Geologic, mineralogic, fluid inclusion and isotope evidence for the genesis of the Bou Jaber Ba-F-Pb-Zn salt diapir-related Mississippi Valley-Type deposit, Tunisia

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Abstract The Bou Jaber Ba-F-Pb-Zn deposit is located at the edge of a Triassic salt diapir in the Salt Diapir Belt of the Tunisian Atlas Foreland. It provides a good example of the close association between Mississippi Valley-type mineralization and evaporite-bearing diapirs. The ores are fault-controlled and occur as subvertical column-shaped bodies developed in dissolution breccias and cavities in Aptian platform/reef limestone, which is covered unconformably by impermeable shale and marl of the Upper Albian-Cenomanian. The limestone host rock is hydrothermally altered to ankerite proximal to and within the ore bodies. Quartz as fine-grained bipyramidal crystal formed during hydrothermal alteration of the host rocks.

The ore mineral assemblage is composed of barite, fluorite, sphalerite and galena in decreasing abundance. The ore zones outline distinct depositional events: sphalerite-galena, barite+ankerite and fluorite. Fluid inclusions, commonly oil-rich, have distinct fluids salinities and homogenization temperatures for each of these events: sphalerite-galena (17 to 24 wt% NaCl eq., and Th from 112° to 136°C; ankerite+ barite (11 to 17 wt% NaCl eq., and Th from 100° to 130°C); fluorite (19 to 21 wt% NaCl eq., Th from 140° to 165°C).

The mean temperatures of the ore fluids in the events decreased from sphalerite (125°C) to barite (115°C) and increased during fluorite deposition (152°C); then decreased to ~110°C during late calcite precipitation. LA-ICP-MS analyses of fluid inclusions show there are at least 2 distinct fluids. Inclusions in fluorite are metal-rich (100’s to 1000’s ppm Pb, Zn, Cu, Fe) but the inclusions in barite are Pb, Zn, Cu, Fe-deficient. No information on metal contents are available. Inclusions in fluorite have Cl/Br and Na/Br ratios of several thousand, consistent with dissolution of halite while the inclusions analysed in barite have values lower than those of seawater which are indicative of a Br-enriched brine derived from the evaporation of seawater plus a component of halite dissolution. The salinity of the barite fluid inclusions is less than obtained simply by the evaporation of seawater to halite saturation and requires a dilution of more than two times for halite saturated fluids. This is consistent with the presence of a component of meteoric water in the brine that deposited barite. The higher K/Na values from fluid inclusions from barite suggest that the brines interacted with K-rich rocks in the basement or in siliciclastic sediments in the basin. Carbonate gangue minerals (ankerite and calcite) have $\delta^{13}$C and $\delta^{18}$O that are close to the Aptian limestone host rock values and indicate fluid equilibrium between carbonate host rocks and warm brines. The $\delta^{34}$S values for sphalerite and galena are positive and very homogeneous. They fall within a narrow range (1 to 10 %o) with a bulk value of 7.5 %o, indicating a homogeneous source of sulfur. The $\delta^{34}$S values of barite are also relatively homogeneous (22 %o), with 6 % higher than the $\delta^{34}$S of local and regional Triassic evaporites (15%). The latter are believed to be the source of sulfate. Temperature of deposition together with sulfur isotopes data indicate that the reduced sulfur in sulfides was derived through the reduction of Triassic sulfate by thermochemical sulfate reduction using hydrocarbons produced probably from Upper Cretaceous source rocks. The $^{87}$Sr/$^{86}$Sr ratio in the Bou Jaber barite (0.709821 to 0.711408) together with the lead isotope values of Bou Jaber galena ($^{206}$Pb/$^{204}$Pb=18.699 to 18.737; $^{207}$Pb/$^{204}$Pb=15.635 to 15.708 and $^{208}$Pb/$^{204}$Pb=38.321 to 38.947) show that
metals were extracted from homogenous crustal source(s). The tectonic setting of the Bou Jaber ore deposit, the carbonate nature of the host rocks, the epigenetic style of the mineralization and the mineral associations, together with sulfur and oxygen isotope data and fluid inclusion data show that Bou Jaber zinc-lead ores of the deposit has the major characteristics of a salt diapir-related MVT Zn-Pb ores with superimposed events of fluorite and of barite deposit. Field relations are consistent with mineral deposition during the Miocene Alpine Orogeny from multiple hydrothermal events: (1) Zn-Pb sulfides formed by the mixing of two fluids: one fluid metal-rich but reduced sulfur-poor and a second fluid reduced sulfur rich; (2) the fluorite precipitated from a more dilute fluid with higher temperatures; (3) barite precipitation involved the influx of a meteoric water component that mixed with a barium-rich fluid. A significant conclusion of the study provides evidence that decouples the mineral assemblages (Zn-Pb, fluorite and barite) into separate and possibly unrelated mineralization events. Consequently, the presence of barite or fluorite mineralization in any diapiric zone does not necessarily suggest the presence of Zn-Pb rich ores.

**Keywords** Fluid inclusions° Laser ablation ICP-MS° C, O, S, Sr, Pb isotopes° diapir-related MVT Ba-F-Pb-Zn deposits° Bou Jaber° Tunisia°
Introduction

Lead-zinc ore deposits associated with evaporite-bearing diapirs are well known and have been exploited for many years in North Africa and the Gulf of Mexico region of the U.S.A. (Sainfeld 1956; Hanna and Wolf 1934; Price and Kyle 1983; Posey et al. 1994). They form a distinct group within the MVT class of deposits, with typically low to high tonnage and modest to high grade (1 to few million tons). Recently high tonnage (with a reserve of approximately 200 million tons of ore grading 6% Zn and 1.3% Pb) are discovered in Jinding, China (e.g., Leach et al 2013). A number of North American studies have characterized some of the processes of formation (e.g., Light et al. 1987; Posey and Kyle 1988; Kyle and Price 1986; Kyle and Posey 1991).

In North Tunisia and adjacent Algeria region, although the numerous Pb-Zn (±Ba-F) deposits located at the edges of Triassic salt-bearing diapirs were exhaustively investigated and explored during the last eight decades, important aspects of the metallogeny of these salt diapir-related metallic deposits remain a subject of debate. Conflicting genetic models involving syngenetic origin, epigenetic origin, or a combination of both have been proposed (e.g., Sainfeld 1956; Rouvier et al. 1985; Gharbi et al. 1985; Charef and Sheppard 1987; Amouri 1989; Orgeval 1994; Sheppard et al. 1996; Bouzenoune and Lécolle 1997; Bouhlel 2005; Bouhlel et al. 2007; Bouhlel et al. 2009).

The Bou Jaber evaporite diapir-related Ba-F-Pb-Zn deposit, is located in central-western Tunisia, 30 km west of Tajerouine city, and lies against the Algerian-Tunisian international border (Fig. 1). It is one of numerous Algerian-Tunisian Pb-Zn-Ba deposits located at the edges of Triassic diapirs and where mineralization is hosted in Cretaceous peridiapiric limestone strata (Sainfeld 1956; Rouvier et al. 1985; Bouhlel 1993). Unlike most of the Tunisian-Algerian salt diapir-related Pb-Zn deposits, the Bou Jaber deposit is barite and fluorite-rich and exhibits a clear spatial relationship with three geo-structural elements: a salt diapir and NW-trending faults limiting Miocene-Pliocene grabens, allowing a possible role of these three ore geological controls in its genesis.

Currently no comprehensive geochemical investigation has been published. Based on mapping, general mineralogical descriptions and limited geochemical database the controversy over the genesis of the Bou Jaber mineralization has mainly included: (i) a syngenetic origin that involved meteoric karstification followed by the deposition of base-metals originating from reworking of continental heavy-metal-rich soil horizons during Upper Aptian period (Fuchs 1973; Amouri 1989); and (ii) an epigenetic origin at Miocene time, that involved replacement of limestones and infilling of hydrothermal dissolution-cavities and open fractures by undefined fluids and precipitation processes (Bouhlel 1987; Bouhlel 1993; Salmi-Laouar et al. 2004). To better define ore controls, the mineralizing event (s); the nature, origin, and evolution of the hydrothermal fluids, metal and sulfur sources, and the processes that control metal precipitation, this study integrates the geologic ore controls, ore textures and paragenesis, fluid inclusions microthermometry,
halogen analyses of fluid inclusions, and stable (C, O) and radiogenic (Sr, Pb) isotope analyses from mineral
separates. The results provide new insights into the origin of the Bou Jaber ore deposit and, in a more general
sense, into the metallogenesis of the diapir-related carbonate-hosted Pb-Zn-Ba-F deposits.
Geological setting and regional mineralization

Bou Jaber deposit is located in the Salt Diapir Belt of the Tunisian Atlas foreland fold-thrust-belt which is a part of the Alpine Atlas mountain ranges extending through Morocco, Algeria and Tunisia, and resulting from the Miocene convergence between the Africa and Europe plates (Fig. 1). With its NE-SW-striking length of 200 km and a fairly constant width of 50 km, the Salt Diapir Belt roughly coincides with the Tunisian Trough (Fig. 1). It is bordered to the North by the Tell thrust belt characterized by Miocene south-directed tangential tectonism of Tellian and Numidian nappes and to the South by the Central Tunisia Platform. The southwestern area of the Salt Diapir Belt and large area of the Central Tunisia Platform are intersected by large number of transverse grabens. The Tell thrust belt and the Tunisian Atlas foreland fold-thrust-belt are formed by about 8-10 km-thick Mesozoic-Tertiary folded cover pieced by a large number of Triassic salt diapirs. At the surface, the Triassic diapirs are mainly composed of chaotic breccias dominantly formed by gypsum with few shale, dolostone and basic volcanic that correspond to insoluble caprocks. The few wells drilled through diapirs encountered massive salt below 200 or 300 m of gypsum. In map view the diapirs occur as elongated SW-NE bodies, typically 10 x 3 km long and 1 to 2 km in width, and are distributed along 3 to 5 distinct parallel NE-SW-directed strike-slip faults that correspond to the reactivation of former Hercynian faults (Perthuisot 1978; Martinez and Truillet 1987; Turki et al. 1988; Chaari 2002). The Bou Jaber diapir is located on one of these diapir-bearing faults (the Tajerouine Fault) (Fig. 1). Almost everywhere in the Salt Diapir Belt, the tectonic contacts between the Triassic salt diapirs and the intruded Cretaceous to Miocene rocks are marked by lens-shaped evaporite-dissolution breccia bodies that are the host of Pb-Zn-Sr mineralization (Rouvier et al. 1985; Sheppard 1996; Bouhlel 1993; Bouhlel et al. 2007). The Triassic substratum is only known in the Saharan Platform by deep petroleum drilling. It is composed of Paleozoic shale, sandstone, arkosic sandstone and Precambrian granite or metamorphic rocks (Mejri et al. 2006). The Jurassic platform carbonate deposition of central and eastern Tunisia has only rarely been observed and is nowhere seen overlying the diapirs. Lower Cretaceous is composed of sandstone, clay and limestone. Upper Cretaceous - Eocene succession is composed of marl and argillaceous limestone. Oligocene and Miocene are discordant and composed of continental clay, sandstone and conglomerate. This Mesozoic-Tertiary succession forms SW-NE-trending folds (acquired since the Oligocene) which are cut by NW-SE-directed faults, limiting grabens filled by Mio-Pliocene continental sediments.

During the Triassic to Lower Tertiary (pre-orogenic period), the instability of the sedimentary basement was almost permanent, related to repeated activity of deep accidents, inherited from Panafrican and Hercynian orogens and reactivated mainly during rifting stages related to the Africa-Europe drift movement (Cohen et al. 1980; Guirand and Maurin (1991). These resulted in a N-S extension that persisted from the Jurassic until Lower Aptian. In this context, the north-central Tunisia corresponded to a rifted continental margin characterized by extensional NE-SW and NW-SE-trending faults limiting horsts, grabens and tilted.
blocks (Boltenhagen 1985; Martinez and Truillet 1987), with particularly the individualization since the Neocomian of two differentiated paleogeographic and sedimentary domains (Figs. 1-2): to the north, a deep rifted basin called the Tunisian Trough (Burollet 1956) and to the south the flat Central Tunisia Platform which is the northern extension of the Saharan Platform (Vially et al. 1994). In the Tunisian Trough, the syn-rift sedimentary sequence is very thick (about 5,000 m in the Cretaceous alone in the El Kef area) and is composed of deep marine sediments mainly marl and argillaceous limestone. On the platform area, the thicknesses are reduced and gaps occur locally in the series; the facies are composed of sandstone and clay with shallow marine limestone and dolostone of Aptian age (Marie et al. 1084; M’Rabet 1987).

