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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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1 Abstract The Bou Jaber Ba-F-Pb-Zn deposit is located at the edge of a Triassic salt diapir in the Salt Diapir 2 Belt of the Tunisian Atlas Foreland. It provides a good example of the close association between Mississippi 3 Valley-type mineralization and evaporite-bearing diapirs. The ores are fault-controlled and occur as 4 subvertical column-shaped bodies developed in dissolution breccias and cavities in Aptian platform/reef 5 limestone, which is covered unconformably by impermeable shale and marl of the Upper Albian-6 Cenomanian. The limestone host rock is hydrothermally altered to ankerite proximal to and within the ore 7 bodies. Quartz as fine-grained bipyramidal crystal formed during hydrothermal alteration of the host rocks. 8 The ore mineral assemblage is composed of barite, fluorite, sphalerite and galena in decreasing abundance. 9 The ore zones outline distinct depositional events: sphalerite-galena, barite+ankerite and fluorite. Fluid 10 inclusions, commonly oil-rich, have distinct fluids salinities and homogenization temperatures for each of 11 these events: sphalerite-galena (17 to 24 wt% NaCl eq., and Th from 112° to 136°C; ankerite+ barite (11 to 12 17 wt% NaCl eq., and Th from 100° to 130° C); fluorite (19 to 21 wt% NaCl eq., Th from 140° to 165° C). 13 The mean temperatures of the ore fluids in the events decreased from sphalerite (125°C) to barite (115°C) and 14 increased during fluorite deposition (152°C); then decreased to ~110°C during late calcite precipitation. LA-15 ICP-MS analyses of fluid inclusions show there are at least 2 distinct fluids. Inclusions in fluorite are metal-16 rich (100's to 1000's ppm Pb, Zn, Cu, Fe) but the inclusions in barite are Pb, Zn, Cu, Fe-deficient. No 17 information on metal contents are available. Inclusions in fluorite have Cl/Br and Na/Br ratios of several 18 thousand, consistent with dissolution of halite while the inclusions analysed in barite have values lower than 19 those of seawater which are indicative of a Br-enriched brine derived from the evaporation of seawater plus a 20 component of halite dissolution. The salinity of the barite fluid inclusions is less than obtained simply by the 21 evaporation of seawater to halite saturation and requires a dilution of more than two times for halite saturated 22 fluids. This is consistent with the presence of a component of meteoric water in the brine that deposited 23 barite. The higher K/Na values from fluid inclusions from barite suggest that the brines interacted with K-rich 24 rocks in the basement or in siliciclastic sediments in the basin. Carbonate gangue minerals (ankerite and 25 calcite) have $\delta^{13}C$ and $\delta^{18}O$ that are close to the Aptian limestone host rock values and indicate fluid 26 equilibrium between carbonate host rocks and warm brines. The δ^{34} S values for sphalerite and galena are 27 positive and very homogeneous. They fall within a narrow range (1 to 10 %) with a bulk value of 7.5 %, 28 indicating a homogeneous source of sulfur. The δ^{34} S values of barite are also relatively homogeneous (22 ‰), 29 with 6 % higher than the δ^{34} S of local and regional Triassic evaporites (15%). The latter are believed to be 30 the source of sulfate. Temperature of deposition together with sulfur isotopes data indicate that the reduced 31 sulfur in sulfides was derived through the reduction of Triassic sulfate by thermochemical sulfate reduction 32 using hydrocarbons produced probably from Upper Cretaceous source rocks. The ⁸⁷Sr/⁸⁶Sr ratio in the Bou 33 Jaber barite (0,709821 to 0.711408) together with the lead isotopes values of Bou Jaber galena 34 (²⁰⁶Pb/²⁰⁴Pb=18.699 to 18.737; ²⁰⁷Pb/²⁰⁴Pb=15.635 to 15.708 and ²⁰⁸Pb/²⁰⁴Pb=38.321 to 38.947) show that

35 metals were extracted from homogenous crustal source(s). The tectonic setting of the Bou Jaber ore deposit, 36 the carbonate nature of the host rocks, the epigenetic style of the mineralization and the mineral associations, 37 together with sulfur and oxygen isotope data and fluid inclusion data show that Bou Jaber zinc-lead ores of 38 the deposit has the major characteristics of a salt diapir-related MVT Zn-Pb ores with superimposed events of 39 fluorite and of barite deposit. Field relations are consistent with mineral deposition during the Miocene 40 Alpine Orogeny from multiple hydrothermal events: (1) Zn-Pb sulfides formed by the mixing of two fluids: 41 one fluid metal-rich but reduced sulfur-poor and a second fluid reduced sulfur rich; (2) the fluorite 42 precipitated from a more dilute fluid with higher temperatures; (3) barite precipitation involved the influx of a 43 meteoric water component that mixed with a barium-rich fluid. A significant conclusion of the study provides 44 evidence that decouples the mineral assemblages (Zn-Pb, fluorite and barite) into separate and possibly 45 unrelated mineralization events. Consequently, the presence of barite or fluorite mineralization in any diapiric 46 zone does not necessarily suggest the presence of Zn-Pb rich ores. 47 Keywords Fluid inclusions° Laser ablation ICP-MS° C, O, S, Sr, Pb isotopes° diapir-related MVT Ba-F-Pb-48 Zn deposits °Bou Jaber ° Tunisia°

49

50 Introduction

51	Lead-zinc ore deposits associated with evaporite-bearing diapirs are well known and have been exploited for
52	many years in North Africa and the Gulf of Mexico region of the U.S.A. (Sainfeld 1956; Hanna and Wolf
53	1934; Price and Kyle 1983; Posey et al. 1994). They form a distinct group within the MVT class of deposits,
54	with typically low to high tonnage and modest to high grade (1 to few million tons). Recently high tonnage
55	(with a reserve of approximately 200 million tons of ore grading 6 % Zn and 1.3 % Pb are discovered in
56	Jinding, China (e.g., Leach et al 2013). A number of North American studies have characterized some of the
57	processes of formation (e.g., Light et al. 1987; Posey and Kyle 1988; Kyle and Price 1986; Kyle and Posey
58	1991).
59	In North Tunisia and adjacent Algeria region, although the numerous Pb-Zn (±Ba-F) deposits located at
60	the edges of Triassic salt-bearing diapirs were exhaustively investigated and explored during the last eight
61	decades, important aspects of the metallogeny of these salt diapir-related metallic deposits remain a subject of
62	debate. Conflicting genetic models involving syngenetic origin, epigenetic origin, or a combination of both
63	have been proposed (e.g., Sainfeld 1956; Rouvier et al. 1985; Gharbi et al. 1985; Charef and Sheppard 1987;
64	Amouri 1989; Orgeval 1994; Sheppard et al. 1996; Bouzenoune and Lécolle 1997; Bouhlel 2005; Bouhlel et
65	al 2007; Bouhlel et al. 2009).
66	The Bou Jaber evaporite diapir-related Ba-F-Pb-Zn deposit, is located in central-western Tunisia, 30 km
67	west of Tajerouine city, and lies against the Algerian-Tunisian international border (Fig. 1). It is one of
68	numerous Algerian-Tunisian Pb-Zn-Ba deposits located at the edges of Triassic diapirs and where
69	mineralization is hosted in Cretaceous peridiapiric limestone strata (Sainfeld 1956; Rouvier et al. 1985;
70	Bouhlel 1993). Unlike most of the Tunisian-Algerian salt diapir-related Pb-Zn deposits, the Bou Jaber deposit
71	is barite and fluorite-rich and exhibits a clear spatial relationship with three geo-structural elements: a salt
72	diapir and NW-trending faults limiting Miocene-Pliocene grabens, allowing a possible role of these three ore
73	geological controls in its genesis.
74	Currently no comprehensive geochemical investigation has been published. Based on mapping, general
75	mineralogical descriptions and limited geochemical database the controversy over the genesis of the Bou
76	Jaber mineralization has mainly included: (i) a syngenetic origin that involved meteoric karstification
77	followed by the deposition of base-metals originating from reworking of continental heavy-metal-rich soil
78	horizons during Upper Aptian period (Fuchs 1973; Amouri 1989); and (ii) an epigenetic origin at Miocene
79	time, that involved replacement of limestones and infilling of hydrothermal dissolution-cavities and open
80	fractures by undefined fluids and precipitation processes (Bouhlel 1987; Bouhlel 1993; Salmi-Laouar et al.
81	2004).To better define ore controls, the mineralizing event (s); the nature, origin, and evolution of the
82	hydrothermal fluids, metal and sulfur sources, and the processes that control metal precipitation, this study
83	integrates the geologic ore controls, ore textures and paragenesis, fluid inclusions microthermometry, Λ
	4

- 84 halogen analyses of fluid inclusions, and stable (C, O) and radiogenic (Sr, Pb) isotope analyses from mineral
- 85 separates. The results provide new insights into the origin of the Bou Jaber ore deposit and, in a more general
- 86 sense, into the metallogenesis of the diapir-related carbonate-hosted Pb-Zn-Ba-F deposits.

