

The calculated model age (T) values are homogenous and range from 9.79 to 9.80 and from 4.08 to 4.12 respectively. The calculated model age (T) is bracketed between 431 and 470 Ma.
be attributed to either an increase in temperature, or the introduction of isotopically lighter fluid.

Using the average δ18O values of the ore calcite, the homogenization temperature range of 60 to 180 °C, and the oxygen isotope fractionation equation of Friedman and O’Neil (1977), the calculated δ18O of the fluid varied between −2.1 and 9.4‰. Such fluid is similar to the basal brines of the MVT ore deposits (δ18O of +4 to +10‰) (e.g., Mc Limans, 1977; Ohmoto, 1986).

The oxygen isotope composition of sulfates (barite and celestite) is closer to that of Mesozoic seawater sulfate (−10–15‰) (Claypool et al., 1980). This indicates that these sulfate minerals precipitated from an 18O-enriched, SO4−-rich fluid derived from Mesozoic seawater.

7.2. Source of metals

The sources of the metals for sediment-hosted, base-metal deposits are a variety of crustal rocks. No special rock type stood out as a preferred source (Leach et al., 2005). The brines leached the metals from the rocks it encountered along their paths of migration.

The galena samples show homogenous Pb isotope compositions with 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb ratios ranging from 18.124 to 18.183, 15.630 to 15.634, and 38.325 to 38.440, respectively. According to the plumbotectonic model of Zartman and Doe (1981), these Pb isotope values plot above the orogene curve in the thorogenic (206Pb/204Pb vs 208Pb/204Pb) diagram, and between the upper crust and the orogene in the uranogenic (207Pb/204Pb vs 206Pb/204Pb) diagram (Fig. 11). This indicates that lead originated from upper crustal and orogenic reservoirs, which is consistent with the geodynamic setting of the High Atlas to which the studied district belongs.

The calculated model age (T) varies from 431 Ma to 470 Ma, and is older than the proposed Eocene–Miocene age (refer to the discussion below). This abnormal older age, typical of numerous MVT ore deposits, is explained by the delay in Pb in-situ growth. This Pb growth retardation is due to the contribution of a low radiogenic material originating most likely from the lower crust and/or the preferential removal of U during orogenic events.

The Paleozoic series consist mainly of siliciclastics, and thus are a suitable source of metals for the Bou Dahar ore deposits. The presence

(iii) the ascent of deeply circulating fluids in basement rocks beneath the deposits (e.g., Upper Silesia and Irish Midlands; Leach et al., 2010).

The salinity values of the ore-forming fluids at Bou Dahar fall within the range of those calculated in the worldwide MVT districts where salinity is typically in the range of 10 to 30 wt.% NaCl eq. (Leach et al., 2005; Leach et al., 2010). These fluids have compositions and temperatures similar to those of oil-field brines (Sverjensky, 1986). The high salinity of these sedimentary basinal brines can be explained by the dissolution of evaporates, incorporation of connate bittern brines, or the infiltration of evaporated surface waters (Hanor, 1979; Carpenter et al., 1974; Viets et al., 1996). For Bou Dahar, the Na–Cl– Br–Li systems of sphalerite-hosted fluid inclusions suggest that the high salinity resulted from evaporated seawater with a contribution of low amounts of halite dissolution (Adil et al., 2004).

The δ34S values of carbonates display a general downward trend in the following sequence: limestone (22.7 to 25.7‰, average = 24.2‰) → ore-calcite (18.4 to 21.6‰, average = 20‰) → post-ore calcite (15.4‰). This trend resembles similar trends that have been observed at other MVT deposits (e.g., Frank and Lohmann, 1987; Nesbitt and Muehlenbachs, 1994; Spangenberg et al., 1995) in which isotopically lighter O is observed in paragenetically late carbonates. Lighter δ18O values of post-ore calcite, relative to the ore-calcite, can