In the trough, with the overburden of Jurassic and Neocomian series, halokinetic movements of the Triassic salt began. In several places of the south-western area of the trough (Tajerouine-Tabessa region), about 300 to 500 m-thick Aptian, and Lower Albian shallow marine bioclastic limestones, including reef development, overlay diapirc structures (e.g., Bou Jaber, Slata, and Ouenza; Perthuisot 1978, Boulhlel 1987). Aptian and Lower Albian limestones, on both Central Tunisia Platform and diapiric structures, are the host of siderite or Pb-Zn-Ba-F mineralization.

Transpression and transtension tectonics occurred during the Middle Albian with the reactivation of syn-rift extensional NE-SW and NW-SE-trending faults, limiting tilted blocks and half-grabens. It were the intersection zones of these fault systems that accelerated salt diapirism and where numerous diapirs intruded their roof and emerged onto the seafloor (Bolze 1954; Perthuisot 1981). Salt diapirs, tilted blocks, and half-grabens will control the distribution and the nature of the sedimentary facies (Boltenhagen 1985; Perthuisot 1981).

During the Upper Albian-Lower Turonian, transgressive post-rift shale and marl pelagic sediments (300 to 1000m-thick) invaded the entire Aptian-Lower Albian platform as well as the Tunisian Trough fossilizing uplifted blocks, half-grabens and salt diapirs. The latter structures, together with the upper Albian unconformity controlled the ore emplacements. The lower part of the transgressive series contains two organic-rich laminated black limestones: Upper Albian Mouelha laminites (~2 % COT) and Cenomanian-Turonian Bahloul laminites (up to 13% COT) (e.g., Saidi and Belayouni 1994; Soua 2009). These rocks are considered as excellent hydrocarbon source rocks for the petroleum system in the region (e.g., Saidi and Belayouni 1994; Soua 2009). Bahloul laminites may also be the host of strata-bound replacement-type sphalerite-rich mineralization as the case in Bou Grine (Boulhlel et al. 2009). The Cretaceous sedimentation continues with the deposition of about 2000 m-thick marl and limestone succession of Middle Turonian to Paleocene. Subsidence and transpressional tectonics caused a second diapiric piercing during the Lower Eocene (Perthuisot 1981).

The tectonic period of the Alpine orogeny in northern Tunisia began in Oligocene time and reached its maximum during the Middle Miocene as a result of collision of microplates rifted off the European margin with the North African margin, and coincided with the progressive elimination of Proto-
Mediterranean lithosphere from west to east along the African margin (Rouvier 1977; Martinez and Truillet 1987). Deformations consist of a NW-SE contraction phase with significant shortening resulting in NE-SW to E-W-trending folds; flow of Triassic salt into the cores of these folds assisted by tectonic loading during fault inversion; NE-SW strike-slip faults resulting from reactivation of syn-rift extensional faults; and setting up in the North of the Tell Thrust Belt composed of major thrust sheets of Oligo-Lower Miocene “Numidian” flysch emplaced over Upper Cretaceous-Eocene “Tellian” nappes. At the base of the nappes, blades of Triassic evaporitic breccias are common; these are due to detachment surfaces or to diapiric extrusions cut and trailed by moving nappes. Basic and acidic igneous rocks are described in several places of the Tell Thrust Belt (e.g. Oued Bélif region and at La Galite island (Bellon 1976; Lardhi-Ouazza 1994) and correspond to Upper Miocene and Pliocene magmatism activities. In the Atlas Foreland, Pliocene reactivation of transpressional movements created NW-SE-trending grabens (Ben Ayed 1986; Chihi 1995) intersecting and cutting across the SW-NE-oriented folds and Triassic diapirs. The grabens were filled by Pliocene continental conglomerate and sandstone sediments. On the Tell Thrust Belt post-orogenic relaxation phase resulted in conglomerate, clay and lacustrine limestone deposition in Upper Miocene basins. Upper Miocene-Pliocene basins in the Atlas Foreland and in the Tell Thrust Belt are the host of some Pb-Zn ore deposits.

Ore deposits

The Pb-Zn ±(Ba, Sr, F) ore deposits in the Salt Diapir Belt and adjacent regions are shown on Figure1. Most of the ore deposits contain low to medium size resources (1 to 8 million tons at about 5 to 15 % Pb+Zn). The ore deposits are classified into four groups based on the ore minerals present in the deposits (Rouvier et al. 1985; Bouhlel 1993; Bouhlel 2005) (Fig. 1). However, we point out in this report that these groups are spatially and genetically distinct from each other. These assemblages are not present in all deposits and where they do occur, they may or may not be present in specific mineralized zones. In all cases, where they occur in the same mineralized zone, there is a consistent paragenetic relationship discussed later. These 4 groups reflect a complex hydrothermal overprinting by up to 4 mineralization events in some deposits. These ore groups are described below:

Group 1: Strata-bound replacement siderite deposits hosted in Aptian limestone (e.g., Ouenza, Bou Khadra and Jerissa deposits) with global resources of about 165 million tons of Fe metal (Pohl et al. 1986; Bouzenoune and Lecolle 1997).

Group 2: Ba±F±(Pb-Zn) strata-bound replacement-type and cavity-filling deposits in Aptian and Lower Albian platform and reef limestones at the edges of Triassic salt diapirs. This group shows two distinct mineral assemblages: group 2a with Ba-F±(Pb-Zn) (e.g., Mesloula, Mzouzia, Belkfif deposits in Algeria; Akrour et al. 1991; and Bou Jaber in Tunisia), and group 2b with Ba±(Pb-Zn) deposits (e.g., Slata, Hamra, Ajred, Trozza, in Tunisia) (Bouhlel 1993; Jrad and Perthuisot 1995; Béjaoui et al. 2013). Furthermore Pb-Zn-Ba mineralization is also present in the Cenomanian-Turonian dolostones (Aïn Nouba), in the Eocene
phosphorite rocks (Sekarna) and even in the Miocene clastic rocks (Aïn Khmouda) (Sainfeld 1956; Fucks 1973; Garnit et al. 2012).

Group 3: Pb-Zn (±celestite) strata-bound replacement-type deposits hosted by dissolution evaporitic breccias at the contact zones between salt diapirs or salt sheets and the surrounding Cretaceous to Miocene rocks (e.g., Fedj el Adoum, Kebbouch, Bou Khil, Garn Halfaya, Zag Ettir, Aguida). The most economic is the Fedj el Adoum deposit that contains about 1.5 Mt of 17% Zn+Pb (Sheppard et al. 1996; Bouhlel et al. 2007). If the barite is present in these deposits, it always cuts the celestite-, and the Pb-Zn ore bodies.

Group 4: Pb-Zn strata-bound replacement-type and vein-type ore deposits that lack Ba, Sr or F are hosted by Upper Cretaceous limestone that envelops the Triassic salt diapirs (Bou Grine, Akhouat, O. Jebs; Schmith 1999; Bouhlel et al. 2009; Béjaoui et al. 2013). Prior to mining operations (1992-2006), the Bou Grine deposit resources were about 7.3 million tons of ore at 15% Zn+Pb (Orgeval 1994).

Group 5: Pb-Zn deposits occur either as strata-bound ores or as veins in continental Miocene rocks (e.g., Sidi Driss in the Tell Thrust Belt and Koudiat Safra and Jebba in the Atlas Foreland) (Rouvier et al. 1985; Decrée et al. 2008).

Field observations indicate that the Zn-Pb-, Ba-F ores may be arranged as follow: a Zn-Pb event, a BaSO4 event (may have trace sphalerite and galena) and a fluorite event with minor barite (may have trace sphalerite and galena). These various mineral assemblages are suggestive of contributions from at least 4 distinct ore fluids and/or ore forming events that variably affected the Triassic diapiric structures. The Bou Jaber deposit contains a mineral assemblage that reflects mineralization from a Zn-Pb event, a barite event and a late fluorite event as discussed below.

The Bou Jaber deposit

The Bou Jaber deposit was first mined for lead and silver by the Romans (2nd to 5th centuries), where galena yielded up to 500g/t Ag. Small and episodic mining activities continued by Arabs and Turks (9th to 17th centuries), and then the French (1890 to 1950). The most recent (1972 to 2004) intermittent mining activities by Tunisian state-owning mining companies focused on underground exploitation with a total production of about 50,000t Pb+Zn, 0.5 Mt barite and minor quantities of fluorite. The production ceased in late 2004 due to difficulties in the economic viability of the mine. The remaining estimated reserves are located mainly at the “Gîte de l’Est” (the east deposit), and are of about 8 Mt with a grade of 1.5% Pb, 3.5% Zn, 33 % BaSO4, and 9% CaF2. In 2015, European Industrial and base metal Limited concluded negotiations with the Tunisian Government and earned a 90% right in the Bou Jaber mine exploitation, while 10% are detained by the Office National des Mines (O.N.M.).

Lithostratigraphy and structural evolution
The geological map, lithostratigraphy and cross sections at Bou Jaber region are presented on Figure 3. The dipiric Triassic salt formation outcrops in the core of a Cretaceous anticline and consists of dissolution-mega breccias composed of chaotic assemblage of gypsum masses containing blocks of variegated argillite. Halite rocks are dissolved at the surface. These gypsum-rich breccias, partly covered by Mio-Pliocene continental sediments and alluvium, are similar of other Triassic outcrops in neighbouring diapirs where deep drill holes showed thick halite-rich zone beneath the gypsum breccia zone.

The Aptian-Lower Albian limestone (Serdj Formation) outcrops at the south flank of the diapir. It is composed of two platform and reef limestone members, respectively Aptian and Lower Albian in age (Dubourdieu 1956, Bouhlel 1993; Vila and Charrière 1993; Braham et al 2002). The Aptian limestone member is composed of 200 m-thick bioclastic limestone thickening up, interbedded by marl sequences (units 1-4,), following is a massive lens-shaped bar 50 to 100 m-thick (unit 5) composed of platform limestone containing rudistid and coral reefs. Following is a marl-rich member of about 100 m-thick (unit 6) consisting essentially of alternating marl, shale, fine-grained sandstone and bioclastic limestone. The Lower Albian limestone member (unit 7) forms a lens-shaped bar (250 to 50 m-thick) composed of metric-thick beds of bioclastic limestone containing abundant debris of Rudistids, Corals and Echinoderms.

In the southern flank of Bou Jaber Mountain, the shales and marls of the Upper Albian over lain from east to west the units 4 to 7 of the Aptian-Lower Albian platform succession (Fig. 3a). This spectacular cartographic discordance corresponds to the Aptian/Upper Albian unconformity (Bouhlel 1993), regionally known as the Austrian unconformity (Mejri et al 2006 and references therein). The Upper Albian-Cenomanian sequence begins with a small “block complex” (1 to 5 m-thick) composed of limestone blocks of 0.5 to 3 m across ripped from the nearby Aptian uplifted blocks, and in turn covered by about 600m-thick shale, finely laminated dark biomicrite limestone and marl (Fahdene Formation including the Mouelha-, and the Bahloul organic-rich laminite members). To the south (outside Fig. 3a), the Upper Cretaceous series continue with marine sediments of the Turonian to Eocene ages, consisting essentially of alternating marl and argillaceous limestone (1000 m-thick). The stratigraphic section continues with the Oligocene-Miocene series. The Oligocene-Early Miocene times is represented by sandstones and clays. The Late Miocene consists of continental molasses, sandstones and clays, 2,000 m thick, discordant on a regional scale, on earlier folded series.

From a structural point of view, The Bou Jaber E-W- to SE-NE-trending diapiric structure corresponds to a complex southeast-overturned anticline formed by Cretaceous marine strata that are pierced by a Triassic salt diapir. This structural organization is the result of a long-live salt diapir halokinesis and piercement that begun during the Aptian and continued during the compression, faulting and thrusting events of the Miocene Alpine orogeny. During these events, the Aptian/Upper Albian unconformity is overprinted
by the E-W to NE-SW-trending Bou Jaber Fault (Bouhlel 1987). Furthermore numerous N-S to NW-SE
trending faults cut the peridiapiric Cretaceous strata into a number of displaced blocks and the NE
termination of the Bou Jaber diapiric structure is intersected by the NW-trending Bou Ghanem graben filled
by Miocene and Pliocene continental conglomerate, sandstone and clay.