87 Geological setting and regional mineralization

88	Bou Jaber deposit is located in the Salt Diapir Belt of the Tunisian Atlas foreland fold-thrust-belt which is a
89	part of the Alpine Atlas mountain ranges extending through Morocco, Algeria and Tunisia, and resulting from
90	the Miocene convergence between the Africa and Europe plates (Fig. 1).With its NE-SW-striking length of
91	200 km and a fairly constant width of 50 km, the Salt Diapir Belt roughly coincides with the Tunisian Trough
92	(Fig. 1). It is bordered to the North by the Tell thrust belt characterized by Miocene south-directed tangential
93	tectonism of Tellian and Numidian nappes and to the South by the Central Tunisia Platform. The south-
94	western area of the Salt Diapir Belt and large area of the Central Tunisia Platform are intersected by large
95	number of transverse grabens. The Tell thrust belt and the Tunisian Atlas foreland fold-thrust-belt are formed
96	by about 8-10 km-thick Mesozoic-Tertiary folded cover pieced by a large number of Triassic salt diapirs. At
97	the surface, the Triassic diapirs are mainly composed of chaotic breccias dominantly formed by gypsum with
98	few shale, dolostone and basic volcanic that correspond to insoluble caprocks. The few wells drilled through
99	diapirs encountered massive salt below 200 or 300 m of gypsum. In map view the diapirs occur as elongated
100	SW-NE bodies, typically 10 x 3 km long and 1 to 2 km in width, and are distributed along 3 to 5 distinct
101	parallel NE-SW- directed strike-slip faults that correspond to the reactivation of former Hercynian faults
102	(Perthuisot 1978; Martinez and Truillet 1987; Turki et al. 1988; Chaari 2002). The Bou Jaber diapir is located
103	on one of these diapir-bearing faults (the Tajerouine Fault) (Fig. 1). Almost everywhere in the Salt Diapir
104	Belt, the tectonic contacts between the Triassic salt diapirs and the intruded Cretaceous to Miocene rocks are
105	marked by lens-shaped evaporite-dissolution breccia bodies that are the host of Pb-Zn-Sr mineralization
106	(Rouvier et al. 1985; Sheppard 1996; Bouhlel 1993; Bouhlel et al. 2007).
107	The Triassic substratum is only known in the Saharan Platform by deep petroleum drilling. It is composed
108	of Paleozoic shale, sandstone, arkosic sandstone and Precambrian granite or metamorphic rocks (Mejri et al.
109	2006). The Jurassic platform carbonate deposition of central and eastern Tunisia has only rarely been
110	observed and is nowhere seen overlying the diapirs. Lower Cretaceous is composed of sandstone, clay and
111	limestone. Upper Cretaceous - Eocene succession is composed of marl and argillaceous limestone. Oligocene
112	and Miocene are discordant and composed of continental clay, sandstone and conglomerate. This Mesozoic-
113	Tertiary succession forms SW-NE-trending folds (acquired since the Oligocene) which are cut by NW-SE-
114	directed faults, limiting grabens filled by Mio-Pliocene continental sediments.
115	During the Triassic to Lower Tertiary (pre-orogenic period), the instability of the sedimentary basement
116	was almost permanent, related to repeated activity of deep accidents, inherited from Panafrican and
117	Hercynian orogens and reactivated mainly during rifting stages related to the Africa-Europe drift movement
118	(Cohen et al. 1980; Guirand and Maurin (1991). These resulted in a N-S extension that persisted from the
119	Jurassic until Lower Aptian. In this context, the north-central Tunisia corresponded to a rifted continental
120	margin characterized by extensional NE-SW and NW-SE-trending faults limiting horsts, grabens and tilted

121 blocks (Boltenhagen 1985; Martinez and Truillet 1987), with particularly the individualization since the 122 Neocomian of two differentiated paleogeographic and sedimentary domains (Figs, 1-2): to the north, a deep 123 rifted basin called the Tunisian Trough (Burollet 1956) and to the south the flat Central Tunisia Platform 124 which is the northern extension of the Saharan Platform (Vially et al. 1994). In the Tunisian Trough, the syn-125 rift sedimentary sequence is very thick (about 5,000 m in the Cretaceous alone in the El Kef area) and is 126 composed of deep marine sediments mainly marl and argillaceous limestone. On the platform area, the 127 thicknesses are reduced and gaps occur locally in the series; the facies are composed of sandstone and clay 128 with shallow marine limestone and dolostone of Aptian age (Marie et al. 1084; M'Rabet 1987). 129 In the trough, with the overburden of Jurassic and Neocomian series, halokinetic movements of the 130 Triassic salt began. In several places of the south-western area of the trough (Tajerouine-Tabessa region), 131 about 300 to 500 m-thick Aptian, and Lower Albian shallow marine bioclastic limestones, including reef 132 development, overlay diapiric structures (e.g., Bou Jaber, Slata, and Ouenza; Perthuisot 1978, Bouhlel 1987). 133 Aptian and Lower Albian limestones, on both Central Tunisia Platform and diapiric structures, are the host of 134 siderite or Pb-Zn-Ba-F mineralization. 135 Transpression and transtension tectonics occurred during the Middle Albian with the reactivation of syn-136 rift extensional NE-SW and NW-SE-trending faults, limiting tilted blocks and half-grabens. It were the 137 intersection zones of these fault systems that accelerated salt diapirism and where numerous diapirs intruded 138 their roof and emerged onto the seafloor (Bolze 1954;Perthuisot 1981). Salt diapirs, tilted blocks, and half-139 grabens will control the distribution and the nature of the sedimentary facies (Boltenhagen 1985; Perthuisot 140 1981). 141 During the Upper Albian-Lower Turonian, transgressive post-rift shale and marl pelagic sediments (300 142 to 1000m-thick) invaded the entire Aptian-Lower Albian platform as well as the Tunisian Trough fossilizing 143 uplifted blocks, half-grabens and salt diapirs. The latter structures, together with the upper Albian 144 unconformity controlled the ore emplacements. The lower part of the transgressive series contains two 145 organic-rich laminated black limestones: Upper Albian Mouelha laminites (~2 % COT) and Cenomanian-146 Turonian Bahloul laminites (up to 13% COT) (e.g., Saidi and Belayouni 1994; Soua 2009). These rocks are 147 considered as excellent hydrocarbon source rocks for the petroleum system in the region (e.g., Saidi and 148 Belayouni 1994; Soua 2009). Bahloul laminites may also be the host of strata-bound replacement-type 149 sphalerite-rich mineralization as the case in Bou Grine (Bouhlel et al. 2009). The Cretaceous sedimentation 150 continues with the deposition of about 2000 m-thick marl and limestone succession of Middle Turonian to 151 Paleocene. Subsidence and transpressional tectonics caused a second diapiric piercement during the Lower 152 Eocene (Perthuisot 1981). 153 The tectonic period of the Alpine orogeny in northern Tunisia began in Oligocene time and reached its 154 maximum during the Middle Miocene time as a result of collision of microplates rifted off the European 155 margin with the North African margin, and coincided with the progressive elimination of Proto156 Mediterranean lithosphere from west to east along the African margin (Rouvier 1977; Martinez and Truillet 157 1987). Deformations consist of a NW-SE contraction phase with significant shortening resulting in NE-SW to 158 E-W-trending folds; flow of Triassic salt into the cores of these folds assisted by tectonic loading during fault 159 inversion; NE-SW strike-slip faults resulting from reactivation of syn-rift extensional faults; and setting up in 160 the North of the Tell Thrust Belt composed of major thrust sheets of Oligo-Lower Miocene "Numidian" 161 flysch emplaced over Upper Cretaceous-Eocene "Tellian" nappes. At the base of the nappes, blades of 162 Triassic evaporitic breccias are common; these are due to detachment surfaces or to diapiric extrusions cut 163 and trailed by moving nappes. Basic and acidic igneous rocks are described in several places of the Tell 164 Thrust Belt (e.g. Oued Bélif region and at La Galite island (Bellon 1976; Lardhi-Ouazza 1994) and 165 correspond to Upper Miocene and Pliocene magmatism activities. In the Atlas Foreland, Pliocene reactivation 166 of transpressional movements created NW-SE-trending grabens (Ben Ayed 1986; Chihi 1995) intersecting 167 and cutting across the SW-NE-oriented folds and Triassic diapirs. The grabens were filled by Pliocene 168 continental conglomerate and sandstone sediments. On the Tell Thrust Belt post-orogenic relaxation phase 169 resulted in conglomerate, clay and lacustrine limestone deposition in Upper Miocene basins. Upper Miocene-170 Pliocene basins in the Atlas Foreland and in the Tell Thrust Belt are the host of some Pb-Zn ore deposits. 171 Ore deposits

172 The Pb-Zn ±(Ba, Sr, F) ore deposits in the Salt Diapir Belt and adjacent regions are shown on Figure 1. Most 173 of the ore deposits contain low to medium size resources (1 to 8 million tons at about 5 to 15 % Pb+Zn). The 174 ore deposits are classified into four groups based on the ore minerals present in the deposits (Rouvier et al. 175 1985; Bouhlel 1993; Bouhlel 2005) (Fig. 1). However, we point out in this report that these groups are 176 spatially and genetically distinct from each other. These assemblages are not present in all deposits and where 177 they do occur, they may or may not be present in specific mineralized zones. In all cases, where they occur in 178 the same mineralized zone, there is a consistent paragenetic relationship discussed later. These 4 groups 179 reflect a complex hydrothermal overprinting by up to 4 mineralization events in some deposits. These ore 180 groups are described below: 181 Group 1: Strata-bound replacement siderite deposits hosted in Aptian limestone (e.g., Ouenza, Bou 182 Khadra and Jerissa deposits) with global resources of about 165 million tons of Fe metal (Pohl et al. 1986; 183 Bouzenoune and Lecolle 1997). 184 Group 2: Ba±F±(Pb-Zn) strata-bound replacement-type and cavity-filling deposits in Aptian and Lower 185 Albian platform and reef limestones at the edges of Triassic salt diapirs. This group shows two distinct 186 mineral assemblages: group 2a with Ba-F±(Pb-Zn) (e.g., Mesloula, Mzouzia, Belkfif deposits in Algeria; 187 Akrour et al. 1991; and Bou Jaber in Tunisia), and group 2b with Ba±(Pb-Zn) deposits (e.g., Slata, Hamra, 188 Ajred, Trozza, in Tunisia) (Bouhlel 1993; Jrad and Perthuisot 1995; Béjaoui et al. 2013). Furthermore Pb-Zn-189 Ba mineralization is also present in the Cenomanian-Turonian dolostones (Aïn Nouba), in the Eocene

8

190 phosphorite rocks (Sekarna) and even in the Mio-Pliocene clastic rocks (Aïn Khmouda) (Sainfeld 1956;

191 Fucks 1973; Garnit et al. 2012).

192 Group 3: Pb-Zn (±celestite) strata-bound replacement-type deposits hosted by dissolution evaporitic

193 breccias at the contact zones between salt diapirs or salt sheets and the surrounding Cretaceous to Miocene

194 rocks (e.g., Fedj el Adoum, Kebbouch, Bou Khil, Garn Halfaya, Zag Ettir, Aguiba). 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.

- 196 2007). If the barite is present in these deposits, it always cuts the celestite-, and the Pb-Zn ore bodies.
- 197 Group 4: Pb-Zn strata-bound replacement-type and vein-type ore deposits that lack Ba, Sr or F are hosted
- 198 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
- 200 deposit resources were about 7.3 million tons of ore at 15% Zn+Pb (Orgeval 1994).

201 Group 5: Pb-Zn deposits occur either as strata-bound ores or as veins in continental Mio-Pliocene strata

202 (e.g., Sidi Driss in the Tell Thrust Belt and Koudiat Safra and Jebba in the Atlas Foreland) (Rouvier et al.