Table 5
Sulfur isotope composition of sulfides and sulfates from the Bou Dahar ore district.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Mineral δ34S (‰, VCDT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCG1</td>
<td>Tountia</td>
<td>Galena</td>
</tr>
<tr>
<td>TCG2</td>
<td>Tountia</td>
<td>Galena</td>
</tr>
<tr>
<td>TOS1</td>
<td>Tountia</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>WG1</td>
<td>Corne Wast</td>
<td>Galena</td>
</tr>
<tr>
<td>WS1</td>
<td>Corne Wast</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>WS2</td>
<td>Corne Wast</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>ChG1</td>
<td>Chitane</td>
<td>Galena</td>
</tr>
<tr>
<td>ChG2</td>
<td>Chitane</td>
<td>Galena</td>
</tr>
<tr>
<td>ChS1</td>
<td>Chitane</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>YG1</td>
<td>Yacoub</td>
<td>Galena</td>
</tr>
<tr>
<td>YG2</td>
<td>Yacoub</td>
<td>Galena</td>
</tr>
<tr>
<td>YG3</td>
<td>Yacoub</td>
<td>Galena</td>
</tr>
<tr>
<td>YS2</td>
<td>Yacoub</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>YS3</td>
<td>Yacoub</td>
<td>Sphalerite</td>
</tr>
<tr>
<td>YB2</td>
<td>Yacoub</td>
<td>Barite</td>
</tr>
<tr>
<td>YB3a</td>
<td>Yacoub</td>
<td>Barite</td>
</tr>
<tr>
<td>YB3b</td>
<td>Yacoub</td>
<td>Barite</td>
</tr>
<tr>
<td>YB3c</td>
<td>Yacoub</td>
<td>Barite</td>
</tr>
<tr>
<td>TaB1</td>
<td>Taboudaharte</td>
<td>Barite</td>
</tr>
<tr>
<td>TaB2</td>
<td>Taboudaharte</td>
<td>Barite</td>
</tr>
<tr>
<td>TaB3</td>
<td>Taboudaharte</td>
<td>Barite</td>
</tr>
<tr>
<td>RCe1</td>
<td>Rich-Khole</td>
<td>Celestite</td>
</tr>
<tr>
<td>RCe2</td>
<td>Rich-Khole</td>
<td>Celestite</td>
</tr>
</tbody>
</table>

Fig. 9. Histogram distribution of the δ34S values for sphalerite, galena, barite and celestite from Bou Dahar district.

Fig. 10. Hand specimen δ34S isotopic composition of sphalerite, galena, and barite in Yacoub.
of Li, as inferred from the eutectic temperatures and the high values of crush-leach molar Li/Na ratio (0.007) in the sphalerite-hosted fluid inclusions (Adil et al., 2004), suggests that the ore-forming fluid interacted with the siliciclastic Paleozoic Li-bearing clays/micas (e.g., Banks et al., 2002). The presence of deep-seated E-W to NE-SW-trending Hercynian faults, entrenched deeply within the Paleozoic basement and remobilized during the Alpine orogeny via a thick-skinned tectonic model, further supports the upper crustal origin of Pb and other metals. These deep-seated faults have acted as pathways for the rising fluids from the Paleozoic basement from which metals were mainly leached and transported to the Liassic carbonate ore reservoir.

Compared to other Pb–Zn ore deposits in the Moroccan–Algerian–Tunisian atlas belt, the Pb isotopic values of the Bou Dahar district and the Pb isotope values of Tigrinine–Taabest district (Rddad and Bouhlel, in preparation), which is located in the Central High Atlas, are less radiogenic than the Pb–Zn Touissit–Bou Beker ore deposits (Bouabdellah et al., 2012). The less radiogenic character of the Bou Dahar district, compared to Touissit–Bou Beker, reflects differences in the composition of the underlying Paleozoic basement. The latter consists of schist in Bou Dahar and of schist with Visean rhyodacites and volcaniclastic rocks in underlying Paleozoic basement. The least radiogenic reservoir is encountered in Morocco while the more evolved, “live” Pb reservoir is found in Tunisia.