Mineralization

The known carbonate-hosted mineralization at Bou Jaber diapiric structure forms several small to medium
size deposits, fault-controlled and hosted by peridiapiric strata of the Aptian and Lower Albian platform
limestone. The deposits are dominated by barite or sphalerite+galena or fluorite: Pb+Zn+Ba at the “gîte du
col”; Pb-calcite at the “gîte du centre”; Pb-Zn+calcite at the “gîte Esperance”; and Ba-F±Pb-Zn at the “gîte
de l’Est” (Fig. 3a). This indicates that the western deposits are dominated by Pb-Zn and the eastern deposits
are dominated by Ba-F (with minor Pb and Zn). Fluorite-rich zones are probably genetically related to the
NW-trending faults limiting the Bou Ghanem graben.

The “gîte de l’Est” mineralization (Fig. 4) is hosted in the unit 5 of the Aptian platform/reef limestone
which is uncomfortably overlain by mid-upper Albian-Cenomanian shale and marl. Mineralization fills
breccia bodies and hydrothermal dissolution cavities distributed along roughly E-W faulted zones
overprinting the Aptian/Upper Albian unconformity. Ore rich zones are often located at the intersection zones
of NE- and NW-trending faults. In the central part of the deposit, near shaft 5, rich ores form three roughly
vertical ore bodies termed A, B and C (Fig. 4d). Each of these ore bodies has a thickness of 5 to 40 m, and is
roughly E-W-striking length of about 500 to 700m and extends to depths greater than 400 m. Underground
mapping and drill holes show that most ore bodies have the following zonation, from the border to the ore
body core: sulfide rich-zone, mixed barite/sulfide zone and late barite rich-zone.

A number of liquid hydrocarbon seeps occur along fractures and within various porous zones of the
permeable Aptian host limestone and as impregnations and residue within the ores. It consists of degraded
liquid hydrocarbons composed of saturated hydrocarbon (18.9%), aromatic (7.2%), asphaltene (55.6%), and
resin (18.3%) (Maameri and Daadouch 1986). The total of the heavy hydrocarbon fraction is about 74%, and
the resin/asphaltene ratio is 0.34% (Maameri and Daadouch 1986). Potential source rocks belong to the Upper
Albian-Cenomanian calcareous shales of the Fahdene Formation, containing ~2 wt% to ~13 wt% COT (Saidi
and Belayouni 1994). This organic-rich formation was buried during the Campanian-Eocene period to a depth
of about 3,000 m and organic maturation processes produced oil and gas as demonstrated by the numerous oil
seeps in the Bou Jaber mine and neighbouring regions and by oil wells sourced from the Aptian limestone in
the Central Tunisian Platform (e.g., Douleb and Semmama oil fields; Belayouni et al. 1992). Oil generation
probably began in the Maastrichtian-Eocene times, resulting from subsidence, but peak petroleum generation
probably occurred in the Miocene and Pliocene (Belayouni et al. 1992) in parallel with the Alpine orogenic
events.
In the absence of direct dates on ore emplacement, constraints on the age of ore formation can be made from geological relationships of the geological controls on the deposits. The ores are strongly controlled by regional faults and therefore the age of ore must be as old as or younger than these faults. The structural elements are: a) the Bou Jaber diapir is located on the regional deep Tajerouine Fault; 2) the ores are located along E-W- to NE-SW-trending faulted zones including the faulted Aptian-Upper Albian unconformity) and ore-rich zones are concentrated at the intersection of the SW-NE with NW-SE faults. These tectonic elements were derived from the Miocene tectonic events of the Alpine orogeny. Thus the timing of the ore emplacement at Bou Jaber must correspond to (or possibly younger than) the Alpine orogeny in the Miocene times (Sainfeld 1956; Bouhlel 1993). Furthermore, this time of mineralization coincides well with the maximum stratigraphic burial and subsequent hydrocarbon generation and migration into the peridiapirc strata.

**Sampling and analytical methods**

About 100 samples of Aptian limestone, ankerite, sphalerite, galena, barite, and calcite were collected from underground, open pit exposures and drill cores. The majority of the samples were collected on the -63, -69 and -95 m levels of the mine and are representative of the A, B, and C ore bodies (Fig. 4d). Within a given ore body, minerals were collected from different zones (e.g., sulfide rich, mixed barite/sulfide and barite rich). Gypsum was obtained from Triassic evaporites outcropping on the north side of Jebel Bou Jaber and from other Triassic evaporite diapirs of the region. Mineral separates for C, O, S, Sr, Pb isotope analysis were prepared by hand-picking or by use of a dental drill.

Ore textures, mineralogy and petrographic relationships were determined on hand samples on thin and polished sections using transmitted and reflected light microscopy.

Fluid inclusion studies were carried out on a variety of minerals from the main stage of mineralization: sphalerite, barite, fluorite, and calcite. Samples were prepared as standard 200- to 500µm-thick doubly polished wafers. The measurements were carried out at the Earth Sciences Department, Faculty of Sciences of Tunis, using a Linkam THM600 freezing-heating stage on a Leitz microscope. The system was calibrated using pure CO$_2$ fluid inclusion (-56.6 °C), the freezing point of H$_2$O (0°C), and melting points of Merck NaCl standards. The precision was ±0.5°C. Fluid salinities were calculated as weight percent NaCl equivalent (wt% NaCl eq.) using the equation of Bodnar (1993). Standard procedures were carried out, with initial petrography to determine inclusion types and paragenesis in order to select material for subsequent micro-thermometric measurements. The 200 to 400µm doubly polished wafers were also examined with an epi-fluorescent microscope to observe the fluorescence of hydrocarbon-bearing inclusions.

Fluid inclusions hosted in fluorite and barite were analysed individually by LA-ICPMS. Inclusions were chosen that were clearly primary, occurring in growth zones, but in addition, fluid inclusion assemblages (FIA’s) that were pseudosecondary and in some cases secondary in origin, were analysed to determine the full
range of possible fluid compositions in the ore-deposit. Individual inclusions, or groups of small related
inclusions were analysed by Laser-ablation inductively-coupled mass-spectrometry (LA-ICPMS) using an
Agilent 7500c mass spectrometer, combined with a Geolas ablation system. This system uses a Compex 103
ArF excimer laser with a wavelength of 193 nm and an energy density between 10 – 15 Jcm⁻² at the sample
surface. The operating frequency of the laser was typically 5Hz with spot sizes of 25µm and 50µ, the main
criteria being that the size was greater than that of the inclusions. Several small inclusions could be ablated
together to provide sufficient mass for analysis if inclusions were very small. The ablated material was
transported from the ablation cell to an Agilent 7500c ICP-MS using 99.9999% He flowing at 2 ml min⁻¹ into
a cyclone mixer where it was combined with the Ar carrier gas flowing at 1.02 ml min⁻¹. The mixer prolongs
the signal from the ablated inclusions and improves precision by increasing the number of cycles through the
selected elements and therefore the number of determinations of their ratio relative to Na. The instrument
was operated in reaction cell mode using 2.5 ml min⁻¹ 99.9999% H₂ to remove interferences from ⁴⁰Ar on
⁴⁰Ca and from ³⁶ArO on ⁵⁶Fe. Element/Na intensity ratios were converted to weight ratios using the NIST
glass standard SRM-610. For K/Na the soda lime standard SRM-1412 was used in addition to SRM-610 as it
has a K/Na ratio of 1 which was closer to the analysed ratios of K/Na in barite while the K/Na ratios in
fluorite are closer to the value of SRM-610. Instrumental drift was checked using SRM-610, which was
insignificant over each day’s analysis. Integration of the standard and sample signals used the SILLS software
package (Guillong et al. 2008). Full details of the analytical protocols and calibration of the instrument are
presented in Allan et al. (2005). The moderate to high salinities of the inclusions and their size enables the
signal from the ablation of fluid inclusions to be easily distinguished from any matrix signal. The ablation of
the host fluorite or barite precedes opening of the inclusions and continues after the inclusion signal has
ceased. Therefore, any signal from the sample matrix is easily observed and can be removed by the SILLS
software. The distinction between inclusion and matrix is based on the sharp rise and then decrease in the
inclusion signal over a period of c. 10-15 seconds, whereas the matrix signal is more constant over the entire
ablation period. In addition, areas of fluorite and barite that were free of inclusions were ablated for a total of
200 pulses to determine if they contained any significant concentrations of the elements to be determined in
the inclusions. In fluorite-hosted samples there was no contamination from the matrix except for Ca and Sr in
one sample. In barite there was considerable contamination from the mineral matrix for elements such as Fe,
Zn, Sr, in addition to Ca and Ba from the fluid inclusion host mineral. This signal from the contamination
could not be resolved from that of the fluid inclusions because it was too erratic.

Stable isotopes analyses were obtained at the U.S.G.S. Crustal Geophysics and Geochemistry Science
Center stable isotope laboratory in Denver following the procedures of McCrea (1950) for carbonates and
Giesemann et al. (1994) for sulfur minerals. Isotopic compositions are reported in δ-notation relative to
VPDB for carbon, VSMOW for oxygen, and VCDT for sulfur. Precision of the analyses is better than ±0.1‰ for carbonates, ±0.2‰ for sulfur, and ±0.5‰ for oxygen in sulfates.

Strontium isotopes analyses were performed on nine barite separates and on one gypsum sample. Sample separates were finely milled, dried for four hours, than leached overnight in 6N HCl at 100°C overnight. Dry residues were dissolved in 2.5N HCl. After centrifugation, strontium was separated using standard cation exchange procedures. Sr isotopes ratios were measured on a thermal ionization mass spectrometer at the Centre Petrographique et Géochimique (CRPG), Nancy, France. Strontium deviation of analysis was usually ±0.00004.

Lead isotopes analyses were performed on galena separates selected by hand picking under a binocular microscope and then rinsed with doubly distilled water. Lead isotopes analysis were performed using the Thermal Ionization Mass spectrometry (TIMS) at the Geochronology and Isotope Geochemistry Laboratory, University of North Carolina, Chapel Hill, following the procedure described by Skaggs et al. (2012) and Garnit et al. (2012).

Results

Ore textures and mineralogy

The ore mineralogy consists of three distinct mineral assemblages representing at least three mineralizing events. (1) breccia-hosted sphalerite-galena ores with rare pyrite and some tetrahedrite micro-inclusions in galena; (2) cavity-fill barite-rich ores; (3) replacive and geodic fluorite (+ minor Pb-Zn sulfides). Post-ore calcite fills thin fractures. Alteration mineral assemblage is represented by ankerite and quartz. A generalized paragenetic sequence for the minerals at the Bou Jaber mine is given in Fig. 5.

Breccia-hosted sphalerite-galena ores (stage 1)

The sphalerite-galena ores are hosted in dissolution-collapse breccias cross-cutting the Aptian limestone strata. Breccia elements are composed of light grey Aptian limestone (2 cm to 2 m across) and are surrounded by black matrix (Fig. 6, a-c). The latter is composed of kaolinitic mudstone, minor fine-grained cubic pyrite (20 to 150 µm in size), calcite relicts, organic matter debris and abundant fine-grained hydrothermal bipyramidal quartz (100-200 µm) (Fig. 6, e-g). This black mudstone matrix is also observed in small veins and stylolites. This matrix is the main host the sulfide concentration (Fig. 6, b-c). Sphalerite occurs as honey to light brown euhedral crystals 1 to 8 mm across, with a dark brown core (Fig. 6, d-f). Galena is less abundant than sphalerite (Fig. 6, b-c ) and precipitated during and after sphalerite deposition as indicated by geometric relationships and overgrowths (Fig. 6g). Minor epigenetic galena crystals, 1 to 2 cm across occur as irregular disseminations that replaced the limestone wall rock. Both sphalerite and galena contain abundant inclusions of micrite grains (up to 200 microns), bipyramidal quartz (100-200 µm), organic
matter (5-20 µm) and pyrite microcrystals (20-50 µm). These insoluble residues were inherited from the
decalcification of the black matrix hosting the sulfide assemblage described below, as well from the
dissolution of Aptian limestone host rocks. Bipyramidal quartz is the first hydrothermal alteration of the host
rocks and pre-date sulfide deposition. Only rare barite (barite-1) aggregates have been observed in the sulfide-rich
ore zones or in laterally equivalent breccias, so it seems unlikely that the sulfides replaced barite in this
deposit. The black mudstone-hosted sulfides may represent limestone insoluble residue, which is common in
most carbonate-hosted deposits and districts where carbonate dissolution breccias are present and commonly
described as internal sediments (Sass-Gustkiewics 1996; Leach and Sangster 1993; Matlock and Misra 1993;
Bouabdellah et al. 1996).