- 203 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

206 sphalerite and galena). These various mineral assemblages are suggestive of contributions from at least 4

207 distinct ore fluids and/or ore forming events that variably affected the Triassic diapiric structures. The Bou

- 208 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.
- 210

211 The Bou Jaber deposit

212

213 The Bou Jaber deposit was first mined for lead and silver by the Romans (2th to 5th centuries), where galena

- 214 yielded up to 500g/t Ag. Small and episodic mining activities continued by Arabs and Turks (9th to 17th
- 215 centuries), and then the French (1890 to 1950). The most recent (1972 to 2004) intermittent mining

216 activitiesby Tunisian state-owning mining companies focused on underground exploitation with a total

217 production of about 50,000t Pb+Zn, 0.5 Mt barite and minor quantities of fluorite. The production ceased in

- 218 late 2004 due to difficulties in the economic viability of the mine. The remaining estimated reserves are
- 219 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%

220 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.).
- 223

224 Lithostratigraphy and structural evolution

225 226 The geological map, lithostratigraphy and cross sections at Bou Jaber region are presented on Figure 3. The 227 dipiric Triassic salt formation outcrops in the core of a Cretaceous anticline and consists of dissolution-mega 228 breccias composed of chaotic assemblage of gypsum masses containing blocks of variegated argillite. Halite 229 rocks are dissolved at the surface. These gypsum-rich breccias, partly covered by Mio-Pliocene continental 230 sediments and alluvium, are similar of other Triassic outcrops in neighbouring diapirs where deep drill holes 231 showed thick halite-rich zone beneath the gypsum breccia zone. 232 The Aptian-Lower Albian limestone (Serdj Formation) outcrops at the south flank of the diapir. It is 233 composed of two platform and reef limestone members, respectively Aptian and Lower Albian in age 234 (Dubourdieu 1956, Bouhlel 1993; Vila and Charrière 1993; Braham et al 2002). The Aptian limestone member 235 is composed of 200 m-thick bioclastic limestone thickening up, interbedded by marl sequences (units 1-4,), 236 following is a massive lens-shaped bar 50 to 100 m-thick (unit 5) composed of platform limestone containing 237 rudistid and coral reefs. Following is a marl-rich member of about 100 m-thick (unit 6) consisting essentially 238 of alternating marl, shale, fine-grained sandstone and bioclastic limestone. The Lower Albian limestone 239 member (unit 7) forms a lens-shaped bar (250 to 50 m-thick) composed of metric-thick beds of bioclastic 240 limestone containing abundant debris of Rudistids, Corals and Echinoderms. 241 In the southern flank of Bou Jaber Mountain, the shales and marls of the Upper Albian overlain from 242 east to west the units 4 to 7 of the Aptian-Lower Albian platform succession (Fig. 3a). This spectacular 243 cartographic discordance corresponds to the Aptian/Upper Albian unconformity (Bouhlel 1993), regionally 244 known as the Austrian unconformity (Mejri et al 2006 and references therein). The Upper Albian-

245 Cenomanian sequence begins with a small "block complex" (1 to 5 m-thick) composed of limestone blocks of

246 0.5 to 3 m across ripped from the nearby Aptian uplifted blocks, and in turn covered by about 600m-thick

247 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

249 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-

251 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

- 257 piercement that begun during the Aptian and continued during the compression, faulting and thrusting events
- 258 of the Miocene Alpine orogeny. During these events, the Aptian/Upper Albian unconformity is overprinted

10

- 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
- 261 termination of the Bou Jaber diapiric structure is intersected by the NW-trending Bou Ghanem graben filled
- 262 by Miocene and Pliocene continental conglomerate, sandstone and clay.

263 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.

271The "gîte de l'Est" mineralization (Fig. 4) is hosted in the unit 5 of the Aptian platform/reef limestone272which is uncomfortably overlain by mid-upper Albian-Cenomanian shale and marl. Mineralization fills

273 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

277 roughly E-W-striking length of about 500 to 700m and extends to a depths greater than 400 m. Underground

278 mapping and drill holes show that most ore bodies have the following zonation, from the border to the ore

279 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

281 permeable Aptian host limestone and as impregnations and residue within the ores. It consists of degraded

282 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
- 288 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

290 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.

293 In the absence of direct dates on ore emplacement, constraints on the age of ore formation can be made 294 from geological relationships of the geological controls on the deposits. The ores are strongly controlled by 295 regional faults and therefore the age of ore must be as old as or younger than these faults. The structural 296 elements are: a) the Bou Jaber diapir is located on the regional deep Tajerouine Fault; 2) the ores are located 297 along E-W- to NE-SW-trending faulted zones including the faulted Aptian-Upper Albian unconformity) and 298 ore-rich zones are concentrated at the intersection of the SW-NE with NW-SE faults. These tectonic elements 299 were derived from the Miocene tectonic events of the Alpine orogeny. Thus the timing of the ore 300 emplacement at Bou Jaber must correspond to (or possibly younger than) the Alpine orogeny in the Miocene 301 times (Sainfeld 1956; Bouhlel 1993). Furthermore, this time of mineralization coincides well with the 302 maximum stratigraphic burial and subsequent hydrocarbon generation and migration into the peridiapiric 303 strata.

304 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.

312 Ore textures, mineralogy and petrographic relationships were determined on hand samples on thin and

313 polished sections using transmitted and reflected light microscopy.

314 Fluid inclusion studies were carried out on a variety of minerals from the main stage of mineralization:

315 sphalerite, barite, fluorite, and calcite. Samples were prepared as standard 200- to 500µm-thick doubly

316 polished wafers. The measurements were carried out at the Earth Sciences Department, Faculty of Sciences of

317 Tunis, using a Linkam THM600 freezing-heating stage on a Leitz microscope. The system was calibrated

318 using pure CO₂ fluid inclusion (-56.6 °C), the freezing point of H₂O (0°C), and melting points of Merck

319 standards. The precision was ±0.5°C. Fluid salinities were calculated as weight percent NaCl equivalent (wt%

320 NaCl eq.) using the equation of Bodnar (1993). Standard procedures were carried out, with initial petrography

321 to determine inclusion types and paragenesis in order to select material for subsequent micro-thermometric

322 measurements. The 200 to 400µm doubly polished wafers were also examined with an epi-fluorescent

323 microscope to observe the fluorescence of hydrocarbon-bearing inclusions.

324 Fluid inclusions hosted in fluorite and barite were analysed individually by LA-ICPMS. Inclusions were

325 chosen that were clearly primary, occurring in growth zones, but in addition, fluid inclusion assemblages

326 (FIA's) that were pseudosecondary and in some cases secondary in origin, were analysed to determine the full

12

327 range of possible fluid compositions in the ore-deposit. Individual inclusions, or groups of small related 328 inclusions were analysed by Laser-ablation inductively-coupled mass-spectrometry (LA-ICPMS) using an 329 Agilent 7500c mass spectrometer, combined with a Geolas ablation system. This system uses a Compex 103 330 ArF excimer laser with a wavelength of 193 nm and an energy density between 10 - 15 Jcm⁻² at the sample 331 surface. The operating frequency of the laser was typically 5Hz with spot sizes of 25µm and 50µ, the main 332 criteria being that the size was greater than that of the inclusions. Several small inclusions could be ablated 333 together to provide sufficient mass for analysis if inclusions were very small. The ablated material was 334 transported from the ablation cell to an Agilent 7500c ICP-MS using 99.9999% He flowing at 2 ml min⁻¹ into 335 a cyclone mixer where it was combined with the Ar carrier gas flowing at 1.02 ml min⁻¹. The mixer prolongs 336 the signal from the ablated inclusions and improves precision by increasing the number of cycles through the 337 selected elements and therefore the number of determinations of their ratio relative to Na. The instrument 338 was operated in reaction cell mode using 2.5 ml min⁻¹ 99.9999% H₂ to remove interferences from ⁴⁰Ar on 339 ⁴⁰Ca and from ⁵⁶ArO on ⁵⁶Fe. Element/Na intensity ratios were converted to weight ratios using the NIST 340 glass standard SRM-610. For K/Na the soda lime standard SRM-1412 was used in addition to SRM-610 as it 341 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 342 fluorite are closer to the value of SRM-610. Instrumental drift was checked using SRM-610, which was 343 insignificant over each day's analysis. Integration of the standard and sample signals used the SILLS software 344 package (Guillong et al. 2008). Full details of the analytical protocols and calibration of the instrument are 345 presented in Allan et al. (2005). The moderate to high salinities of the inclusions and their size enables the 346 signal from the ablation of fluid inclusions to be easily distinguished from any matrix signal. The ablation of 347 the host fluorite or barite precedes opening of the inclusions and continues after the inclusion signal has 348 ceased. Therefore, any signal from the sample matrix is easily observed and can be removed by the SILLS 349 software. The distinction between inclusion and matrix is based on the sharp rise and then decrease in the 350 inclusion signal over a period of c. 10-15 seconds, whereas the matrix signal is more constant over the entire 351 ablation period. In addition, areas of fluorite and barite that were free of inclusions were ablated for a total of 352 200 pulses to determine if they contained any significant concentrations of the elements to be determined in 353 the inclusions. In fluorite-hosted samples there was no contamination from the matrix except for Ca and Sr in 354 one sample. In barite there was considerable contamination from the mineral matrix for elements such as Fe, 355 Zn, Sr, in addition to Ca and Ba from the fluid inclusion host mineral. This signal from the contamination 356 could not be resolved from that of the fluid inclusions because it was too erratic. 357 Stable isotopes analyses were obtained at the U.S.G.S. Crustal Geophysics and Geochemistry Science 358 Center stable isotope laboratory in Denver following the procedures of McCrea (1950) for carbonates and 359 Giesemann et al. (1994) for sulfur minerals. Isotopic compositions are reported in δ -notation relative to

360 VPDB for carbon, VSMOW for oxygen, and VCDT for sulfur. Precision of the analyses is better than $\pm 0.1\%$

361 (1 σ) for carbonates, $\pm 0.2\%$ for sulfur, and $\pm 0.5\%$ for oxygen in sulfates.

362 Strontium isotopes analyses were performed on nine barite separates and on one gypsum sample. Sample
363 separates were finely milled, dried for four hours, than leached overnight in 6N HCl at 100°C overnight. Dry
364 residues were dissolved in 2.5N HCl. After centrifugation, strontium was separated using standard cation
365 exchange procedures. Sr isotopes ratios were measured on a thermal ionization mass spectrometer at the
366 Centre Petrographique et Géochimique (CRPG), Nancy, France. Strontium deviation of analysis was usually
367 ±0.00004.