### 7.3. Source of sulfur

Sulfur isotope values of MVT sulfides throughout the world indicate that sulfur generated from a variety of crustal sources (Ohmoto and Rye, 1979; Sangster, 1990; Leach et al., 2010). Individual deposits or districts can have one or more possible sources of sulfur that may include sulfate-bearing evaporates, connate seawater, diagenetic sulfides, sulfur-bearing organic material, or H2S reservoir gas (Leach et al., 2010). The ultimate source of the sulfur is seawater sulfate trapped by the sediments in various minerals and/or connate water that was subsequently reduced by one or more processes (Sangster, 1990; Leach et al., 2010).

For Bou Dahar, the δ34S values in celestite and barite, ranging between ~15 and 20‰ (Table 4), fall within the range of Mesozoic seawater sulfate (13–20‰) (e.g., Triassic seawater +11 to 20‰; Jurassic seawater +14 to 18‰) (Fig. 12). The δ34S values of barite and celestite are also close to those of Triassic gypsum (13.0 to 15.6‰) reported in the Touissit–Bou Beker ore district (Bouabdellah et al., 2012). The most obvious source of sulfur for the Bou Dahar ores is the Triassic sulfates underlying the Jurassic carbonate of the Moroccan High Atlas.

The reduced sulfur in sphalerite and galena was derived from dissolved sulfate through thermochemical sulfate reduction (TSR) or bacterial sulfate reduction (BSR) processes. Beyond this basic point, the geochemical pathways by which reduced sulfur was formed and how it was introduced into the ore zone remain problematic. BSR
takes place under low temperatures, generally below 80 °C (Dixon and Davidson, 1996; Jørgensen et al., 1992; Machel, 1987). Conversely, TSR occurs via a reaction involving hydrocarbons at a temperature environment (80–100 °C < T < 150–200 °C) fluctuating mainly between 80 and 130 °C (Orr, 1974; Krouse et al., 1988; Machel, 1987). Sulfur isotope compositions of sulfides generated through BSR are around 40‰ lower than those of the original sulfates (Ohmoto and Rye, 1979; Ohmoto, 1986). However, fractionation induced by TSR can produce sulfides with δ34S values around 15‰ lighter than those of the parent sulfates (Orr, 1974). If sulfide precipitation follows sulfate reduction, the difference between the δ34S_{SO_4} and δ34S_{S_{i,S}} is approximately 14 to 24‰ (Krouse et al., 1988). For Bou Dhah, the difference Δ_{sulfate–sulfide} (δ34S_{Sulfate} − δ34S_{Sulfide}) fluctuates from 8.6‰ to 24.4‰. These values are within the range of 14 to 24‰ produced by TSR, and thus are consistent with the reduction of sulfates through TSR. The separation δ_{sulfate–sulfide} is generally around +5‰ for in situ-formation of H2S in a shallow environment (Ohmoto et al., 1985). This separation, however, oscillates between 0 and +10‰ for H2S generated in depth and transported to the ore site (Ohmoto et al., 1985). It follows that the observed δ_{sulfate–sulfide} values at Bou Dahar indicate that the reduced sulfur was produced in depth by TSR distant from the orebodies. Subsequently, this reduced sulfur was carried toward the loci of ore deposition.

However, the overall positive δ34S values of sphalerite and galena, and the small deviation from the isotopic values of Mesozoic seawater sulfate (13–20‰, mean ≈ 15‰) can also be produced by BSR in a closed system, or through the mixing of reduced sulfur from multiple sources involving more than one reduction process. Because the temperature of ore deposition generally exceeded the conditions capable of sustaining efficient bacterial processes, biogenic sulfate reduction could have occurred away from the ore zone and/or prior to the hydrothermal event.

7.4. Processes of ore deposition

The new data presented here reveal that the carbonate-hosted Bou Dahar Zn–Pb–Ba ores have many geological and geochemical features that are typical of MVT lead–zinc ore deposits (e.g., Sverjensky, 1986; Leach et al., 2005). There are three historically proposed models that account for the precipitation of MVT ore deposits: the reduced-sulfur model, the sulfate-reduction model, and the mixing model.

In the sulfate reduction model, ore metals and sulfates are transported together. The precipitation of ore occurs during the reduction of sulfate via thermochemical sulfate reduction and/or bacterial sulfate reduction in the presence of organic matter or methane (Anderson, 1983; Macqueen and Powel, 1983).