Barite- and ankerite-rich ore (stage 2)

Barite-rich ores fill hydrothermal dissolution cavities up to several meters in diameter (Fig. 7a). The wall
rocks of the cavities have been partly to completely replaced by coarse-grained ankerite (ank-1) that forms 5
to 20 cm-thick halos lining the barite-rich ore bodies. Ankerite-1 occurs as aggregates of well-formed
rhombohedral crystals, 1 to 5 mm across (Fig. 7b). In numerous places, the barite-rich ores consist of
alternations of white and black coloured bands (Fig. 7, c-d). The black bands are composed of black
mudstone similar to that described above in the sulfide stage containing fine-grained quartz-barite1-
sphalerite-galena assemblage overprinted by aggregates of stage 2 ankerite (ankerite-2) which is often
replaced by black fluorite-1 (see fluorite stage below). The white bands, 2 to 20 cm in thickness, are
essentially composed of stacked or intergrown tabular barite crystals (barite-2), 0.5 to 3cm-thick and 2 to
20cm-long. In the central part of the barite-rich ore bodies, late-stage barite (barite-3) forms spectacular very
large white to transparent barite crystals (50 cm to up to 1.5 meter-long and up 10 to 30 cm-thick) that
occupy 80 to 90% of the cavities (Fig. 7e).

Fluorite (+minor sulfides) stages and post-ore calcite (stage 3)

Massive dark to black fluorite (fluorite-1), with small amounts of sphalerite and galena, most commonly fills
polygonal spaces between intergrown barite crystals. In detail the fluorite-1 has partially to completely
replaced the calcite and ankerite that previously cemented sulfides and barite crystals (Fig. 7f). The black-
colour of this fluorite is due to abundant solid inclusions (e.g., sphalerite, micrite, ankerite, black clay, and
fine-grained hydrothermal bipyramidal quartz), and to abundant oil inclusions. Following the fluorite-1 stage,
fluorite-2 (with minor sulfides) forms geodic cubic crystals from few mm to 5 cm across, which are
colourless or purple. This fluorite is commonly coated by rhombohedral crystals of ankerite up to 5 mm
across (ank-3), and by late stage calcite occurring as large scalenoedral crystals calcite up to 5 cm across.
Post-ore spar calcite occurs in thin open fractures (5 to 20 cm wide) crosscutting the previous described ores and the host rocks.

**Fluid inclusions petrography and microthermometry**

Few fluid inclusions are observed in sphalerite; however barite-, fluorite-, and late-stage calcite contain numerous primary and secondary fluid inclusions suitable for fluid inclusion study. In these minerals primary fluid inclusions were identified in the context of Roedder (1984) and Goldstein and Reynolds (1994). They are classified in three types (Fig. 8): (1) Liquid water + vapour (Lw+V); (2) Liquid petroleum + Vapour (Lp+V); (3) Liquid water + Liquid petroleum + Vapour (Lw+Lp+V).

**Aqueous fluid inclusions microthermometry**

The microthermometric data derived from the primary fluid inclusions in sphalerite, barite, and fluorite from the Bou Jaber “Gîte de l’Est” are given in Table 1. Sphalerite contains small (5- to 20 µm size) Lw+V and Lp+V fluid inclusions. Microthermometric analysis performed on the Lw+V inclusions yielded first melting temperature (Tfm) values in the range of −40° and −30 °C. The final ice melting temperatures (Tmice) vary from −18° to −13°C with a mode at −16°C. The homogenization temperatures (Th) range from 120 to 136°C with a mode at 128°C (± 5°C). Calculated salinities range from 17 to 20 wt% NaCl eq. with a mode at 19 wt% NaCl eq. (± 1%).

Transparent and geodic barite crystals (barite-2 and barite-3) contain numerous two-phase inclusions (Lw+V) (5- to 200µm size) that form locally abundant clusters. Fluid inclusions indicating stretching or necking down (Roedder 1984; Ulrich and Bodnar 1988) are not measured. It is well known that barite is susceptible to stretching of the fluid inclusions by modest heating beyond their trapping temperature (Ulrich and Bodnar 1988). Therefore, only sets of primary fluid inclusions that had the same Th values are reported. Nevertheless, there is an unknown level of uncertainty regarding the Th data for barite, consequently the reported Th values should be considered “maximum” temperatures for fluid trapping. In general the (Lw+V) inclusions present generally the same volumetric proportion of the liquid to vapour phases (L = 90 to 95 %; V = 5 to 10 %). The first melting temperature (Tfm) values range between about −45 to −19 °C (ave. −34±7°C, n=36). The final ice melting temperatures (Tmice) range from −14 to −8°C (ave. −10±1°C; n=31). The homogenization temperatures (Th) range from 100 to 130°C (ave. 114±10°C). Calculated salinities range from 11 to 15 wt% NaCl eq. (ave. 13 wt% NaCl eq. ± 1%).

Fluorite-1 and fluorite-2 samples contain abundant two-phase inclusions (Lw+V) (5- to 200µm size). The Tfm recorded temperatures range from −45° to −28°C. The final ice melting temperature (Tmice) values vary from −20° to −12 °C with a mode of −17°C. The homogenization temperatures range from 140° to 165°C.
(mean = 152±7°C). Calculated salinities range from 16 to 23 wt% NaCl eq. with a mean =20±1.5 wt% NaCl eq.

Transparent late-stage calcite crystals (calcite-2), overlapping fluorite in druses and caves, contain small but numerous two-phase inclusions (L_w+V) of about 5- to 50- µm size. The first melting temperature (T_{f_{m}}) values range between −33 to −30 °C. The final ice melting temperatures (T_{m_{icl}}) were in the range of −18° to −15.5°C with a mode of −17°C. The homogenization temperatures (T_h) range from 109° to 117°C (ave. 114±2°C). Calculated salinities range from 19 to 21 wt% NaCl eq., with a mode of 20 wt% NaCl eq.

Petroleum fluid inclusions

Liquid hydrocarbon fluid inclusions are observed in sphalerite and are abundant in fluorite. The inclusions in sphalerite are less than 5 to 10µm in size. Large inclusions (80 to 200 µm) are observed in the core- or along growth zones of fluorite crystals. In black fluorite crystals, petroleum-bearing inclusions represent more than 30% of the total inclusions. The black coloured fluorite is due to petroleum inclusion abundances.

Two types of primary fluid inclusions are observed: L_p+V and L_w+L_p+V fluid inclusions that are isolated or distributed along growth zones. These inclusions may coexist in the same mineral zones with aqueous inclusions (L_w+V). Secondary L_w+V and L_p+V fluid inclusions are located along fractures, cracks and cleavage planes. In transmitted light, liquid hydrocarbon inclusions are usually brown- to yellow-colored. In epifluorescence observations, most of the hydrocarbon inclusions show fluorescence emissions in the light yellow to light or deep blue colours.

Primary L_p+V inclusions recorded homogenization temperatures that range between 97° to 140°C, and are lower than the T_h values of coexisting aqueous inclusions (100° to 165°C). The differences in homogenization temperatures are about 20°C which probably reflects differences in pressure corrections caused by the greater compressibility of oil than water (Roedder 1963).

Semi-quantitative compositions of hydrocarbon inclusions trapped in barite and fluorite crystals were determined by infrared microscopy and microfluorometry, as described in Guilhaumou et al. (1990). Both techniques show the presence of aliphatic and aromatic components in the oil, but microfluorometry shows that in barite the components are aliphatic dominant and in fluorite aromatic compounds dominate. The transition from aliphatic-rich oil inclusions to more aromatic components correlates with the timing and temperature of barite to fluorite depositions. The temperatures associated with the deposition of barite are low at around 100° to 130°C, whereas in fluorite the temperature is higher at around 140° to 165°C. In addition, fluorite, being paragenetically later than barite indicates there was more time for the oil to mature.
Homogenization temperatures—salinity relationships

Salinities and homogenization temperatures from primary fluid inclusions (L+V) in sphalerite, barite, fluorite and calcite are shown in Fig. 9. The data indicate that sphalerite, barite, fluorite, and late stage calcite were probably deposited from fluids with homogenization temperatures of between 100 to 165°C (ave. 130°C±18°C) and salinities in the range of 11 to 22 wt% NaCl eq. (ave. 17.5±3 wt% NaCl eq.).

Based on the mineral paragenesis and the defined mineralization stages, the brine fluids are of three types: (1) the fluid that deposited sphalerite (A fluid) is characterized by high salinities (17 to 24 wt% NaCl eq.), and homogenization temperatures (112° to 136°C); (2) the fluid responsible for barite deposition (B fluid) is characterized by low salinities (11 to 17 wt% NaCl eq.), and low temperatures (Th = 100° to 130°C); (3) fluorite was deposited by fluids (C fluid) with salinities ranging from 19 to 21 wt% NaCl eq. (ave. 20%), and relatively high homogenization temperatures of 140° to 165°C; and (4) late-stage calcite was deposited by a fluid (D fluid) with Th ranging from 109° to 117°C and calculated salinities between 19 to 21 wt% NaCl eq. (mode at 20 wt% NaCl eq). The mean temperatures of the ore fluids decreased from sphalerite (125°C) to barite (115°C) and increased during fluorite deposition (152°C); then decreased to ~110°C during the late stage calcite precipitation.

Composition of fluid inclusions using LA-ICPMS

Approximately 200 fluid inclusions hosted in fluorite and barite were analysed individually by LA-ICPMS. A summary of the element/Na weight ratios for individual fluid inclusions and their reproducibility (based on more than 30 measurements for each sample) is presented in Table 2. The average weight ratios have also been converted to elemental concentrations (ppm) based on the average salinity of the inclusions in fluorite (18 equiv. wt% NaCl) and barite (13 equiv. wt% NaCl) determined by microthermometry (Banks et al. 2000). The accuracy of the calculation relies on the ability to measure all of the cation/Na ratios in the inclusion which are impossible for Ca and Ba because these are the cation in the host mineral. In fluorite it was possible to estimate the Ca/Na ratio from the ice and hydrohalite melting temperatures and using the NaCl-CaCl2-H2O phase diagram to calculate the Na/Ca ratio, which was found to be approximately 0.5. In barite, Ca is present as CaCO3 and CaF2 solid inclusions in the mineral matrix and contaminates the fluid analyses. It was also not possible to observe the ice-hydrohalite melting relationship in these inclusions; therefore it was not possible to directly estimate the Ca/Na ratio of these inclusions. Based on similarities between other elements in fluorite and barite hosted inclusions, we assume the Ca/Na ratio to be similar to that in fluorite. In the barite the ratios of Ba, Zn, and Sr to Na were also unreasonable high and were clearly from contamination in the host mineral.

The fluid inclusions in fluorite are dominated by Na>Ca>K>Mg, with the concentrations of Sr, Fe and Zn each being equivalent to that of Mg. Concentrations of ore metals such as Cu are 250 to 450 ppm, Zn 850...
to 2100 ppm, and Pb150 to 430 ppm. The difference in the concentrations between the different fluorite-hosted fluids are, in the majority of cases, statistically significant and not due to the precision of the replicate analyses. The composition of the major cations in the barite-hosted inclusions are different to those in fluorite. These are dominated by K>Na>Ca>Mg, with Cu and Pb at significantly lower concentrations than in fluorite. Due largely to the different K/Na ratios, bivariate plots of pairs of individual inclusions analyses (Fig. 10, a-l) show there are 2 distinct fluid compositions, whereas other ratios, such as Mg, Li, Sr, Cu, Pb and Mn/Na are broadly similar. The elemental ratios of the 3 fluorite samples largely overlap indicating a common fluid. Differences in the Mg/Na and K/Na between samples BJ9612 and the other samples are real but not significant enough to indicate these inclusions contain another distinct fluid.