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

374 Ore textures and mineralogy

- 375 The ore mineralogy consists of three distinct mineral assemblages representing at least three mineralizing
- 376 events. (1) breccia-hosted sphalerite-galena ores with rare pyrite and some tetrahedrite micro-inclusions in
- 377 galena; (2) cavity-fill barite-rich ores; (3) replacive and geodic fluorite (+ minor Pb-Zn sulfides). Post-ore
- 378 calcite fills thin fractures. Alteration mineral assemblage is represented by ankerite and quartz. A generalized
- 379 paragenetic sequence for the minerals at the Bou Jaber mine is given in Fig. 5.
- 380 Breccia-hosted sphalerite-galena ores (stage 1)
- 381 The sphalerite-galena ores are hosted in dissolution-collapse breccias cross-cutting the Aptian limestone
- 382 strata. Breccia elements are composed of light grey Aptian limestone (2 cm to 2 m across) and are
- 383 surrounded by black matrix (Fig. 6, a-c). The latter is composed of kaolinitic mudstone, minor fine-grained
- 384 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
- 386 small veins and stylolites. This matrix is the main host the sulfide concentration (Fig. 6, b-c). Sphalerite
- 387 occurs as honey to light brown euhedral crystals 1 to 8 mm across, with a dark brown core (Fig. 6, d-f).
- 388 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
- 390 across occur as irregular disseminations that replaced the limestone wall rock. Both sphalerite and galena
- 391 contain abundant inclusions of micrite grains (up to 200 microns), bipyramidal quartz (100-200 µm), organic

392 matter (5-20 µm) and pyrite microcrystals (20-50 µm). These insoluble residues were inherited from the 393 decalcification of the black matrix hosting the sulfide assemblage described below, as well from the 394 dissolution of Aptian limestone host rocks. Bipyramidal quartz is the first hydrothermal alteration of the host 395 rocks and pre-date sulfide deposition. Only rare barite (barite-1) aggregates have been observed in the sulfide-396 rich ore zones or in laterally equivalent breccias, so it seems unlikely that the sulfides replaced barite in this 397 deposit. The black mudstone-hosted sulfides may represent limestone insoluble residue, which is common in 398 most carbonate-hosted deposits and districts where carbonate dissolution breccias are present and commonly 399 described as internal sediments (Sass-Gustkiewics 1996; Leach and Sangster 1993; Matlock and Misra 1993; 400 Bouabdellah et al. 1996).

401 Barite- and ankerite-rich ore (stage 2)

402 Barite-rich ores fill hydrothermal dissolution cavities up to several meters in diameter (Fig. 7a). The wall 403 rocks of the cavities have been partly to completely replaced by coarse-grained ankerite (ank-1) that forms 5 404 to 20 cm-thick halos lining the barite-rich ore bodies. Ankerite-1 occurs as aggregates of well-formed 405 rhomohedral crystals, 1 to 5 mm across (Fig. 7b). In numerous places, the barite-rich ores consist of 406 alternations of white and black coloured bands (Fig. 7, c-d). The black bands are composed of black 407 mudstone similar to that described above in the sulfide stage containing fine-grained quartz-barite1-408 sphalerite-galena assemblage overprinted by aggregates of stage 2 ankerite (ankerite-2) which is often 409 replaced by black fluorite-1 (see fluorite stage below). The white bands, 2 to 20 cm in thickness, are 410 essentially composed of stacked or intergrown tabular barite crystals (barite-2), 0.5 to 3cm-thich and 2 to 411 20cm-long. In the central part of the barite-rich ore bodies, late-stage barite (barite-3) forms spectacular very 412 large white to transparent barite crystals (50 cm to up to 1.5 meter-long and up 10 to 30 cm-thick) that 413 occupie 80 to 90% of the cavities (Fig. 7e). 414 Fluorite (+minor sulfides) stages and post-ore calcite (stage 3)

- 415 Massive dark to black fluorite (fluorite-1), with small amounts of sphalerite and galena, most commonly fills
- 416 polygonal spaces between intergrown barite crystals. In detail the fluorite-1 has partially to completely
- 417 replaced the calcite and ankerite that previously cemented sulfides and barite crystals (Fig. 7f). The black-
- 418 colour of this fluorite is due to abundant solid inclusions (e.g., sphalerite, micrite, ankerite, black clay, and
- 419 fine-grained hydrothermal bipyramidal quartz), and to abundant oil inclusions. Following the fluorite-1 stage,
- 420 fluorite-2 (with minor sulfides) forms geodic cubic crystals from few mm to 5 cm across, which are
- 421 colourless or purple. This fluorite is commonly coated by rhombohedral crystals of ankerite up to 5 mm
- 422 across (ank-3), and by late stage calcite occurring as large scalenoedral crystals calcite up to 5 cm across.

- 423 Post-ore spar calcite occurs in thin open fractures (5 to 20 cm wide) crosscutting the previous described ores
- 424 and the host rocks.

425 Fluid inclusions petrography and microthermometry

- 426 Few fluid inclusions are observed in sphalerite; however barite-, fluorite-, and late-stage calcite contain
- 427 numerous primary and secondary fluid inclusions suitable for fluid inclusion study. In these minerals primary
- 428 fluid inclusions were identified in the context of Roedder (1984) and Goldstein and Reynolds (1994). They
- 429 are classified in three types (Fig. 8): (1) Liquid water + vapour (L_w+V); (2) Liquid petroleum + Vapour
- 430 (L_P+V) ; (3) Liquid water + Liquid petroleum + Vapour (L_W+L_P+V) .
- 431 Aqueous fluid inclusions microthermometry
- The microthermometric data derived from the primary fluid inclusions in sphalerite, barite, and fluorite from 433 the Bou Jaber "Gîte de l'Est" are given in Table 1. Sphalerite contains small (5- to 20 μ m size) L_w+V and 434 L_P+V fluid inclusions. Microthermometric analysis preformed on the L_w+V inclusions yielded first melting 435 temperature (T_{fm}) values in the range of -40° and -30° C. The final ice melting temperatures (T_{mice}) vary 436 from -18° to -13°C with a mode at -16°C. The homogenization temperatures (Th) range from 120 to 136°C 437 with a mode at 128°C (± 5°C). Calculated salinities range from 17 to 20 wt% NaCl eq. with a mode at 19
- 438 wt% NaCl eq. $(\pm 1\%)$

432

439 Transparent and geodic barite crystals (barite-2 and barite-3) contain numerous two-phase inclusions 440 (Lw+V) (5- to 200µm size) that form locally abundant clusters. Fluid inclusions indicating stretching or 441 necking down (Roedder 1984; Ulrich and Bodnar 1988) are not measured. It is well known that barite is 442 susceptible to stretching of the fluid inclusions by modest heating beyond their trapping temperature (Ulrich 443 and Bodnar 1988). Therefore, only sets of primary fluid inclusions that had the same Th values are reported. 444 Nevertheless, there is an unknown level of uncertainty regarding the Th data for barite, consequently the 445 reported Th values should be considered "maximum" temperatures for fluid trapping. In general the (Lw+V)

- 446 inclusions present generally the same volumetric proportion of the liquid to vapour phases (L = 90 to 95 %; V
- 447 = 5 to 10 %). The first melting temperature (T_{fm}) values range between about -45 to -19 °C (ave. -34±7°C,
- 448 n=36). The final ice melting temperatures (Tm_{ice}) range from -14 to -8°C (ave. -10±1°C; n=31). The
- 449 homogenization temperatures (Th) range from 100 to 130°C (ave. 114±10°C). Calculated salinities range
- 450 from 11 to 15 wt% NaCl eq. (ave. 13 wt% NaCl eq. \pm 1%).

451 Fluorite-1 and fluorite-2 samples contain abundant two-phase inclusions (Lw+V) (5- to 200µm size). The

- 452 T_{fm} recorded temperatures range from -45° to -28°C. The final ice melting temperature (T_{mi}) values vary
- 453 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.

- 456 Transparent late-stage calcite crystals (calcite-2), overlapping fluorite in druses and caves, contain small
- 457 but numerous two-phase inclusions (L_W+V) of about 5- to 50- μ m size. The first melting temperature (T_{fm})
- 458 values range between -33 to -30 °C. The final ice melting temperatures (Tm_{ice}) were in the range of -18° to
- 459 –15.5°C with a mode of –17°C. The homogenization temperatures (Th) range from 109° to 117°C (ave.
- 460 114±2°C). Calculated salinities range from 19 to 21 wt% NaCl eq., with a mode of 20 wt% NaCl eq.
- 461 Petroleum fluid inclusions
- 462 Liquid hydrocarbon fluid inclusions are observed in sphalerite and are abundant in fluorite. The inclusions in
- 463 sphalerite are less than 5 to 10μm in size. Large inclusions (80 to 200 μm) are observed in the core- or along
- 464 growth zones of fluorite crystals. In black fluorite crystals, petroleum-bearing inclusions represent more than
- 465 30% of the total inclusions. The black coloured fluorite is due to petroleum inclusion abundances.
- 466 Two types of primary fluid inclusions are observed: $L_{p}+V$ and $L_{w}+L_{p}+V$ fluid inclusions that are isolated
- 467 or distributed along growth zones. These inclusions may coexist in the same mineral zones with aqueous
- 468 inclusions (L_w+V). Secondary L_w+V and L_P+V fluid inclusions are located along fractures, cracks and
- 469 cleavage planes. In transmitted light, liquid hydrocarbon inclusions are usually brown- to yellow-colored. In
- 470 epifluorescence observations, most of the hydrocarbon inclusions show fluorescence emissions in the light
- 471 yellow to light or deep blue colours.
- 472 Primary L_p+V inclusions recorded homogenization temperatures that range between 97° to 140°C, and
- 473 are lower than the Th values of coexisting aqueous inclusions (100° to 165°C). The differences in
- 474 homogenization temperatures are about 20°C which probably reflects differences in pressure corrections
- 475 caused by the greater compressibility of oil than water (Roedder 1963).
- 476 Semi-quantitative compositions of hydrocarbon inclusions trapped in barite and fluorite crystals were
- 477 determined by infrared microscopy and microfluorometry, as described in Guilhaumou et al. (1990). Both
- 478 techniques show the presence of aliphatic and aromatic components in the oil, but microfluorometry shows
- 479 that in barite the components are aliphatic dominant and in fluorite aromatic compounds dominate. The
- 480 transition from aliphatic-rich oil inclusions to more aromatic components correlates with the timing and
- 481 temperature of barite to fluorite depositions. The temperatures associated with the deposition of barite are low
- 482 at around 100° to 130°C, whereas in fluorite the temperature is higher at around 140° to 165°C. In addition,
- 483 fluorite, being paragenetically later than barite indicates there was more time for the oil to mature.