In the reduced sulfur model, ore metals and the reduced sulfur are transported in the same fluid. The amounts of metals and sulfur transported are very limited due to the constraint on the solubility of metals in the presence of sulfur. The precipitation of the ore occurs due to the PH change, cooling, and/or dilution by a superficial fluid (Anderson, 1973; Helgeson, 1970; Sverjensky, 1981).

In the mixing model, ore metals are transported by one fluid while sulfur is separately transported by another fluid. The precipitation occurs as a result of the mixing of these two fluids at the site of deposition (Anderson, 1973; Beales and Jackson, 1966; Anderson and Macqueen, 1988; Sverjensky, 1986; Plumlee et al., 1994). Another variant of this model is the possibility of a metal-bearing fluid encountering a reduced sulfur source such as H2S reservoir gas, diagenetic iron sulfides, or sulfur associated with organic matter (Beales and Jackson, 1966; Sverjensky, 1986).

For the Bou Dahar district, transport of metals together with reduced sulfur (reduced sulfur model) in a carbonate environment (Liassic carbonate aquifer) is highly unlikely. In fact, the transport of reduced sulfur requires acidic conditions, which are difficult to maintain in a Liassic carbonate aquifer through which fluids have migrated over large distances. Similarly, the metal-bearing fluid, migrating upward, cannot carry sulfates (sulfate reduction model) because of the low solubility of Ba and Sr in an SO_{4}^{2-}–rich fluid. It follows that the plausible transport scenario is that deep-seated fluids carried metals, while SO_{4}^{2-} was supplied by another shallower and cooler fluid (mixing model). The reduced sulfur must, then, have been generated via TSR of dissolved seawater sulfate (SO_{4}^{2-}), and delivered to the site of ore deposition where it was mixed with the ore-bearing hot fluid causing the precipitation of the ore.

The trend δ34S_{PbS} < δ34S_{ZnS} is observed for all ore deposits except Toutia and Corne Wast, which suggests that ore precipitated under disequilibrium conditions that are typical of ore formation at temperatures well below 250 °C (Ohmoto and Rye, 1979; Ohmoto, 1986). For Corne Wast and Toutia, the sulfur isotopic composition trend (PbS < ZnS) may indicate equilibrium conditions. The fractionation factors between sphalerite–galena pairs in Corne Wast and Toutia have an average value of 2.3‰ and 4.7‰, respectively. Using the equation α_{ZnS–PbS} = (0.73/T)^{2} \times 10^{6} (T in Kelvin) (Ohmoto and Rye, 1979), the calculated average temperatures are about 290 °C and 121 °C for Corne Wast and Toutia, respectively. The calculated temperature for Toutia (121 °C) is within the range of those reached through the fluid-inclusion studies (T_{f} = 142–180 °C). This may suggest that the precipitation of sphalerite and galena took place at/near equilibrium conditions in this deposit. However, the calculated temperature for Corne Wast (290 °C) is higher than the homogenization temperature range of 106–180 °C, obtained from the fluid inclusions. This observation together with the general trend δ34S_{PbS} < δ34S_{ZnS} indicate that the ores were, overall, precipitated under disequilibrium conditions resulting from fluid mixing (Ohmoto, 1986). At the hand specimen scale, the enrichment trend of δ34S along the paragenetic sequence ZnS < PbS < BaSO_{4} is observed. This isotopic composition trend indicates that δ34S of the generated H2S is lighter in the beginning, and becomes progressively heavier with time. This is consistent with heavy δ34S and δ18O measured in sulfates (barite and celestite). It follows that these sulfate minerals precipitated from a 34S– and 18O-enriched sulfate reservoir.

The proposed fluid mixing mechanism is supported by fluid inclusions and stable isotope results. In fact, the similarity between the δ34S values of gangue carbonates and those of the host rocks points to the mixing of metal-bearing and reduced sulfur-bearing fluids at the site of deposition. A similar conclusion was reached for Polaris ore deposits, Canada (Savard et al., 2000). The pre-ore wall–rock silification indicates that hot fluids underwent conductive cooling as they encountered carbonate host rocks (Fournier, 1985) prior to this fluid mixing process.