Isotope geochemistry

Carbon and oxygen isotopes in carbonates

The isotopic results for barren Aptian limestone (n=4), mineralized limestone (n=9), ore ankerite (n=8) and post ore calcite (n=18) are listed in Table 3 and shown on Fig. 11. The limestone have δ¹³C values ranging from -2 to 3.9 ‰ and δ¹⁸O values ranging from 26.2 to 30.1‰, within the ranges typical of marine limestones of Cretaceous age (Veizer and Hoefs 1976; Land 1980). The values are comparable to values reported for Aptian limestones elsewhere in Central Tunisia and eastern Algeria (M’Rabet1987; Bouzenoune and Lecolle1997).

Ankerite-1 (n=3) which precipitated after the sulphide stage and before barite, has δ¹³C values of 2.7 to 3.6‰ and δ¹⁸O values of 26.8 to 26.9‰. Ankerite-2 (n=3), which precipitated after barite, has δ¹³C values of 2.4 to 3.6‰ and δ¹⁸O values of 26 to 27‰. Ankerite-3 (n=3), which precipitated in geodes after fluorite, has δ¹³C values of -0.5 to 1.5‰ and δ¹⁸O values of 19.6 to +22.9‰.

Five samples of early calcites (calcite-1), which precipitated in geodes after fluorite-2 and ank-3, have δ¹³C values of 1.3 to 3.8‰ and δ¹⁸O values of 18.8 to +23.1‰. Late calcite (calcite-2) (n=11) has δ¹³C values of 2.6 to 6.2‰ and δ¹⁸O values of 24.8 to 27.4‰. Calcite-2 occurs in late thin fractures and appears to be precipitated after the end of the mineralized hydrothermal system.

The pre-barite ankerite (ankerite-1) and post-barite ankerite (ankerite-2) show similar ranges of δ¹⁸O values, 26.8–26.9‰ and 26–27‰, respectively, isotopically similar to the lowest δ¹⁸O Aptian limestone (26.2–30.1‰); whereas the fluorite–ankerite-3–calcite-1 sequence contains the ankerite and calcite with lower δ¹⁸O values, 18.8–23.1‰ and 19.6–22.9‰, respectively, although there is greater isotopic variation in the hydrothermal carbonates (ankerite-1,2,3 and calcite-1) (18–27‰) than in the Aptian limestones (26.2–30.1‰) (Fig.11).
The δ¹³C values of host limestones and hydrothermal ankerites are quite uniform: 2.0±1.9‰ for the limestones, 3.1±0.5‰ for pre-barite ankerite, 2.6±0.3‰ for post-barite ankerite, and 0.5±1‰ for post-fluorite ankerite. The isotopic similarity indicates that carbon in all three ankerite generations was derived from the local Aptian limestones, and that carbon isotopic equilibrium was established between hydrothermal fluids and the host limestones during the main stages of ankerite and sulfide precipitation. Late stage calcite shows higher δ¹³C values (3.6±1‰).

Oxygen isotopic compositions of limestone host rock are restricted to a narrower range (26.2–30.1‰) than the hydrothermal ankerite and calcite generations (19.6–27.4‰). The limestones represent the isotopically heaviest carbonates. The δ¹⁸O values of carbonates display a general downward trend in the following sequence: limestone (26.2–30.1‰) → pre-barite ankerite (26.8–26.9‰) ≈ post-barite ankerite (26.8–26.9‰) → post-fluorite ankerite (19.6–22.9‰) ≈ post-fluorite calcite (18.8–23.1‰). This trend resembles similar trends that have been observed at other MVT deposits (e.g., Frank and Lohmann 1986; Nesbitt and Muehlenbachs 1994; Spangenberg et al. 1996) in which isotopically lighter O is seen in paragenetically late carbonates compared to the unaltered host carbonates. The carbonates exhibit a positive covariation in a δ¹³C vs δ¹⁸O plot.

Sulfur isotope characteristics in sulfides and sulfates

Sulfur isotopic compositions were determined on 18 sphalerite, 43 galena, 3 pyrite, 45 barite and 22 gypsum samples (Table 4, Fig. 12). The pyrites have δ³⁴S values of about 16‰, and sphalerites range from 8.4 to 9.8‰. There are no significant differences in sphalerite compositions among different sampled ore bodies, or within ore zones in a single ore body, or even among sulfide stages. Galenas associated with the analyzed sphalerites range from 1.1 to 9.6‰. Most of the galena δ³⁴S values occupy a narrow interval between 5 and 6‰. There is no significant difference between the galena that replaced the breccia matrix in dissolution cavities-type ores (1.1–8.2‰; ave. 5.7‰), and epigenetic galena porphyroblasts in the host rocks or galena associated with the fluorite stage event (3.2–9.6‰; ave. 6.6‰).

The δ³⁴S values of Triassic gypsum range from 13.4 to 17.0‰ (ave. 15‰, n=12) similar to previously reported compositions for Triassic gypsum of the Diapir Belt (Sheppard et al. 1996; Salmi-Laouar et al. 2007). These values match the δ³⁴S values of Triassic seawater (13–16‰) (Claypool et al. 1980; Kampschulte and Strauss 2004).

The δ³⁴S values of barite range from 18.4 to 24.5‰ (ave. 22‰, n=45) (Table 4, Fig. 12, a-b). Despite their wide spatial distribution, either within a single ore body or throughout the three ore bodies, the barites show a relatively narrow range of δ³⁴S values.
Oxygen isotope characteristics in sulfate minerals

The δ¹⁸O values for Triassic gypsum range from 13 to 16‰, in good agreement with the δ¹⁸O value of marine sulfate in Triassic time (Claypool et al. 1980). The δ¹⁸O values of barites vary between 19.6 and 23.5‰ (ave. 22‰, n=13). The higher values imply that barite did not form simply by dissolution and re-precipitation of Triassic evaporite minerals. In fact, the barite δ¹⁸O values are higher than the value of marine sulfate of any age (Claypool et al. 1980). Thus, rather than reflecting the source of the sulfate, the values reflect either isotopic exchange, possibly involving oxygen exchange with H₂O driven by hydrothermal heating, or a reservoir effect associated with partial reduction of a fixed sulfate pool.

Radiogenic isotopes

87Sr/86Sr ratio in barite and gypsum

In order to constrain the origin of high-barium fluids and to monitor possible changes in fluid composition during barite deposition, nine samples of barite from the main barite stages were selected for ⁸⁷Sr/⁸⁶Sr analysis. In addition one sample of anhydrite from the Triassic diapir was analysed. Results of the ⁸⁷Sr/⁸⁶Sr analysis are listed in Table 5 and presented on Fig. 13. Regional ⁸⁷Sr/⁸⁶Sr ratios for Cretaceous sediments (Calvez et al. 1986) are also shown for comparison. A slight trend of ⁸⁷Sr-enrichment is observed from early to late generations of barite crystals. This trend indicates extensive exchange reactions between hydrothermal fluids and source rocks. A similar trend was observed in calcite generations in carbonate-hosted Pb-Zn deposits (Lange et al. 1983; Spangenberg et al. 1996).

Bou Jaber barites show Sr isotope compositions ranging from 0.709821 to 0.711408; these values are radiogenic compared to Triassic anhydrite with a ⁸⁷Sr/⁸⁶Sr ratio of 0.70800, which is close to the estimated ratio for seawater during Triassic times (0.7073–0.7080; Veizer and Compston 1974; Burke et al. 1982). The barite Sr-isotopes values are also more radiogenic than the Tunisian Cretaceous sediments (0.707400 to 0.707600; Orgeval 1994) that are close to the ratios of 0.70730 to 0.70750 for Cretaceous seawater (Koepenick et al. 1985). The radiogenic strontium of the Bou Jaber barite might reflect leaching of a feldspar-rich reservoir containing rocks and/or rubidium-rich minerals.

Lead isotopes

Sixteen samples of galena were collected from the Bou Jaber ore deposit for lead isotope analysis. Results are presented in Table 6 and plotted in Fig. 14, and are compared to fields of sulfide lead compositions from 24 Tunisian Pb-Zn deposits of the Tell thrust zone and the Atlas Foreland (Bouhlel et al. 2013) and to the Pb-isotope compositions of a 15 Ma biotite microgranite sample from the Nefza region (Decrée 2008) and from
the Galite island in the Tunisian offshore (Juteau et al. 1986), about 120 Km and 150 km north of Bou Jaber
area, respectively (Fig. 1).

Bou Jaber galenas have $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ values ranging from 18.697–18.786 (ave. 18.729), 15.643–15.762 (ave. 15.679), and 38.7057–39.228 (ave. 38.842) respectively. Results show
remarkable homogeneity of lead isotope compositions that plot within a narrow field, indicating a single or
homogenous source and suggesting a short duration of the mineralization event.

Lead isotope compositions form an elliptic field in both $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$
versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots. The majority of the analyzed galena samples plot in a field below the upper crust
evolution curve in the orogenic plot (Fig. 1a) and above the orogen curve (Fig. 1b) indicating the
dominance of continental crustal sources. In the orogenic plot, some of the galena samples plot clearly above
the upper crust curve (i.e. high $\mu$), indicating a large component of a radiogenic source. Some others plot
below the upper crust curve (i.e. low $\mu$), indicating a large component of non-radiogenic sources. The lead
field of Bou Jaber lies within the lead isotope field defined by the major Tunisian Pb-Zn deposits (Bouhlel et
al. 2013).

Given the homogenous Pb-isotopic compositions of the Bou Jaber galena samples, it is reasonable to
propose that the Bou Jaber ores were formed from fluids that passed through the same well-mixed source
rock(s) over a relatively restricted period of time. Bou Jaber is located on the SW-NE-trending Tajerouine
Fault (Fig. 1), reflecting the main Paleozoic-basement structural features that enabled diapirism and probably
influenced fluid migration. It is possible that the lead may have been extracted from the basement or from
siliciclastic feldspar-rich rocks in the basin, consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in barite.

The Pb-Zn isotopic lead field also overlaps that of the Miocene felsic rocks of the Galite Island and the
Nefza region. These rocks, related to Miocene anatexis, were derived from a metaluminous basement
(Belayouni et al. 2010). This feature may indicate that the ore lead and the felsic rocks were originally from
similar source rocks, and/or probably extracted at the same period.

The Bou Jaber galena samples give $^{207}\text{Pb}/^{206}\text{Pb}$ model ages from the plumbotectonic model of Zartman
and Doe (1981), between 400 and 300 Ma (Fig. 1a), older than the proposed Miocene age of the Atlasic
metallognic events (Sainfeld 1956; Rouvier et al. 1985; Bouhlel 2005). This retardation which is was also
observed for the Miocene felsic rocks (Decrée 2008) may be due to the contribution of a less radiogenic
material with low uranium content such as the lower crust).

Discussion

The Bou Jaber Ba-F-Pb-Zn deposit is located adjacent to a Triassic salt diapir in the Salt Diapir Belt (Fig 1).
Although there are more than 100 diapirs in this belt, only a relatively few have spatially associated economic
ore deposits. The diapir-related ore deposits in the Salt Diapir Belt contain three distinct ore assemblages
dominated by sphalerite and galena, barite, or fluorite. Some deposits like Bou Jaber contain ores of all three
assemblages (Fig. 1) whereas others contain only one assemblage (i.e., Bou Grine with sphalerite and galena;
Bouhlel et al. 2009). The presence of the three paragenetically distinct ore assemblages in a single diapiric
zone at Bou Jaber provides an opportunity to better understand how if at all, these mineral assemblages may
be related and insights into regional controls on the Zn-Pb-barite-fluorite mineralization.

Comparison to similar ores of the world

Until the recent studies at the giant Jinding diapir-hosted deposit in China (Leach et al. 2013), the resources
of diapir-related Zn-Pb ores were considered to be relatively small as well as uncommon relative to the
abundance of diapirs worldwide. Other than Jinding) the most significant diapir related ores were at the Bou
Grine Zn-Pb deposit (about 7 million tons 12% combined Zn+Pb). Other well-known diapir related
mineralization is also known from the Gulf Coast, United States with the Hockley Dome being well studied
(e.g., Kyle and Posey, 1991 and references therein). Due to the relatively small number of mineralized diapir-
related ores, there are few observations and data about the fundamental ore controls.