484 Homogenization temperatures-salinity relationships

485 Salinities and homogenization temperatures from primary fluid inclusions (L_w+V) in sphalerite, barite,

- 486 fluorite and calcite are shown in Fig. 9. The data indicate that sphalerite, barite, fluorite, and late stage calcite
- 487 were probably deposited from fluids with homogenization temperatures of between 100 to 165°C (ave.
- 488 130°C±18°C) and salinities in the range of 11 to 22 wt% NaCl eq. (ave. 17.5±3 wt% NaCl eq.).
- 489 Based on the mineral paragenesis and the defined mineralization stages, the brine fluids are of three
- 490 types: (1) the fluid that deposited sphalerite (A fluid) is characterized by high salinities (17 to 24 wt% NaCl
- 491 eq.), and homogenization temperatures (112° to 136°C); (2) the fluid responsible for barite deposition (B
- 492 fluid) is characterized by low salinities (11 to 17 wt% NaCl eq.), and low temperatures (Th = 100° to 130° C);
- 493 (3) fluorite was deposited by fluids (C fluid) with salinities ranging from 19 to 21 wt% NaCl eq. (ave. 20%),
- 494 and relatively high homogenization temperatures of 140° to 165°C; and (4) late-stage calcite was deposited
- 495 by a fluid (D fluid) with Th raging from 109° to 117°C and calculated salinities between 19 to 21 wt% NaCl
- 496 eq. (mode at 20 wt% NaCl eq). The mean temperatures of the ore fluids decreased from sphalerite (125°C) to
- 497 barite (115°C) and increased during fluorite deposition (152°C); then decreased to ~110°C during the late
- 498 stage calcite precipitation.

499 Composition of fluid inclusions using LA-ICPMS

500 Approximately 200 fluid inclusions hosted in fluorite and barite were analysed individually by LA-ICPMS. A 501 summary of the element/Na weight ratios for individual fluid inclusions and their reproducibility (based on 502 more than 30 measurements for each sample) is presented in Table 2. The average weight ratios have also 503 been converted to elemental concentrations (ppm) based on the average salinity of the inclusions in fluorite 504 (18 equiv. wt% NaCl) and barite (13 equiv. wt% NaCl) determined by microthermometry (Banks et al. 2000). 505 The accuracy of the calculation relies on the ability to measure all of the cation/Na ratios in the inclusion 506 which are impossible for Ca and Ba because these are the cation in the host mineral. In fluorite it was possible 507 to estimate the Ca/Na ratio from the ice and hydrohalite melting temperatures and using the NaCl-CaCl2-H2O 508 phase diagram to calculate the Na/Ca ratio, which was found to be approximately 0.5. In barite, Ca is present 509 as CaCO3 and CaF2solid inclusions in the mineral matrix and contaminates the fluid analyses. It was also not 510 possible to observe the ice-hydrohalite melting relationship in these inclusions; therefore it was not possible 511 to directly estimate the Ca/Na ratio of these inclusions. Based on similarities between other elements in 512 fluorite and barite hosted inclusions, we assume the Ca/Na ratio to be similar to that in fluorite. In the barite 513 the ratios of Ba, Zn, and Sr to Na were also unreasonable high and were clearly from contamination in the 514 host mineral.

515The fluid inclusions in fluorite are dominated by Na>Ca>K>Mg, with the concentrations of Sr, Fe and516Zn each being equivalent to that of Mg. Concentrations of ore metals such as Cu are 250 to 450 ppm, Zn 850

- 517 to 2100 ppm, and Pb150 to 430 ppm. The difference in the concentrations between the different fluorite-
- 518 hosted fluids are, in the majority of cases, statistically significant and not due to the precision of the replicate
- 519 analyses. The composition of the major cations in the barite-hosted inclusions are different to those in

520 fluorite. These are dominated by K>Na>Ca>Mg, with Cu and Pb at significantly lower concentrations than in

- 521 fluorite. Due largely to the different K/Na ratios, bivariate plots of pairs of individual inclusions analyses
- 522 (Fig. 10, a-l) show there are 2 distinct fluid compositions, whereas other ratios, such as Mg, Li, Sr, Cu, Pb
- 523 and Mn/Na are broadly similar. The elemental ratios of the 3 fluorite samples largely overlap indicating a
- 524 common fluid. Differences in the Mg/Na and K/Na between samples BJ9612 and the other samples are real
- 525 but not significant enough to indicate these inclusions contain another distinct fluid.

526 Isotope geochemistry

- 527 Carbon and oxygen isotopes in carbonates
- 528 The isotopic results for barren Aptian limestone (n=4), mineralized limestone (n=9), ore ankerite (n=8) and 529 post ore calcite (n=18) are listed in Table 3 and shown on Fig. 11.
- 530 The limestone have δ^{13} C values ranging from -2 to 3.9 ‰ and δ^{18} O values ranging from 26.2 to 30.1‰,
- 531 within the ranges typical of marine limestones of Cretaceous age (Veizer and Hoefs 1976; Land 1980). The
- 532 values are comparable to values reported for Aptian limestones elsewhere in Central Tunisia and eastern
- Algeria (M'Rabet1987; Bouzenoune and Lecolle1997).
- 534 Ankerite-1 (n=3) which precipitated after the sulphide stage and before barite, has δ^{13} C values of 2.7 to
- 535 3.6‰ and δ^{18} O values of 26.8 to 26.9‰. Ankerite-2 (n=3), which precipitated after barite, has δ^{13} C values of
- 536 2.4 to 3.6 ‰ and δ^{18} O values of 26 to 27 ‰. Ankerite-3 (n=3), which precipitated in geodes after fluorite, has
- 537 δ^{13} C values of -0.5 to 1.5‰ and δ^{18} O values of 19.6 to +22.9‰.
- 538 Five samples of early calcites (calcite-1), which precipitated in geodes after fluorite-2 and ank-3, have
- 539 δ^{13} C values of 1.3 to 3.8% and δ^{18} O values of 18.8 to +23.1%. Late calcite (calcite-2) (n=11) has δ^{13} C values
- 540 of 2.6 to 6.2 % and δ^{18} O values of 24.8 to 27.4 %. Calcite-2 occurs in late thin fractures and appears to be
- 541 precipitated after the end of the mineralized hydrothermal system.
- 542 The pre-barite ankerite (ankerite-1) and post-barite ankerite (ankerite-2) show similar ranges of δ^{18} O
- 543 values, 26.8–26.9 ‰ and 26–27 ‰, respectively, isotopically similar to the lowest δ^{18} O Aptian limestone
- 544 (26.2–30.1‰); whereas the fluorite–ankerite-3 –calcite-1 sequence contains the ankerite and calcite with
- 545 lower δ^{18} O values, 18.8–23.1‰ and 19.6–22.9‰, respectively, although there is greater isotopic variation in
- 546 the hydrothermal carbonates (ankerite-1,2,3 and calcite-1) (18–27‰) than in the Aptian limestones (26.2–
- 547 30.1‰) (Fig.11).

548 The δ^{13} C values of host limestones and hydrothermal ankerites are quite uniform: 2.0±1.9‰ for the 549 limestones, 3.1±0.5‰ for pre-barite ankerite, 2.6±0.3‰ for post-barite ankerite, and 0.5±1‰ for post-fluorite 550 ankerite. The isotopic similarity indicates that carbon in all three ankerite generations was derived from the 551 local Aptian limestones, and that carbon isotopic equilibrium was established between hydrothermal fluids 552 and the host limestones during the main stages of ankerite and sulfide precipitation. Late stage calcite shows 553 higher δ^{13} C values (3.6±1‰). 554 Oxygen isotopic compositions of limestone host rock are restricted to a narrower range (26.2-30.1‰) 555 than the hydrothermal ankerite and calcite generations (19.6-27.4‰). The limestones represent the 556 isotopically heaviest carbonates. The δ^{18} O values of carbonates display a general downward trend in the 557 following sequence: limestone (26.2–30.1‰) \rightarrow pre-barite ankerite (26.8–26.9‰) \approx post-barite ankerite 558 $(26.8-26.9\%) \rightarrow \text{post-fluorite}$ ankerite $(19.6-22.9\%) \approx \text{post-fluorite}$ calcite (18.8-23.1%). This trend 559 resembles similar trends that have been observed at other MVT deposits (e.g., Frank and Lohmann 1986; 560 Nesbitt and Muehlenbachs 1994; Spangenberg et al. 1996) in which isotopically lighter O is seen in 561 paragenetically late carbonates compared to the unaltered host carbonates. The carbonates exhibit a positive 562 covariation in a δ^{13} C vs δ^{18} O plot. 563 Sulfur isotope characteristics in sulfides and sulfates 564 Sulfur isotopic compositions were determined on 18 sphalerite, 43 galena, 3 pyrite, 45 barite and 22 gypsum 565 samples (Table 4, Fig.12). The pyrites have δ^{34} S values of about 16‰, and sphalerites range from 8.4 to 566 9.8‰. There are no significant differences in sphalerite compositions among different sampled ore bodies, or 567 within ore zones in a single ore body, or even among sulfide stages. Galenas associated with the analyzed 568 sphalerites range from 1.1 to 9.6‰. Most of the galena $\delta^{34}S$ values occupy a narrow interval between 5 and 569 6‰. There is no significant difference between the galena that replaced the breccia matrix in dissolution 570 cavities-type ores (1.1–8.2‰; ave. 5.7‰), and epigenetic galena porphyroblasts in the host rocks or galena 571 associated with the fluorite stage event (3.2–9.6 ‰; ave. 6.6‰). 572 The δ^{34} S values of Triassic gypsum range from 13.4 to 17.0% (ave. 15%, n=12) similar to previously 573 reported compositions for Triassic gypsum of the Diapir Belt (Sheppard et al. 1996; Salmi-Laouar et al.

574 2007). These values match the δ^{34} S values of Triassic seawater (13–16‰) (Claypool et al. 1980;

575 Kampschulte and Strauss 2004).

576 The δ^{34} S values of barite range from 18.4 to 24.5‰ (ave. 22‰, n=45) (Table 4, Fig. 12, a-b). Despite 577 their wide spatial distribution, either within a single ore body or throughout the three ore bodies, the barites 578 show a relatively narrow range of δ^{34} S values.

- 579 Oxygen isotope characteristics in sulfate minerals
- 580 The δ^{18} O values for Triassic gypsum range from 13 to 16%, in good agreement with the δ^{18} O value of marine
- 581 sulfate in Triassic time (Claypool et al. 1980). The δ^{18} O values of barites vary between 19.6 and 23.5% (ave.
- 582 22‰, n=13). The higher values imply that barite did not form simply by dissolution and re-precipitation of
- 583 Triassic evaporite minerals. In fact, the barite δ^{18} O 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
- 585 isotopic exchange, possibly involving oxygen exchange with H₂O driven by hydrothermal heating, or a
- 586 reservoir effect associated with partial reduction of a fixed sulfate pool.