In the early hydrothermal stage, the mixing of the deep-seated, ascending, ore-forming, 18O-enriched hot brines with a shallow, cooler, less saline, H2S-rich fluid (trend 1) (Fig. 13) occurred at the site of deposition. H2S was generated through TSR processes at elevated
temperatures away from the ore site. Such mixing accounts for the wide range of salinity and the homogenization temperatures obtained from sphalerite-hosted fluid inclusions. During this mineralization event, the brine/shallow-fluid mixing ratio was high and resulted in hot (~143°C) and saline (~23 wt.% NaCl eq.) brine from which sulfides precipitated. The metal-bearing fluid was supersaturated in iron, and mixing led to the rapid precipitation of pyrite as indicated by its colloform texture (Roedder, 1968) (e.g., Yacoub). The medium- to coarse-grained texture of sphalerite and galena, observed in the studied ore deposits, suggests a relatively slow precipitation of sphalerite and galena from a relatively less saturated fluid. With time, the mixing proportion of the brine relative to superficial fluid decreased as the cool superficial SO\(_4^{2-}\)-rich fluid started to dominate the hydrothermal system. This is evident from the overall cooling trend (Trend 2) (Fig. 12). At this waning stage, the SO\(_4^{2-}\) could not be reduced most likely because of lower temperatures that hindered the TSR processes, and thus the production of H\(_2\)S (Kiyosu and Krouse, 1990; Machel et al., 1995).

The inhibition of TSR reaction contributed to the end of the sulfide mineralizing stage. The unreduced SO\(_4^{2-}\) combined with Ba leading to the precipitation of barite from a cooler (T\(_b\) < 50 °C, −40 °C) and moderately saline fluid (~17 wt.% NaCl eq.). The precipitation of barite was slow as revealed by its coarse-grained texture. At the final waning stage of the evolution of the hydrothermal fluid system, the cooler fluid became dominant and more pronounced giving rise to a cooler (T\(_b\) < 50 °C, −40 °C) and diluted fluid (~5 wt.% NaCl eq.). As a result of this cooling-dilution process, Sr combined with the unreduced SO\(_4^{2-}\) causing the slow precipitation of celestite (Trend 2) (Fig. 13). The presence of iron-oxide inclusions in celestite reflects the oxidative nature of the fluid system during the last waning stage.

7.5. Ore controls, timing of mineralization, and fluid migration

Lithostratigraphy, faults, and local paleostructures have guided the ore emplacement in the Bou Dahar district. The E-W to NE-SW trending faults at the margins and across the Bou Dahar plateau (Fig. 1) were a major control for ore deposition. Faulting activities during the first Liassic rifting had created a paleohigh structure, adjacent to deep basins, which promoted the development of the Lower and Middle Liassic carbonate platforms. It is within these highly porous carbonates that the strata bound-type and the vein-type ore deposits are confined. During the second Liassic–Jurassic rifting, the Liassic carbonates were drowned and sealed with the Toarcian–Bajocian impermeable marls. The latter acted as an aquitard focalizing the mineralizing fluids within the Liassic carbonates. Later on, these faults and fractures were reactivated during the Alpine orogeny and acted as migration conduits for the ascending metal-carrying fluids. Beside these structural and lithological controls, brecciation, dolomitization, and silicification had also enhanced porosity for ore emplacement.

The age of ore emplacement at Bou Dahar cannot be determined precisely. Ore deposition, however, must have taken place after the fracturing and faulting of the Jurassic platform. These faulting activities are related to Eocene–Miocene Alpine orogeny. The ore deposits are mainly hosted in Middle Liassic carbonates. In some ore deposits, however, the ore is hosted in Aalenian black shale/mudstones filling the fractures within the Liassic limestone. Therefore, the ore is post-Aalenian (post- Early Dogger), and thus post-Jurassic rifting. In the Tirisht Pb–Zn ore deposit, the genesis of the mineralization is post-Jurassic (Gaia, 1968).