The new data presented here show that the diapir-related Bou Jaber lead-zinc ores have many geological,
textural and geochemical features of MVT lead-zinc ore deposits (e.g., Sverjenski 1986; Leach et al. 2005).
However, the presence of coeval barite or fluorite with the Zn-Pb ores is rare in MVT ores (e.g., Leach and
Sangster 1993; Leach et al. 2005). Where minor barite does occur in MVT ores, it is either early or late in the
paragenetic sequence and typically has distinctly different sulphur isotopic compositions from sulphide
minerals and different fluid inclusion compositions from associated sulphide- or gangue minerals, consistent
with different mineralizing events (e.g., Leach et al. 2005). In the giant Ozark MVT province in the
midcontinent of the United States, the world-class Southeast Missouri Zn-Pb district is devoid of barite or
fluorite occurrences. However, large barite deposits in the region formed from compositionally distinct fluids
and the ores are stratigraphically, spatially and temporally distinct. Ore fluids that transport and deposit MVT
or Clastic Dominated (CD) Zn-Pb ores can contain oxidized sulphur (and insignificant amounts of reduced
sulfur) that significantly limits Ba transport with significant sulphate (Cooke et al. 2000). Barite and or
celestite are present in minor amounts in the Hockley-, and Jinding Pb-Zn mineralization, however the barite
in these ores is interpreted to represent separate events related to the diagenetic transformation of the original
gypsum/anhydrite and not directly with Zn-Pb mineralization. In view of the world occurrences of
mineralized diapirs, the presence of abundant barite and fluorite in the Tunisian Salt Diapir Belt is unusual.

Perhaps the best examples of coeval fluorite with carbonate-hosted Zn-Pb mineralization are the fluorite-
dominated districts of southern Illinois and Central Kentucky of the United States. These deposits have been
considered a sub-type of a larger family of MVT ores because they are commonly associated with continental
rifts and are suspected of being related to a magmatic component of fluorine that mixed with basinal brines
assemblage overprints the main Zn-Pb MVT event in the Central Tennessee MVT district but this is likely to be related to the nearby Illinois fluorite event. There are many small Zn-Pb MVT ores in France and a few deposits have a late fluorite event, which is considered to represent an event superimposed on an older Zn-Pb event (Macquar et al. 1990).

Other than the Bou Jaber deposit, fluorite is not present in the Pb-Zn rich ore bearing diapirs either in Tunisia (e.g. Bou Grine, Fedj el Adoum) or in China (Jinding) nor is it reported from the Gulf Coast diapirs. Fluorite-rich diapirs, low in Zn-Pb mineralization are known both in Tunisia (e.g., the Zaghouan district; Bouhlel 1982; Bouhlel et al. 1988) and Morocco (e.g., Tirremi; Bouabdellah et al. 2013). However, a fluorite + barite (low Zn-Pb) ± calcite-dolomite-quartz mineral assemblage is more common in some vein deposits (e.g., U.S. Central Tennessee, Leach and Sangster, 1993; Zaghouan district, Tunisia, Bouhlel 1982; Bouhlel 1985; Bouhlel et al. 1988) and the Cevennes area, France; Macquar et al. 1990), particularly where basement-connected vein deposits cut the cover rock sequences.

Evidence for separate mineralizing events at Bou Jaber

The Bou Jaber ores display three mineral assemblages that are spatially and temporary distinct: (1) Pb-Zn sulfides within breccia bodies; (2) barite with early minor sulfides in dissolution cavities, (3) fluorite ores with minor sulfides that invade and crosscut the sulfide and barite ores and (4) three distinct fluids as shown from the mineral paragenesis and fluid inclusion microthermometry. Figure 5 shows the paragenetic relations of these three events: the main stage of sphalerite and galena was followed by the barite event and finally by the fluorite event. The combined fluid inclusion temperature-salinity plot (Fig. 10) clearly shows three distinct groups based on salinities and temperatures for sphalerite, barite and fluorite: a higher temperature-salinity field for fluorite, lower temperature-salinity field for barite and an intermediate field for sphalerite. Although this distribution could possibly be interpreted as a cooling and dilution trend of a single fluid, the LA-ICPMS analyses show the fluid inclusions in barite and fluorite have two different fluid compositions; no data are available on sphalerite. Inclusions in fluorite are metal-rich (100’s to 1000’s ppm Pb, Zn, Cu, Fe) but the inclusions in barite are metal-deficient. Bi-variant plots of pairs of individual inclusions analyses (Fig. 10, a-l) show there are 2 distinct fluid compositions based largely on the different K/Na ratios while other ratios, such as Mg, Li, Sr, Cu, Pb and Mn/Na are broadly similar.

Source of the ore fluids

The origin of high salinity brines that form sediment-hosted Zn-Pb ores is generally attributed to evaporated seawater with or without involving some minor amount of dissolved halite. Although information on the composition of ore fluids in diapir-related ores are scarce, data for two diapir-related metallic deposits, the Orduña-Murgía deposits in Basque-Cantabrian basin Northern Spain (Grandia et al. 2003) and the Jbel...
Tirremi fluorite-barite deposit in Morocco (Bouabdellah et al. 2013) show the ore fluids were dominated by high salinity brines representing a mixture of evaporated seawater and dissolved halite.

Unfortunately, there are no data on the composition of the Zn-Pb ore fluids other than the fluid salinity from the fluid inclusions. Therefore, nothing can be concluded about the origin of the Zn-Pb fluids other then they plot in a temperature-salinity space (Fig. 9) that differs from the fluorite and barite fluids. Inclusions in fluorite from the Bou Jaber deposit have Cl/Br and Na/Br ratios of several thousand, consistent with dissolution of halite whereas the inclusions analysed in barite have values lower than those of seawater which are indicative of a Br-enriched brine derived from the evaporation of seawater plus a component of halite dissolution. The Bou Jaber fluorite ore fluids are Na-Ca dominated with low Mg concentrations indicating significant dolomitization of limestone by the fluids. The salinity of the barite fluids could be the result of evaporation of seawater prior to halite saturation or by the dilution of a more saline fluid with meteoric water.

Furthermore, the higher K/Na values of fluid inclusions from barite suggest the brines interacted with K-rich rocks in the basement or in siliciclastic sediments in the basin. Oxygen isotope compositions of the ore fluid calculated from late stage calcite indicate that the δ18O of the fluid varied between ≈ +3 and ≈ +8‰. Such a fluid most likely originated from formation waters in isotopic equilibrium with the host rocks. The oxygen isotopic composition of the fluids that deposited the Bou Jaber Ba-F-Pb-Zn ores are similar to that of modern sedimentary basinal brines and MVT deposits (e.g., Mc Limans 1975; Mc Limans 1977) as well as in the nearby Fedj el Adoum deposit (Charef and Sheppard 1987).

Sources of the metals

The sources of metals in sediment-hosted ores are poorly understood. An extensive analysis of lead isotopes from sediment-hosted Zn-Pb ores (Leach et al. 2005) concluded that no single host rock type could explain the lead isotopic compositions of galena in the deposits. In many examples, the lead isotopic compositions of the ores suggest that the ore fluids may have interacted with the basement rock, the weathered regolith or basal sandstones or with detritus in the sediment cover rocks that contains material weathered from the basement rocks.

Interpretations of the lead isotope data from Bou Jaber indicates that the lead was derived from upper crustal rocks and it is reasonable to assume that these rocks were also the source of Zn, Fe and Ba. In Figure 14, the isotopic data for Bou Jaber lies within the large field defined by Pb-Zn deposits of the Tell Thrust Belt and the Atlas Foreland. These regions have the same Paleozoic basement rocks, which suggest that the basement rocks or sediment derived from the basement may have contributed metals in both regions. This suggestion is consistent with compilations of lead isotope compositions from global MVT ores (Leach et al., 2005) that suggest a relationship between the isotopic compositions of ores in the district and the compositions of the basement rocks.
Bou Jaber barites have Sr isotope compositions that are radiogenic compared to Triassic anhydrite or the estimated ratio for seawater during the Triassic and are also more radiogenic than the marine Tunisian Cretaceous sediments. The most likely source for the more radiogenic strontium in the barite is feldspar-rich rocks and/or Rb-rich minerals.

The possible sources for fluorine are problematic. The common spatial association of world fluorite deposits with continental rift basins leads to the speculation that fluorine was possibly derived from deep-seated basement sources (i.e., mantle gases as in the Illinois fluorite district; Plumlee et al. 1994; Kendrick et al. 2002). This suggestion is consistent with the abundance of fluorite deposits adjacent to Mio-Pliocene graben structures in the Tunisian Atlas Foreland (Fig. 1). Note that Bou Jaber lies along the border of the one of these grabens at the intersection with a salt diapir.

**Sources of Sulfur**

Based simply on proximity, gypsum in the nearby Triassic evaporite diapirs is the most obvious sulfur source for the Bou Jaber ores. However, sulfate minerals or sulfate-bearing formation waters within overlying, younger strata would also be plausible sources inasmuch as ore formation did not occur until Miocene–Pliocene time.

The reduced sulfur in sphalerite and galena was most likely produced by thermochemical sulfate reduction (TSR). The evidence supporting this interpretation is two-fold. First, the minerals show relatively narrow isotopic ranges and relatively high $\delta^{34}S$ values compared with the ranges and values that commonly result from bacterial sulfate reduction (BSR) in marine sediments or marine rocks (Machel et al. 1995).

Second, the fluid inclusion microthermometry indicates that temperatures were sufficient to drive abiotic reactions between sulfate and organic matter ($80–100^\circ C \times 150–200^\circ C$, Machel et al. 1995), the presence of which is confirmed by organic inclusions in sphalerite. Additional evidence for favourable temperatures for TSR are found in the isotopic results for 13 sphalerite-galena pairs, which yield consistent isotopic equilibration temperatures in the range 118–200°C (Table 4).

The mean $\delta^{34}S$ values for sphalerite and galena, 9 and 6‰, respectively, are 6–9‰ lower than the average value for the Triassic evaporites (15‰, Table 4). The offset in values is smaller than the kinetic isotope effect associated with TSR (−10 to −20‰; Machel et al. 1995), which implies that TSR consumed a substantial fraction of the available sulfate causing the isotope effect to be only partly preserved (Machel et al. 1995).

Thermochemical reduction of younger marine sulfate would also be compatible with the data. For example, the isotopic offset of sphalerite and galena from marine sulfate of Miocene age ($\delta^{34}S$~22‰; Paytan et al. 1998) would be 13–16‰, consistent with the full expression of the kinetic isotope effect.

The mean $\delta^{34}S$ value for barite (22‰) matches Miocene marine sulfate (~22‰) better than Triassic gypsum (~15‰, Table 4), but the Triassic cap rock is more likely to have been the source of barite sulfate.
The supporting evidence can be seen in a plot of $\delta^{34}$S versus $\delta^{18}$O (Fig. 12), which shows that the barite data extend toward the measured composition of Triassic gypsum rather than the composition of Miocene marine sulfate ($\delta^{34}$S~22‰, $\delta^{18}$O~11‰; Paytan et al. 1998; Turchyn and Schrag 2004). The colinearity of gypsum and barite strongly suggests that Triassic cap rock was the source of sulfate for barite formation and that the sulfate was isotopically modified by sulfate-consuming chemical reactions and possibly also by oxygen isotopic exchange reactions. Qualitatively, the isotopic modifications are what would be expected where TSR operated under conditions of limited sulfate supply, the increase in $\delta^{34}$S reflecting the kinetically-controlled preferential reduction of $^{34}$S-depleted sulfate and the increase in $\delta^{18}$O reflecting either preferential reduction of $^{18}$O-depleted sulfate or thermally-driven oxygen exchange between sulfate (or reduction intermediates) and H$_2$O. In that they show effects consistent with TSR under conditions of limited sulfate supply, the isotopic compositions suggest that barite may have formed from sulfate that remained at the site of ore formation after sphalerite and galena had precipitated. Thus, the simplest interpretation of the data is that Triassic evaporites furnished sulfur for both the sulfide and the barite event.