587 Radiogenic isotopes

- 588 ⁸⁷Sr/⁸⁶Sr ratio in barite and gypsum
- 589 In order to constrain the origin of high-barium fluids and to monitor possible changes in fluid composition
- 590 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
- 593 (Calvez et al. 1986) are also shown for comparison. A slight trend of ⁸⁷Sr-enrichment is observed from early
- 594 to late generations of barite crystals. This trend indicates extensive exchange reactions between hydrothermal
- 595 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).
- 597 Bou Jaber barites show Sr isotope compositions ranging from 0.709821 to 0.711408; these values are
- radiogenic compared to Triassic anhydrite with a⁸⁷Sr/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
- 601 0.707600; Orgeval 1994) that are close to the ratios of 0.70730 to 0.70750 for Cretaceous seawater
- 602 (Koepenick et al. 1985). The radiogenic strontium of the Bou Jaber barite might reflect leaching of a feldspar-
- 603 rich reservoir containing rocks and/or rubidium-rich minerals

604 Lead isotopes

- 605 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
- 607 Tunisian Pb-Zn deposits of the Tell thrust zone and the Atlas Foreland (Bouhlel et al. 2013) and to the Pb-
- 608 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 Jaberarea, respectively (Fig. 1).

611 Bou Jaber galenas have ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb values ranging from 18.697–18.786 (ave.

612 18.729), 15.643–15.762 (ave. 15.679), and 38.7057–39.228 (ave. 38.842) respectively. Results show

- 613 remarkable homogeneity of lead isotope compositions that plot within a narrow field, indicating a single or
- 614 homogenous source and suggesting a short duration of the mineralization event.
- 615 Lead isotope compositions form an elliptic field in both ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb
- 616 versus ²⁰⁶Pb/²⁰⁴Pb plots. The majority of the analyzed galena samples plot in a field below the upper crust
- 617 evolution curve in the orogenic plot (Fig. 14a) and above the orogen curve (Fig. 14b) indicating the

618 dominance of continental crustal sources. In the orogenic plot, some of the galena samples plot clearly above

619 the upper crust curve (i.e. high μ), indicating a large component of a radiogenic source. Some others plot

620 below the upper crust curve (i.e. low μ), indicating a large component of non-radiogenic sources. The lead

- 621 field of Bou Jaber lies within the lead isotope field defined by the major Tunisian Pb-Zn deposits (Bouhlel et
- 622 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 ⁸⁷Sr/⁸⁶Sr 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 ²⁰⁷Pb/²⁰⁶Pb model ages from the plumbotectonic model of Zartman and Doe (1981), between 400 and 300 Ma (Fig. 14a), older than the proposed Miocene age of the Atlassic 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).

638 Discussion

- 639 The Bou Jaber Ba-F-Pb-Zn deposit is located adjacent to a Triassic salt diapir in the Salt Diapir Belt (Fig 1).
- 640 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

642 dominated by sphalerite and galena, barite, or fluorite. Some deposits like Bou Jaber contain ores of all three

643 assemblages (Fig. 1) whereas others contain only one assemblage (i.e., Bou Grine with sphalerite and galena;

644 Bouhlel et al. 2009). The presence of the three paragenetically distinct ore assemblages in a single diapiric

545 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.
- 647 Comparison to similar ores of the world
- 648 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

- 651 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
- 653 (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
- 658 Sangster 1993; Leach et al. 2005). Where minor barite does occur in MVT ores, it is either early or late in the
- 659 paragenetic sequence and typically has distinctly different sulphur isotopic compositions from sulfide
- 660 minerals and different fluid inclusion compositions from associated sulfide- or gangue minerals, consistent
- with different mineralizing events (e.g., Leach et al. 2005). In the giant Ozark MVT province in the

662 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

667 celestite are present in minor amounts in the Hockley-, and Jinding Pb-Zn mineralization, however the barite

- 668 in these ores is interpreted to represent separate events related to the diagenetic transformation of the original
- 669 gypsum/anhydrite and not directly with Zn-Pb mineralization. In view of the world occurrences of
- 670 mineralized diapirs, the presence of abundant barite and fluorite in the Tunisian Salt Diapir Belt is unusual.
- 671 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
- 673 considered a sub-type of a larger family of MVT ores because they are commonly associated with continental
- 674 rifts and are suspected of being related to a magmatic component of fluorine that mixed with basinal brines
- 675 (Plumlee et al. 1994; Leach and Sangster 1993, Kendrick et al. 2002; Leach, et al. 2005). A late fluorite-barite

assemblage overprints the main Zn-Pb MVT event in the Central Tennessee MVT district but this is likely to

- 677 be related to the nearby Illinois fluorite event. There are many small Zn-Pb MVT ores in France and a few
- 678 deposits have a late fluorite event, which is considered to represent an event superimposed on an older Zn-Pb

event (Macquar et al. 1990).

- 680 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.
- 682 Fluorite-rich diapirs, low in Zn-Pb mineralization are known both in Tunisia (e.g., the Zaghouan district;
- 683 Bouhlel 1982; Bouhlel et al. 1988) and Morocco (e.g., Tirremi; Bouabdellah et al. 2013). However, a fluorite
- $684 + barite (low Zn-Pb) \pm calcite-dolomite-quartz mineral assemblage is more common in some vein deposits$
- 685 (e.g., U.S. Central Tennessee, Leach and Sangster, 1993); Zaghouan district, Tunisia, Bouhlel 1982; Bouhlel
- 686 1985; Bouhlel et al. 1988) and the Cevennes area, France; Macquar et al. 1990), particularly where basement-
- 687 connected vein deposits cut the cover rock sequences.
- 688 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
- 690 sulfides within breccia bodies; (2) barite with early minor sulfides in dissolution cavities, (3) fluorite ores
- 691 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-
- 696 salinity field for fluorite, lower temperature-salinity field for barite and an intermediate field for sphalerite.
- 697 Although this distribution could possibly be interpreted as a cooling and dilution trend of a single fluid, the
- 698 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,
- 701 a-1) 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.
- 703 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
- 706 composition of ore fluids in diapir-related ores are scarce, data for two diapir-related metallic deposits, the
- 707 Orduña-Murgía deposits in Basque-Cantabrian basin Northern Spain (Grandia et al. 2003) and the Jbel

708 Tirremi fluorite-barite deposit in Morocco (Bouabdellah et al. 2013) show the ore fluids were dominated by 709 high salinity brines representing a mixture of evaporated seawater and dissolved halite. 710 Unfortunately, there are no data on the composition of the Zn-Pb ore fluids other than the fluid salinity 711 from the fluid inclusions. Therefore, nothing can be concluded about the origin of the Zn-Pb fluids other then 712 they plot in a temperature-salinity space (Fig. 9) that differs from the fluorite and barite fluids. Inclusions in 713 fluorite from the Bou Jaber deposit have Cl/Br and Na/Br ratios of several thousand, consistent with 714 dissolution of halite whereas the inclusions analysed in barite have values lower than those of seawater which 715 are indicative of a Br-enriched brine derived from the evaporation of seawater plus a component of halite 716 dissolution. The Bou Jaber fluorite ore fluids are Na-Ca dominated with low Mg concentrations indicating 717 significant dolomitization of limestone by the fluids. The salinity of the barite fluids could be the result of 718 evaporation of seawater prior to halite saturation or by the dilution of a more saline fluid with meteoric water. 719 Furthermore, the higher K/Na values of fluid inclusions from barite suggest the brines interacted with K-rich 720 rocks in the basement or in siliciclastic sediments in the basin. Oxygen isotope compositions of the ore fluid 721 calculated from late stage calcite indicate that the δ^{18} O of the fluid varied between $\approx +3$ and $\approx +8\%$. Such a 722 fluid most likely originated from formation waters in isotopic equilibrium with the host rocks. The oxygen 723 isotopic composition of the fluids that deposited the Bou Jaber Ba-F-Pb-Zn ores are similar to that of modern 724 sedimentary basinal brines and MVT deposits (e.g., Mc Limans 1975; Mc Limans 1977) as well as in the 725 nearby Fedj el Adoum deposit (Charef and Sheppard 1987).

726 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.

733 Interpretations of the lead isotope data from Bou Jaber indicates that the lead was derived from upper 734 crustal rocks and it is reasonable to assume that these rocks were also the source of Zn, Fe and Ba. In Figure 735 14, the isotopic data for Bou Jaber lies within the large field defined by Pb-Zn deposits of the Tell Thrust Belt 736 and the Atlas Foreland. These regions have the same Paleozoic basement rocks, which suggest that the 737 basement rocks or sediment derived from the basement may have contributed metals in both regions. This 738 suggestion is consistent with compilations of lead isotopes compositions from global MVT ores (Leach et al., 739 2005) that suggest a relationship between the isotopic compositions of ores in the district and the 740 compositions of the basement rocks.

741Bou Jaber barites have Sr isotope compositions that are radiogenic compared to Triassic anhydrite or the742estimated ratio for seawater during the Triassic and are also more radiogenic than the marine Tunisian743Cretaceous sediments. The most likely source for the more radiogenic strontium in the barite is feldspar-rich744rocks 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 deepseated 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.

751 Sources of Sulfur

752 Based simply on proximity, gypsum in the nearby Triassic evaporite diapirs is the most obvious sulfur source

753 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-

755 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 δ^{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).

760 Second, the fluid inclusion microthermometry indicates that temperatures were sufficient to drive abiotic

761 reactions between sulfate and organic matter (80–100<T<150–200°C, Machel et al. 1995), the presence of

762 which is confirmed by organic inclusions in sphalerite. Additional evidence for favourable temperatures for

763 TSR are found in the isotopic results for 13 sphalerite-galena pairs, which yield consistent isotopic

requilibration temperatures in the range 118–200°C (Table 4).

The mean δ^{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).

769 Thermochemical reduction of younger marine sulfate would also be compatible with the data. For example,

- 770 the isotopic offset of sphalerite and galena from marine sulfate of Miocene age (δ^{34} S~22‰; Paytan et al.
- 1998) would be 13–16‰, consistent with the full expression of the kinetic isotope effect.

The mean δ^{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.