In the Eastern High Atlas, Pb–Zn ore deposits are hosted in rocks ranging in age from Liassic to Lower Cenomanian (Rajlich et al., 1983). It is widely accepted that ore deposition in the High Atlas region was post-Cretaceous (Agard and Du Dresnay, 1965; Bazin, 1968; Le Blanc, 1968; Dupuy, 1984; Rddad, 1998). Moreover, the ore was emplaced prior to the onset of the supergene oxidation of the sulfides, which took place in the last 20 Ma (Choulet et al., 2014).

There is an increasing agreement that major sediment-hosted Zn–Pb ores are formed as a result of large-scale tectonic triggers (Leach et al., 2010) that released deep-seated fluids into favorable geochemical traps. This is the most plausible mechanism behind large-scale fluid circulation in the Bou Dahar district and other ore deposits of the High Atlas foreland belt. A post-Cretaceous compressional tectonic event (Alpine orogeny) took place during the collision between the European and African plates. The Atlasic compressional tectonic event was not continuous, but rather consisted of a succession of periods of shortening alternating with periods of tectonic quiescent (Frizon de Lamotte et al., 2009). Consequently, the timing of ore deposition in the studied area can be related to the first major Atlasic compressional event which started during the Middle–Eocene age (~50 Ma–35 Ma) and continued during the second compressional event of the Late Miocene (Tortonian) age (~12 Ma). This age range is consistent with the ones proposed for the Touissit–Bou Beker ore district (Bouabdellah et al., 2012) and for the Tunisian Pb–Zn ore districts (Bouhlel et al., 2013).

This major tectonic event has caused N–S trending compression of the High Atlas, which resulted in creating a topographic gradient. Compression and topography-driven processes are found to be effective mechanisms in remobilizing and transporting large amounts of orogenic, metal-rich brines from the basin to adjacent platforms (Garven and Freeze, 1984; Garven, 1985; Kesler, 1994). This mechanism is well established in the genesis of the Pb–Zn–Ba MVT in the Ozark Plateau in USA (Leach, 1994; Appold and Garven, 1999; Leach et al., 2005; Leach et al., 2010). Thrusting, regional E–W and NE–SW deep-seated faults acted as pathways for the flow and migration of fluids. The Alpine orogeny as a driving force for the circulation of large-scale fluids was also proposed for the Pb–Zn–Ba MVT ores in the Tunisian Atlasic belt (Bouhlel, 2005) and for the MVT Pb–Zn–Ba–(±Sr) ores in the Moroccan High Atlas (Rddad, 1998; Rddad, 2012).

The proposed mechanism of the orogenically-driven circulation of brines in crustal rocks, followed by the ascent of and reaction with fluids in the overlying cover rocks has striking similarities to the mechanisms through which other MVT deposits formed as a consequence of the plate tectonic collisions (Bradley and Leach, 2003).

8. The Bou Dahar ore genesis model

Based on the geochemical studies, in combination with geological and mineralogical characteristics, salient physico-chemical metallogenic parameters can be drawn for the Bou Dahar ore genesis. These parameters include temperature and salinity during ore formation, the character and source of hydrothermal fluids, and the sources of sulfur and metals. These constraints are used to establish the following genetic model for the origin of the Bou Dahar ore deposits.

The Eocene–Miocene Alpine orogeny caused the compression of the High Atlas basin, via a thick-skin model (Teixell et al., 2003), and the development of a topographic gradient. The deep-seated, ore-forming fluids were expelled during sediment compaction (Noble, 1963; Beales and Jackson, 1966) and subsequently remobilized to higher platform zones (e.g., Bou Dahar paleohigh) by the Alpine tectonic orogeny and topographic gradient (e.g., Garven and Freeze, 1984). These basal fluids are brines as indicated by microthermometric and stable isotope characteristics. The ore-forming brines, driven by the Alpine tectonic orogeny, acquired their high salinity mainly from evaporated seawater trapped in sediments, with a minor contribution from halite dissolution. During their migration, the bittern brines evolved to Pb–Zn–Ba–rich fluids through the interaction with the Paleozoic and the Mesozoic siliciclastic rocks. The overpressured, orogenic, metal-rich fluids were, subsequently, channeled through the inherited deep-seated E–W to NE–SW faulted zones. Ultimately, they migrated through the confined Liassic carbonate reservoir that contained H\(_2\)S-rich fluid generated through TSR processes away from the ore site. The mixing of these two fluids triggered the precipitation of the sulfide ores. During the late stage, the hydrothermal system was open to continual influx of SO\(_4^{2-}\) rich fluids, resulting in an increase in the proportion of the SO\(_4^{2-}\).
rich, cooler fluid relative to the brine. At this waning stage, barium and strontium reacted with $\text{SO}_4^{2-}$ leading to the precipitation of barite and celestite respectively.