Processes of ore deposition

**Sphalerite-galena stage:** At the temperatures of ore deposition in the diapiric zone of a carbonate-rich sequence, ore-forming concentrations of Zn and Pb are possible in brine where the ratio of sulfate to reduced sulfur is very high. The deposition of the sphalerite-galena assemblage was most likely achieved by mixing this metal-bearing brine from deep in the basin with a reservoir of reduced sulfur already present in the diapir area. In this scenario, TSR processes involving organic matter in the diapir rocks had reduced sulfate in the diapir or in the fluids residing in the peridiapiric strata prior to the influx of the metaliferous brines. It is possible that some TSR processes may have contributed to the reduced sulfur budget by in situ TSR of sulfate in the inbound metaliferous fluid by local organic matter. Mixing processes of a metal-rich brine with reduced sulfur not only precipitates sulfides but also generates large amounts of acid that must be buffered by the carbonate host rocks. This process is shown by the abundance of dissolution breccia and collapse-breccia, caves, and enhanced pore space, host rock replacements and extensive vuggy porosity in the host rocks. Cooling of the ore fluid, as suggested by the crystallization of fine-grained bipyramidal quartz, may have also contributed to the precipitation of sulfides, but to a lesser degree.

**Barite stage:** The previous discussion of sulfur isotopes show that the colinearity of sulfur isotopes for gypsum and barite strongly suggests that Triassic cap rock was the source of sulfate for barite formation and that the sulfate was isotopically modified by sulfate-consuming chemical reactions (i.e., TSR) and possibly also by oxygen isotopic exchange reactions. Therefore, barite deposition must have been produced when a Ba-rich fluid with low Zn, Pb and perhaps with high-reduced sulfur mixed with the sulfate brine in the area of...
the diapir. Acid is also produced in this reaction that also led to the concurrent dissolution of the carbonate host rocks.

Fluorite stage (+ minor Pb-Zn sulfide): The high temperature of fluids responsible for fluorite deposition, and the dominance of a Na-rich fluid derived from the dissolution of halite are permissive for the formation of CaF-complexes. The high temperatures also account for the high metal contents measured in the fluid inclusions. At high temperatures, some reduced sulfur can be transported together with Zn and Pb (Yardley 2005). A fluid with this metal load and fluorine transport as a CaF complex can deposit fluorite together with sphalerite and galena simply by cooling and fluid dilution.

Timing of mineralization, structural controls, tectonic triggers and fluid migration

It is clear that multiple fluid reservoirs that include hydrocarbon-bearing fluids, evaporated seawater, halite dissolution brines as well as a presumed meteoric component were involved in the three distinct ore events at Bou Jaber (Fig. 14). The interactions of these fluids with other fluid reservoirs containing reduced sulfur (H$_2$S) or oxidized sulphur (SO$_4$) were essential to precipitate sulfides and barite. Assuming the evaporated seawater component formed during the deposition of the Triassic evaporites, these very dense and low viscosity brines probably migrated into the deep parts of the basin, including the Palaeozoic basement rocks. Given that fluid mixing was likely an important depositional process, the ascent of the dense, deep basinal fluid into upper stratigraphic levels required exceptional hydrological events. Although hydrological modelling of fluids in and about salt diapirs show complex fluid regimes such as thermohaline and density convection, release of geopressed fluids and focusing of fluids along impermeable evaporites and diapiric structures (e.g., Kyle and Price 1986; Evans et al. 1991), we suggest that normal basin and diapir-controlled fluid migration was not singularly responsible for ore deposition. If the Tunisian diapir-related ores formed from normal basin processes involving diapirs, then we would expect that there should be many more diapiric related ore deposits in the Tunisia Diapir Belt as well as in the Tethyan diapirs of Central Algeria- and Western Morocco parts of North Africa, as well as in Europe and other diapirs provinces in the world.

There is an increasing appreciation that major sediment-hosted Zn-Pb ores ore formed as a result of large-scale tectonic triggers (Leach et al. 2010) that released deep-seated fluids into favourable geochemical traps. This may be the situation for Bou Jaber and the other ore deposits of the Tunisia salt diapir belt. The first significant tectonic event after evaporite formation was mid-Cretaceous rifting during the Africa-Europe plate separation that produced tilted blocks, half-grabens and salt diapirism. There is no evidence for ore emplacement during this tectonic and diapirism period. However we suspect that the compressional event in mid-Miocene (Rouvier 1977) related to the African European plates subduction-collision that produced thrusting, SW-NE-trending folds and the return of salt diapirism, may have been the tectonic trigger that brought deep-seated brines into the upper parts of the diapir body and into the peridiapiric cover rocks. The
ascent of deep-seated Zn-Pb brines would have interacted with sources of reduced sulfur and hydrocarbons and precipitated the main-stage sphalerite and galena ores.

The diapirs may have focused fluid flow along the southeast flanks of the diapirs that define the Alpine thrusting. Diapir development was also responsible for the development of fracture permeability and creation of hydrocarbon and reduced sulfur chemical traps in the cover rocks. Furthermore, peak oil generation occurred in the Miocene and Pliocene (Belayouni et al. 1992) during accelerated burial in parallel with the Alpine orogenic events. About 50 km south of the Bou Jaber mine, the main oil fields produce hydrocarbons from the Aptian limestones reservoir, similar to that hosting the Bou Jaber ores. Perhaps the reason for mineralization in some diapirs and not others could be the “quality” of the chemical traps or the involvement of some “special” steeply dipping deep-seated faults (perhaps the NW-SE faults that cut the NE-SW trend of the diapirs). The proposed migration of the deep-seated brines during the Alpine orogeny, related to the effects of Alpine collision, provided uplift of the basin and over pressured fluids from thrust stacking and burial maturation of organic matter.

The previous discussion on deposition of the Zn-Pb rich ores proposed a fluid-mixing precipitation model that applies to many sediment hosted Zn-Pb ores (e.g., Cooke et al, 2000; Leach et al, 2005). However, an enigmatic question is how do the barite and fluorite events connect or not to the Zn-Pb ores at Bou Jaber? Although Zn-Pb, barite and fluorite ores do occur together in some ore zones in Bou Jaber, this association is inconsistent within the deposit as well as in the region (few mineralized diapirs contain all three mineral assemblages). The three mineral assemblages are clearly geochemically and paragenetically distinct but yet they were controlled by the same diapiric structures related to the Alpine orogeny in the Miocene-Pliocene times. As pointed out previously, the geochemical constraints on a hot basinal brine in a carbonate platform limits the ability of a single fluid to transport ore-grade amounts of Zn, Pb, Ba and F. Consequently, we suggest that an evolving tectonic and structural regime during the Alpine orogeny, resulted in the ascent of fluids from distinctly different fluid reservoirs. Zn-Pb rich ores formed by the mixing of an oxidized Zn-Pb brine into a hydrocarbon reduces sulphur gas reservoir, barite formed by the mixing of a Ba-rich fluid with sulphate-rich fluids and meteoric water in the diapiric zone and fluorite was deposited in the diapiric zone from a Na-rich brine by cooling, dilution, pH change in the diapiric zone.

Exploration Implications

Given the abundance of salt diapirs in the region, an obvious question is why do only a few have significant Zn-Pb mineralization? A likely factor that determines whether mineralization will occur in a diapir zone is the quality and size of the hydrocarbon and reduced sulfur reservoir. The essential role of a salt diapir in the mineralization process is the formation of a structural trap or reservoir around the diapir for hydrocarbon and reduced sulfur gases. The hydrocarbon and reduced sulfur-rich reservoir in the peridiapiric zone provides a
chemical trap for ascending metalliferous brines. Factors that influence the quality of the trap are the
abundance of gypsum/anhydrite in the mother salt, the size of the structural trap and the permeability and
porosity of the reservoir. The traps at Bou Jaber may have involved the diapir itself or the Albian shale as the
reservoir “seal” in the peridiapiric zone. Additionally, contacts between the Triassic evaporites and the
Cretaceous shale (on both sides of the evaporite diapir) are potentially important traps that have not been
recognized in the past.

The ores at Bou Jaber and other large tonnage deposits in the diapir belt are located in -or adjacent to-
organic-rich peridiapiric rocks along the south-eastern flank of northwest dipping diapirs. Mineralization is
especially common at the NE and SW extremities of the diapir. The locations of the ores appear to coincide
with the possible intersections of the SW-NE deep basement faults and NW-trending faults limiting Miocene-
Pliocene NW-trending grabens were controlled by the interaction of NW-SE to EW trending, deep seated and
steeply dipping faults that may have been the vertical pathway for ascending metalliferous brines that
precipitated ores in the peridiapiric zone. Therefore, the connectivity of faults in the basement with the upper
diapiric zones must have been essential. Lacking the connectivity, a salt diapiric zone would remain sterile in
sulfide mineralization.

A significant conclusion of the study provides evidence that decouples the mineral assemblages (Zn-Pb,
fluorite and barite) into separate and genetically unrelated mineralization events. Consequently, the presence
of barite or fluorite mineralization in any diapiric zone does not necessarily suggest the presence of Zn-Pb
rich ores.

Conclusions

This paper provides new insights into the ore-forming environment, sources of the ore components and
geological controls that produced the sphalerite, galena, barite and fluorite ores of the Bou Jaber deposit. In
contrast to previous authors, we show that the Zn-Pb, barite and fluorite mineral assemblages were produced
by at least three separate and possibly unrelated mineralization events. However, it is unclear how these
separate events are related to specific tectonic events and structural controls.

The exact ages of the ores are uncertain. Field relations are consistent with mineral deposition during the
Miocene Alpine Orogeny from multiple hydrothermal events: (1) Zn-Pb sulfides formed the mixing of two
fluids: one fluid metal-rich but reduced sulfur-poor and a second fluid containing reduced sulfur; (2) the
fluorite precipitated during from a more dilute fluid with higher temperatures; (3) barite precipitation
involved the influx of a meteoric water component that mixed with a barium-rich fluid.

Although the Bou Jaber ores are hosted in peridiapiric rocks, the fundamental genetic characteristics of
the ore deposit are remarkably similar to those for the MVT family. There are no obvious connections to
igneous events. The presence of abundant barite and fluorite with the Zn-Pb ores is unusual for a MVT deposit; however they overprinted a distinct and older Zn-Pb event. Therefore, the ores of Bou Jaber can clearly be classified as “MVT” or as a “MVT sub-type” or as Salt Diapir-related Zn-Pb ores.

The deposition of Zn-Pb ores was determined by the presence of a hydrocarbon-reduced sulphur reservoir about the salt diapir. Undoubtedly, the quality of the sulphur trap played a major role in the endowment of Zn-Pb of the deposit. Factors that influence the quality of the trap are the abundance of gypsum/anhydrite in the mother salt, the size of the structural trap and the permeability and porosity of the hydrocarbon-reduced sulphur reservoir.

The Zn-Pb ores at Bou Jaber resulted from the mixing of metalliferous sedimentary brine with reduced hydrocarbon-reduced sulfur reservoir in the peridiapiric environment. Consequently, a deep-seated (basement?) fluid component must have an efficient fluid pathway to ascend into the chemical sink in the peridiapiric zone. Therefore, the connectivity of faults in the basement with the upper diapiric zones was essential.

The studies presented here provide new insights into the genesis of the Bou Jaber Pb-Zn-Ba-F ore deposit and suggest that new research will be needed to improve our understanding of MVT ores in diapiric environments both in Tunisia and globally. In view of the giant diapiric ores of Jinding China, future discoveries of large resources of diapir-related ores in North Africa and globally require an increased focus on exploration in the peridiapiric environment.