774 The supporting evidence can be seen in a plot of δ^{34} S versus δ^{18} O (Fig. 12), which shows that the barite data 775 extend toward the measured composition of Triassic gypsum rather than the composition of Miocene marine 776 sulfate (δ^{34} S~22‰, δ^{18} O~11‰; Paytan et al. 1998; Turchyn and Schrag 2004). The colinearity of gypsum 777 and barite strongly suggests that Triassic cap rock was the source of sulfate for barite formation and that the 778 sulfate was isotopically modified by sulfate-consuming chemical reactions and possibly also by oxygen 779 isotopic exchange reactions. Qualitatively, the isotopic modifications are what would be expected where TSR 780 operated under conditions of limited sulfate supply, the increase in δ^{34} S reflecting the kinetically-controlled 781 preferential reduction of ³⁴S-depleted sulfate and the increase in δ^{18} O reflecting either preferential reduction 782 of ¹⁸O-depleted sulfate or thermally-driven oxygen exchange between sulfate (or reduction intermediates) and 783 H₂O. In that they show effects consistent with TSR under conditions of limited sulfate supply, the isotopic 784 compositions suggest that barite may have formed from sulfate that remained at the site of ore formation after 785 sphalerite and galena had precipitated. Thus, the simplest interpretation of the data is that Triassic evaporites 786 furnished sulfur for both the sulfide and the barite event.

787 Processes of ore deposition

788 Sphalerite-galena stage: At the temperatures of ore deposition in the diapiric zone of a carbonate-rich 789 sequence, ore-forming concentrations of Zn and Pb are possible in brine where the ratio of sulfate to reduced 790 sulfur is very high. The deposition of the sphalerite-galena assemblage was most likely achieved by mixing 791 this metal-bearing brine from deep in the basin with a reservoir of reduced sulfur already present in the diapir 792 area. In this scenario, TSR processes involving organic matter in the diapir rocks had reduced sulfate in the 793 diapir or in the fluids residing in the peridiapiric strata prior to the influx of the metaliferous brines. It is 794 possible that some TSR processes may have contributed to the reduced sulfur budget by in situ TSR of sulfate 795 in the inbound metaliferous fluid by local organic matter. Mixing processes of a metal-rich brine with reduced 796 sulfur not only precipitates sulfides but also generates large amounts of acid that must be buffered by the 797 carbonate host rocks. This process is shown by the abundance of dissolution breccia and collapse-breccia, 798 caves, and enhanced pore space, host rock replacements and extensive vuggy porosity in the host rocks. 799 Cooling of the ore fluid, as suggested by the cristallization of fine-grained bipyramidal quartz, may have also 800 contributed to the precipitation of sulfides, but to a lesser degree. 801 Barite stage: The previous discussion of sulfur isotopes show that the colinearity of sulfur isotopes for 802 gypsum and barite strongly suggests that Triassic cap rock was the source of sulfate for barite formation and 803 that the sulfate was isotopically modified by sulfate-consuming chemical reactions (i.e., TSR) and possibly

- 804 also by oxygen isotopic exchange reactions. Therefore, barite deposition must have been produced when a
- 805 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 carbonatehost rocks.
- 808 <u>Fluorite stage (+minor Pb-Zn sulfide)</u>: 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
- 810 CaF- complexes. The high temperatures also account for the high metal contents measured in the fluid
- 811 inclusions. At high temperatures, some reduced sulfur can be transported together with Zn and Pb (Yardley
- 812 2005). A fluid with this metal load and fluorine transport as a CaF complex can deposit fluorite together with
- 813 sphalerite and galena simply by cooling and fluid dilution.

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

815 It is clear that multiple fluid reservoirs that include hydrocarbon-bearing fluids, evaporated seawater, halite 816 dissolution brines as well as a presumed meteoric component were involved in the three distinct ore events at 817 Bou Jaber (Fig. 14). The interactions of these fluids with other fluid reservoirs containing reduced sulfur 818 (H₂S) or oxidized sulphur (SO₄) were essential to precipitate sulfides and barite. Assuming the evaporated 819 seawater component formed during the deposition of the Triassic evaporites, these very dense and low 820 viscosity brines probably migrated into the deep parts of the basin, including the Palaeozoic basement rocks. 821 Given that fluid mixing was likely an important depositional process, the ascent of the dense, deep basinal 822 fluid into upper stratigraphic levels required exceptional hydrological events. Although hydrological 823 modelling of fluids in and about salt diapirs show complex fluid regimes such as thermohaline and density 824 convection, release of geopressured fluids and focusing of fluids along impermeable evaporites and diapiric 825 structures (e.g., Kyle and Price 1986; Evans et al. 1991), we suggest that normal basin and diapir-controlled 826 fluid migration was not singularly responsible for ore deposition. If the Tunisian diapir-related ores formed 827 from normal basin processes involving diapirs, then we would expect that there should be many more diapiric 828 related ore deposits in the Tunisia Diapir Belt as well as in the Tethyan diapirs of Central Algeria- and 829 Western Morocco parts of North Africa, as well as in Europe and other diapirs provinces in the world. 830 There is an increasing appreciation that major sediment-hosted Zn-Pb ores ore formed as a result of large-831 scale tectonic triggers (Leach et al. 2010) that released deep-seated fluids into favourable geochemical traps. 832 This may be the situation for Bou Jaber and the other ore deposits of the Tunisia salt diapir belt. The first 833 significant tectonic event after evaporite formation was mid-Cretaceous rifting during the Africa-Europe plate 834 separation that produced tilted blocks, half-grabens and salt diapirism. There is no evidence for ore 835 emplacement during this tectonic and diapirism period. However we suspect that the compressional event in 836 mid-Miocene (Rouvier 1977) related to the African European plates subduction-collision that produced 837 thrusting, SW-NE-trending folds and the return of salt diapirism, may have been the tectonic trigger that 838 brought deep-seated brines into the upper parts of the diapir body and into the peridiapiric cover rocks. The

839 ascent of deep-seated Zn-Pb brines would have interacted sources of reduced sulfur and hydrocarbons and840 precipitated the main-stage sphalerite and galena ores.

841 The diapirs may have focused fluid flow along the southeast flanks of the diapirs that define the Alpine 842 thrusting. Diapir development was also responsible for the development of fracture permeability and creation 843 of hydrocarbon and reduced sulfur chemical traps in the cover rocks. Furthermore, peak oil generation 844 occurred in the Miocene and Pliocene (Belayouni et al. 1992) during accelerated burial in parallel with the 845 Alpine orogenic events. About 50 km south of the Bou Jaber mine, the main oil fields produce hydrocarbons 846 from the Aptian limestones reservoir, similar to that hosting the Bou Jaber ores.Perhaps the reason for 847 mineralization in some diapirs and not others could be the "quality" of the chemical traps or the involvement 848 of some "special" steeply dipping deep-seated faults (perhaps the NW-SE faults that cut the NE-SW trend of 849 the diapirs). The proposed migration of the deep-seated brines during the Alpine orogeny, related to the 850 effects of Alpine collision, provided uplift of the basin and over pressured fluids from thrust stacking and 851 burial maturation of organic matter. 852 The previous discussion on deposition of the Zn-Pb rich ores proposed a fluid-mixing precipitation model 853 that applies to many sediment hosted Zn-Pb ores (e.g., Cooke et al, 2000; Leach et al, 2005). However, an 854 enigmatic question is how do the barite and fluorite events connect or not to the Zn-Pb ores at Bou Jaber? 855 Although Zn-Pb, barite and fluorite ores do occur together in some ore zones in Bou Jaber, this association is 856 inconsistent within the deposit as well as in the region (few mineralized diapirs contain all three mineral 857 assemblages). The three mineral assemblages are clearly geochemically and paragenetically distinct but yet 858 they were controlled by the same diapiric structures related to the Alpine orogeny in the Miocene-Pliocene 859 times. As pointed out previously, the geochemical constraints on a hot basinal brine in a carbonate platform 860 limits the ability of a single fluid to transport ore-grade amounts of Zn, Pb, Ba and F. Consequently, we 861 suggest that an evolving tectonic and structural regime during the Alpine orogeny, resulted in the ascent of 862 fluids from distinctly different fluid reservoirs. Zn-Pb rich ores formed by the mixing of an oxidized Zn-Pb 863 brine into a hydrocarbon reduces sulphur gas reservoir, barite formed by the mixing of a Ba-rich fluid with 864 sulphate-rich fluids and meteoric water in the diapiric zone and fluorite was deposited in the diapiric zone 865 from a Na-rich brine by cooling, dilution, pH change in the diapiric zone.

866 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 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.

878 The ores at Bou Jaber and other large tonnage deposits in the diapir belt are located in -or adjacent to-879 organic-rich peridiapiric rocks along the south-eastern flank of northwest dipping diapirs. Mineralization is 880 especially common at the NE and SW extremities of the diapir. The locations of the ores appear to coincide 881 with the possible intersections of the SW-NE deep basement faults and NW-trending faults limiting Miocene-882 Pliocene NW-trending grabens were controlled by the interaction of NW-SE to EW trending, deep seated and 883 steeply dipping faults that may have been the vertical pathway for ascending metalliferous brines that 884 precipitated ores in the peridiapiric zone. Therefore, the connectivity of faults in the basement with the upper 885 diapiric zones must have been essential. Lacking the connectivity, a salt diapiric zone would remain sterile in 886 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.

891 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 age/s 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

903 the ore deposit are remarkably similar to those for the MVT family. There are no obvious connections to

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904 igneous events. The presence of abundant barite and fluorite with the Zn-Pb ores is unusual for a MVT 905 deposit; however they overprinted a distinct and older Zn-Pb event. Therefore, the ores of Bou Jaber can 906 clearly be classified as "MVT" or as a "MVT sub-type" or as Salt Diapir-related Zn-Pb ores 907 The deposition of Zn-Pb ores was determined by the presence of a hydrocarbon-reduced sulphur reservoir 908 about the salt diapir. Undoubtedly, the quality of the sulphur trap played a major role in the endowment of 909 Zn-Pb of the deposit. Factors that influence the quality of the trap are the abundance of gypsum/anhydrite in 910 the mother salt, the size of the structural trap and the permeability and porosity of the hydrocarbon-reduced 911 sulphur reservoir. 912 The Zn-Pb ores at Bou Jaber resulted from the mixing of metalliferous sedimentary brine with reduced 913 hydrocarbon-reduced sulfur reservoir in the peridiapiric environment. Consequently, a deep-seated 914 (basement?) fluid component must have an efficient fluid pathway to ascend into the chemical sink in the 915 peridiapiric zone. Therefore, the connectivity of faults in the basement with the upper diapiric zones was 916 essential. 917 The studies presented here provide new insights into the genesis of the Bou Jaber Pb-Zn-Ba-F ore deposit 918 and suggest that new research will be needed to improve our understanding of MVT ores in diapiric 919 environments both in Tunisia and globally. In view of the giant diapiric ores of Jinding China, future 920 discoveries of large resources of diapir-related ores in North Africa and globally require an increased focus on 921 exploration in the peridiapiric environment. 922 Acknowledgements - We wish to thank Fethi M'Barek, director of the Bou Jaber mine, for his assistance to made 923 possible underground ore examinations and sampling. We wish also to thank Cyndi Kester, for assistance during the C, O 924 and S isotopes analysis. The authors thank the following individuals for helpful discussions on the geology and halokinesis 925 of the Bou Jaber diapir: Habib Belayouni, Saïd Tlig; Ali Zaier from the University of Tunis El Manar; Ahmed Brahem 926 from the Office National des Mines Tunisia and Larbi Raddad from the College of the City University of New York. 927 Discussions with Pr. Habib Belayounion the organic matter and mineralisation relationships were strongly helpful. Review 928 by Karen Kelley, from the USGS Denver, significantly improved the manuscript. Financial aid was provided to Salah 929 Bouhlel by a research grant from the C.I.E.S/U.S.A, Fulbright program.