The Bou Dahar ore district exhibits striking similarities to the Central and Southeast Missouri MV7 districts in terms of its fluid characteristics. In these districts, the sphalerite-hosted fluid inclusions indicate homogenization temperature in the range of 80 to 110 °C, and a salinity of more than 22 wt.% NaCl eq. (Leach, 1980). Because of the contrasting salinity and temperature values in the fluids forming sphalerite and barite, Leach (1980) argued that the precipitation of barite is unrelated to and superimposed on sulfide mineralization. For the Bou Dahar district, although sulfides and sulfates show distinct fluid temperatures, they reflect an overlap in salinity values. Therefore, the sulfide and sulfate hydrothermal stages were likely related, and were formed from the same evolving hydrothermal brine. The proposed ore genesis model, which involves the interaction between basement-derived ore fluids and shallower H$_2$S-rich fluids, bears similarities to numerous MV7 ore deposits worldwide (e.g., Ozarks, USA; Leach, 1994; Pine Point Canada, Rhodes et al., 1984).

9. Concluding remarks

Geological, mineralogical, fluid-inclusion, and C–O–S–Pb isotope studies allow a better understanding of the genesis of the Bou Dahar Pb–Zn–Ba–(±Sr) ore district. The following are insights into the genesis of the mineralization:

1. The carbonate reservoir developed during the liassic period and fractured during the Eocene–Late Miocene orogeny. It was sealed with thick, mainly marls and argillaceous limestone of Middle and Late Jurassic. The carbonate reservoir provided circulation pathways and a favorable site of ore deposition while the overlapping marls provided a trap for fluid circulation.

2. The sulfur needed for the precipitation of the sulfide ore deposits was generated through TSR of dissolved Mesozoic sulfate away from the site of mineralization. Ultimately, the sulfur was delivered to the loci of ore deposition.

3. The bittern fluids evolved to Pb–Zn–Ba–rich fluids through the interaction with the Paleozoic siliciclastic basement and the Mesozoic cover. The post-Cretaceous Alpine orogeny triggered the remobilization and circulation of these metal-carrying fluids along E–W to NE-SW faulted zones toward the site of deposition.

4. At the site of ore precipitation, the ore-forming fluids mixed and reacted with a subsurface cooler H$_2$S-rich fluid to form sulfides. During the waning hydrothermal stage, the excess of unreduced sulfur and the continual influx of dissolved sulfate reacted with barium and strontium to form barite and celestite.

The geological, mineralogical, and geochemical characteristics of the Bou Dahar mining district allow its integration into the large class of Mississippi-Valley-Type ore deposits. The Bou Dahar district is characterized with those of other Pb–Zn MV7 districts and provinces documented in other regions in the world (e.g., Ozarks, USA; Leach, 1994; Appalachian, USA; Kesler, 1996; Pine Point Canada, Rhodes et al., 1984; High Atlas, Rddad, 1998; Recoin, Spain, Velasco et al., 2003; Touissit–Bou Beker district; Moroccan–Algerian confines, Bouabdellah et al., 2012; and Tunisia Alpine Pb–Zn districts, Bouhlel, 2005).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.oregeorev.2015.08.011. These data include the Google map of the most important areas described in this article.

References


Appôllo, M.S., Garven, G., 1999. The hydrology of ore formation in the Southeast Missouri district: numerical models of topography-driven fluid flow during the Ouachita orogeny. Econ. Geol. 94, 913–935.


1086


Friedman, I., O'Neil, J.R., 1977.


1756

above 100 °C in deep-sea hydrothermal

Haut Atlas central (Maroc) corrélations lithostratigraphiques, éléments de datation et

sary, Symposium 3, pp. 155