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Fig. 1 Simplified structural and paleogeographic map of the Tunisian Salt Diapir Belt and adjacent regions showing the distribution of the Pb-Zn-Fe-Ba-Sr-F deposit groups discussed in text. Most of the ore deposits are spatially connected to Triassic diapirs. Bou Jaber is located at the SW area of the Salt Diapir Belt that corresponded to the SW margin of the Tunisian Trough. A-B line is cross section shown in Figure 2. Regional location is shown on inset map.
Fig. 2 Present day interpretative N-S structural section of northern-central Tunisia. For location see A-B line in Figure 1.
Fig. 3 Geology map of the Bou Jaber Triassic salt diapiric structure showing stratigraphy, principal structural elements and the main F-Ba-Pb-Zn deposits. Circled numbers (1 to 5) correspond to the cross sections in figure 4. b Present day NW-SE cross section showing the geometry of the Triassic salt intrusion trough the Tajerouine SW-NE-tending Fault (Cross section is located by the A-B line in figure 3a and the Tajerouine Fault is shown in Figure 1). c Interpretative N-S cross section of the Bou Jaber diapiric structure at the end of the Middle Miocene Alpine compression (not to scale)
Fig. 4 NW-SE cross sections a, b, c, d of the Bou Jaber “Gîte de l’Est”, illustrated on the basis of field mapping in mining open pits, underground working exposures and drill holes. The sections show some of the vertical and lateral variations in volumes of the dissolution-cavities filled with the Pb-Zn-Ba-F ore cross-cutting the Aptian limestone strata. (for location see a, b, c and d lines in Figure 3b).
Fig. 5 Schematic paragenetic sequence of the ore-, and mineral alteration assemblages in the Bou Jaber (Gîte de l’Est) Pb-Zn-Ba-F deposit. Bars thicknesses reflect abundance of minerals. Hydrocarbons occur as oil seepage in the ore and as oil-bearing fluid inclusions in the sulfide- and fluorite stages.
Fig. 6 Drill core samples of zinc-lead rich-ore from dissolution cavities where sphalerite and galena occur by replacement of carbonaceous breccia-matrix. a Dissolution breccia sphalerite-rich: Breccia fragments are grey Aptian limestone and black mudstone. The matrix is composed of fine-grained bipyramidal quartz, fine-grained honey sphalerite, galena, minor fine grained barite-1 and calcite. Liquid hydrocarbon (HG) fills cavities in the calcite aggregations. b Core sample of high grade massive sphalerite and galena. c Core sample of high-grade sphalerite (honey euhedral sphalerite crystals) aggregation in black mudstone breccia calcite-, quartz-, and organic matter-rich. d Detail from c showing sphalerite crystals cemented by calcite (red-S coloured). e detail from c showing aggregations of euhedral sphalerite crystals in a quartz- and calcite-rich matrix; quartz is white and calcite is red-S coloured. f Euhedral sphalerite in a matrix of calcite and quartz. Calcite is partly replaced by fluorite. g Euhedral galena containing bipyramidal quartz relicts of the replaced quartz-, calcite-rich sulfide matrix. d and e polished sections, transmitted light //; f and g polished sections, reflected light //. 
Fig. 7 Hydrothermal dissolution and ankeritization of the Aptian limestones (unit 5) followed by barite deposition in the gîte de l’Est deposit. a Hydrothermal dissolution of the Aptian limestones developed large irregular cavities, meter- to plurimeteric-size. An ankerite halo (ank-1), 5- to 50 cm-thick, lines the hydrothermal alteration of the host rock. The infilling material of cavities is composed of ankerite-2 and barite postdating minor sphalerite and galena. b SEM photograph of the euhedral coarse-grained ankerite crystals (ank-1) (sample from the ankerite halo). c Banded rich barite ore in dissolution cavity, showing horizontal banding compared to the 70° deeping of the Aptian limestones strata. White bands are barite and dark bands are a complex assemblage of ankerite-2, sphalerite, galena and fluorite. d Sample of banded barite-rich ore. The black matter is composed of ankerite and sulfide where most part of the ankerite is replaced by fluorite (as shown on Fig. 8f). The white bands are composed by tabular cm-size crystals of barite developed often orthogonally to the dark bands. e Barite zone formed by large barite crystals (central part of the hydrothermal dissolution cavities, underground working at level -95 m). Barite forms tabular crystals 5- to 20 cm-thick and 50- to 100 cm-length (scale is also shown by the hammer). f Fluorite-1 replacing ankerite matrix of sphalerite and galena crystals, polished section, reflected light //.
Fig. 8 a and b Primary L\textsubscript{w}+V fluid inclusions in fluorite. c Primary L\textsubscript{w}+V fluid inclusions in barite. d Primary L\textsubscript{w}+L\textsubscript{p}+V fluid inclusion in fluorite. e Large primary L\textsubscript{p} + V fluid inclusion in fluorite. f Same as Fig e but under epifluorescence microscope. L\textsubscript{w}=water; V= vapour; L\textsubscript{p} = Petroleum.

Fig. 9 Plot of Th versus salinity derived from microthermometric studies of fluid inclusions in sphalerite, fluorite, barite and calcite.
Fig 10 Bi-variate cation/Na weight ratios as determined by LA-ICPMS of fluid inclusions. Inclusions hosted in barite are distinctly different to those in fluorite indicating two fluids involved in mineralization. Analyses from individual samples are tightly clustered and for different fluorite samples largely overlap.
Fig. 11 Diagram $\delta^{13}$C (PDP) vs $\delta^{18}$O (SMOW) showing values for ankerite and calcite compared to the Aptian limestone host rock (Bou Jaber deposit).
Fig. 12 a Box plot of $\delta^{34}$S values for sphalerite, galena, pyrite and barite at Bou Jaber, and $\delta^{34}$S values for regional Triassic gypsum and anhydrite. The sulfur isotope compositions shown are isotopically relatively homogeneous with a composition near 6 ‰ for galena, 9 ‰ for sphalerite, 22 ‰ for barite and 15 ‰ for Triassic gypsum. b Histogram distribution of the $\delta^{34}$S values for sphalerite, galena, pyrite, barite and Triassic gypsum. c Plot of $\delta^{18}$O vs $\delta^{34}$S of Bou Jaber barites. The $\delta^{18}$O, $\delta^{34}$S of Triassic anhydrite are also plotted for comparison with barites.
Fig. 13 Strontium isotope ratio diagram comparing Bou Jaber barite ores with Triassic evaporite, Triassic sea water, Cretaceous sea water and with Tunisian Cretaceous sediments ($^{87}\text{Sr}/^{86}\text{Sr}$ values for Cretaceous sediments are from Orgeval 1994).
Fig. 14: Lead isotope ratios of galena sample from Bou Jaber Pb-Zn-Ba-F deposit reported in \( ^{206}\text{Pb}/^{204}\text{Pb} \) and \( ^{207}\text{Pb}/^{204}\text{Pb} \) diagram (uranium derived Pb) (14a) and in the \( ^{208}\text{Pb}/^{204}\text{Pb} \) and \( ^{207}\text{Pb}/^{204}\text{Pb} \) diagram (14b). Isotope composition are present-day values are not corrected to age. The upper crust, lower crust, orogen, mantle evolution curves are from Zartman and Doe (1981). Bou Jaber Lead isotope ratios fill in the field of sulfide lead compositions the Tellian thrust belt- and the Tunisian Atlas foreland Pb-Zn deposits (Bouhlel et al. 2013). The Bou Jaber Pb-isotope compositions are also compared to Pb ratios of Tunisian Miocene granite (values are from Juteau et al. 1986 and Decrée 2008.
Table 1: Summary of the microthermometric data derived from the studies of primary fluid inclusions (Lw+V) in sphalerite, barite and fluorite from the Bou Jaber “Gîte de l’Est”.

<table>
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<th>Sample</th>
<th>Mineral</th>
<th>Nbr IF</th>
<th>Te °C</th>
<th>Tm ice °C</th>
<th>Salinity Wt% NaCl equiv.</th>
<th>Th °C</th>
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<td>2525C1</td>
<td>Sphal</td>
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<td>-39 to -32</td>
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<td>112–133 (123)</td>
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<td>Sphal</td>
<td>34</td>
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<td>6921D</td>
<td>Sphal</td>
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<td>17.4–19.99 (18.1)</td>
<td>116–136 (128)</td>
</tr>
<tr>
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<td>17.2–21.47 (19.1)</td>
<td>112–136 (125)</td>
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<td>101–110 (105)</td>
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<td>110–114 (112)</td>
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<td>100–131 (119)</td>
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<td>15.6–17.4 (16.7)</td>
<td>115–118 (117)</td>
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<td></td>
<td>Total</td>
<td></td>
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<td>11.2–17.4 (13.9°)</td>
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<td>-18.2 to -15.5</td>
<td>19.0–21.1 (20.5)</td>
<td>109–126 (116)</td>
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Table 2 LA-ICPMS analyses of individual fluid inclusions in fluorite and barite from levels – 69 m and 95 m.

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<th>BJ6925 Fluorite</th>
<th>BJ9533 Barite</th>
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<td>StdDev</td>
<td>%RSD ppm</td>
<td>Average wt/wt</td>
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<tr>
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Concentrations in fluorite are based on a salinity of 18 wt% NaCl, barite salinity of 13 wt% NaCl. Ca/Na wt ratio is based on hydrohalite-ice melting temperatures in fluorite and assumed to be the same for inclusions in barite (not possible to measure).
Table 3 Carbon and oxygen isotopes compositions of Aptian limestone host rock, hydrothermal ankerite and calcite from Bou Jaber. Analysis marked with asterisk are from Salmi-Louar 2004; and Salmi-Laouar et al 2007

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<th>δ¹⁸O</th>
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<td>(‰, PDP)</td>
<td>(‰, SMOW)</td>
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Table 4 Sulfur and oxygen isotopes compositions sphalerite, Galena, pyrite and barite from the different ore bodies collected from different ore zones at levels (~63, ~69, and ~95 m) of the Bou Jaber mine (gîte de l’Est), Epigenetic galena and pyrite disseminated in Aptian limestones; and sulfur and oxygen isotopes compositions of Triassic gypsum collected from different salt diapirs of the area. Analysis marked with an asterisk are from Salmi-Louar 2004 and Salmi-Laouar et al. 2007). Calculated Temperatures are obtained using the equation \( \delta \text{ZnS-\deltaPbS} = (0.73/T^2) \times 10^6 \) (Ohimoto and Rye 1979).

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<th>Ore zones</th>
<th>Level (m)</th>
<th>Samples</th>
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<th>34/O%o (SMOW)</th>
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Sulfide/barite zone  -69  66/25Gn  Gn  4.9
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Sulfide/barite zone  -69  68/36Gn  Gn  6.0
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Barite zone  -69  70/31Ba  Barite  22.5
Barite zone  -69  71/32Ba1  Barite  22.5
Barite zone  -69  72/32Gn  Gn  5.5
Barite zone  -69  73/32Ba2  Barite  20.8
Barite zone  -69  74/BJDBa  Barite  22.4
Barite zone  -69  75/2G1Ba1  Barite  22.6
Barite zone  -69  76/50Ba  Barite  23.7
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Sulfide-rich zone  -95  79/5AGn2  Gn  5.6
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Sulfide-rich zone  -95  81/5Aba  Barite  18.7
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Sulfide-rich zone  -95  83/514B2  Barite  22.8  23.1
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Barite zone  -95  99/98K3Ba  Barite  23.4  23.4
Barite zone  -95  100/31Ba  Barite  21.3
Barite zone  -95  101/60 int  Barite  23.0  21.8
Barite zone  -95  102/60 ext  Barite  22.0  19.6
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Aptian limestone  Open pit  104*  Pyrite  15.2
Aptian limestone  Open pit  105*  Pyrite  16.2
Aptian limestone  Open pit  106BJ1*  Gn  5.7
Aptian limestone  Open pit  107CN*  Gn  7.2
Aptian limestone  Open pit  108BJ2*  Gn  7.2
Aptian limestone  Open pit  109N6*  Gn  9.6
Aptian limestone  Open pit  110B2*  Gn  3.2
Triassic sulfate  Ouenza  112 SA870*  Gypsum  16.0
Triassic sulfate  Ouenza  113SA8729*  Gypsum  13.4
Triassic sulfate  Ouenza  114SA8731*  Gypsum  14.3
Triassic sulfate  Mesloula  115SA8792*  Gypsum  15.4
Triassic sulfate  Mesloula  116SA8734*  Gypsum  15.2
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Triassic sulfate  Fedj el Adoum  132FH  Gypsum  17.1  12.9
Triassic sulfate  Fedj el Adoum  133FH  Gypsum  16.8  16.1
Table 5 Strontium isotope compositions of different barite generations from Bou Jaber (levels –69 m and –95 m) and of Triassic gypsum from the Bou Jaber Triassic salt diapir.

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<th>Mineral</th>
<th>87Sr/86Sr Std dev.</th>
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Table 6 Lead isotope composition of galena samples from Bou Jaber collected mine levels –69m and –95m.

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