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Figures



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 paragentic 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 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 the70° 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_w+V fluid inclusions in fluorite. **c** Primary L_w+V fluid inclusions in barite. **d** Primary L_w+L_p+V fluid inclusion in fluorite. **e** Large primary L_p+V fluid inclusion in fluorite. **f** Same as Fig e but under epifluorescence microscope. $L_w=$ water; V= vapour; $L_p=$ Petrolium.



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 δ^{13} C (PDP) vs δ^{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 δ^{34} S values for sphalerite, galena, pyrite and barite at Bou Jaber, and δ^{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 δ^{34} S values for sphalerite, galena, pyrite, barite and Triassic gypsum. **c** Plot of δ^{18} O vs δ^{34} S of Bou Jaber barites. The δ^{18} O, δ^{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 (⁸⁷Sr/⁸⁶Sr 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 ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb diagram (uranium derived Pb) (14**a**) and in the ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb diagram (14**b**). 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.

Sample	Mineral	Nbr IF	Te °C	Tm ice °C	Salinity Wt% NaCl equiv.	Th °C
2525C1	Sphal	38	-39 to -32	-16.8 to -14.8	18.5–19.1 (19.2)	112–133 (123)
2525C3	Sphal	34	-40 to-30	-18.7 to -13.4	17.3–21.5 (19.13)	115–136 (125)
6921D	Sphal	28	-40 to -37	-1.7 to -13.6	17.4–19.99 (18.1)	116–136 (128)
	<u>Total</u>		-40 to -30	-18.7 to -13.4	17.2–21.47 (19.1)	112–136 (125)
6925B1	Barite	20	-40 to -39	-11 to -7.8	11.5–15 (13.3)	101–110 (105)
9514BA	Barite	10	-43 to -40	-11.4 to -7.6	11–15 (13.6)	116–124 (120)
95J1	Barite	16	-40 to -38	-10.4 to -8.8	12.6–14.4 (13.2)	110–114 (112)
9533B	Barite	25	-42 to -36	-10 to -8.8	12.6–13.9 (13.4)	100–131 (119)
63WA	Barite	18	-45 to -41	-13.6 to -11.6	15.6–17.4 (16.7)	115–118 (117)
	Total	89	-45 to -36	-13.6 to -7.6	11.2–17.4 (13.9)°	100–131 (114)
8511	Fluorite	34	-42 to -28	-18 to -14	21.5–18.1 (20.1)	140–165 (155)
B8512	Fluorite	60	-42 to -28	-13.8 to 19.4	22–17.6 (19.8)	144–163 (154)
9514AF	Fluorite	52	-32 to -28	-19.6 to -15.8	22.1–19.3 (20.6)	140–163 (150)
95514BF	Fluorite	60	-32 to -28	-20.5 to -15	22.6–18.6 (20.5)	144–162 (153)
9533BF	Fluorite	40	-45 to -40	-18.2 to -12.4	21.1–16.3 (17)	146–154 (145)
	Total	246	-45 to -28	-20.4 to -12.4	16.3 –22.6 (20)	140–165 (152)
63WB	calcite	25	-33.3 to - 30	-18.2 to -15.5	20-0.9 (20.8)	113–126 (118)
63WC	calcite	22	-33.3 to -	-18 to -17	21.1–19.0 (20)	109–117 (113)
	<u>Total</u>	45	-33 to -30	-18.2 to -15.5	19.0–21.1 (20.5)	109–126 (116)

Table 1: Summary of the microthermometric data derived from the studies ofprimary fluid inclusions (Lw+V) in sphalerite, barite and fluorite from the BouJaber "Gîte de l'Est".

		BJ9533 Fluor	rite BJ6921 Fluorite BJ6925 Fluorite				BJ9533 Barite									
	Average wt/wt	StdDev	%RSD	ppm	Average wt/wt	StdDe v	%RS D	ppm	Average wt/wt	StdDev	%RSD	ppm	Average wt/wt	StdDe v	%RSD	ppm
Li	0.00595	0.0020	35.1	243	0.00415	0.0013	31.9	164	0.00685	0.0019	28.1	275	0.00433	0.0020	48.4	84
N a	1	0	0	4091 4	1	0	0	3952 7	1	0	0	40076	1	0	0	19334
M g	0.01926	0.0143	74.5	788	0.05365	0.0259	48.4	2121	0.03236	0.0041	12.9	1297	0.03417	0.0169	49.5	661
K	0.09236	0.0740	80.2	3779	0.05780	0.0200	34.7	2285	0.13307	0.0842	63.3	5333	1.08053	0.3561	33.0	20891
C a	0.5			2045 7	0.5			1976 4	0.5			20038	0.5			9667
M n	0.00364	0.0018	50.0	149	0.00529	0.0034	64.4	209	<0.0059 5			<238	0.00714	0.0065	91.7	138
F e	0.02681	0.0189	70.5	1097				0	0.04296	0.0325	75.8	1722	0.00974	0.0141	144.8	188
C u	0.00624	0.0073	118.3	255	0.00935	0.0041	44.7	370	0.01115	0.0004	3.9	447	0.00745	0.0043	57.8	144
Z n	0.02107	0.0092	43.7	862	0.05745	0.0196	34.2	2271	0.02813	0.0325	115.8	1127				0
S r	0.03196	0.0120	37.8	1308	0.05385	0.0195	36.3	2129				0				0
A g	0.00005	0.0000	85.7	2	0.00024	0.0002	88.8	9	0.00067	0.0006	101.4	27	0.00037	0.0003	83.7	7
B a	0.01409	0.0078	56.0	576	0.04720	0.0221	47.0	1866	0.00690	0.0038	56.2	276				0
P b	0.01072	0.0085	79.8	439	0.00382	0.0021	55.9	151	0.00589	0.0060	103.3	236	0.00193	0.0008	41.4	37
U	0.00001	0.0000	95.5	0.3	0.00013	0.0001	141.8	5	0.00043	0.0003	72.9	17	0.00005	0.0000	26.1	1

Table 2 LA-ICPMS analyses of individual fluid inclusions in fluorite and barite from levels – 69 m and 95 m,

Concentrations in fluorite are based on a salinity of 18wt%NaCl, barite salinity of 13wt% 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).

Samples	Description	δ ¹³ C	δ ¹⁸ O		
		(‰, PDP)	(‰, SMOW)		
6928	Aptian limestone	-1.9	30.1		
B6930A	Aptian limestone	2.7	29.6		
B6929	Aptian limestone	2.6	29.9		
9523U5	Aptian limestone	3.3	28.3		
9549BC1	Aptian limestone	-2	27.9		
69U5C1	Aptian limestone	2.7	26.9		
69U5C2	Aptian limestone	3.9	26.2		
6929U5	Aptian limestone	2.6	28		
BJU5	Aptian limestone	1.8	27.3		
BJU5 cte2	Aptian limestone	1.6	26.7		
6939U5	Aptian limestone	2.9	26.7		
9518U5	Aptian limestone	3	27.3		
6937A	Aptian limestone	3.5	27		
B9514	Ankerite 1	2.7	26.8		
9534B1	Ankerite 1	3.6	26.9		
9534B2	Ankerite 1	3.1	26.9		
9534A2	Ankerite 2	3	27		
B9517A	Ankerite 2	2.5	26.3		
B9517B	Ankerite 2	2.4	25.9		
9575A	Ankerite 3	-0.4	19.6		
9575B	Ankerite 3	0.3	21.2		
B63W	Ankerite 3	1.5	22.9		
BJ901 cte	Calcite 1	1.3	18.8		
B8511G	Calcite 1	1.3	21.7		
C18015*	Calcite 1	3.1	22.9		
C18128*	Calcite 1	3.3	21.3		
B92H	Calcite 1	3.8	23.1		
B9530B	Calcite 2	3.1	24.8		
B6911B	Calcite 2	3.1	26		
9502	Calcite 2	2.6	25.6		
9505	Calcite 2	3.7	25.9		
6904A	Calcite 2	2.9	25.5		
C18028*	Calcite 2	3.6	26.9		
C1830*	Calcite 2	3.8	27.1		
C18020*	Calcite 2	3.8	27.4		
BJ2295	Calcite 2	6.2	26.4		
9549B	Calcite 2	3.5	25.6		
B6937B	Calcite 2	3.3	27.3		

Table 3 Carbon and oxygen isotopes compositions of Aptian limestone host rock, hydrothermalankerite and calcite from Bou Jaber. Analysis marked with asteriskare from Salmi-Louar 2004; and Salmi-Laouar et al 2007

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 asterisk are from Salmi-Louar 2004 and Salmi-Laouar et al. 2007). Calculated Temperatures are obtained using the equation $\delta ZnS - \delta PbS = (0.73/T^2).10^6$ (Ohmoto and Rye1979).

Ore zones	Level	Samples	Mineral	δ ³⁴ (‰	δ ¹⁸ O‰.	⊿ Sph-Gn	T°C
	(m)			(CDT)	(SMOW)	%	
Sulfide-rich zone	-63	1/P4Ba	Barite	21.5	21.3		
Sulfide-rich zone	-63	2/89NGn	Gn	5.8		3.6	176
Sulfide-rich zone	-63	3/89NGn1	Gn	6.0		3.5	180
Sulfide-rich zone	-63	4/89NSP1	Sph	9.4			
Sulfide-rich zone	-63	5/89NSP1	Sph	9.5		3.7	168
Sulfide-rich zone	-63	6/89NBa1	Barite	22.6	21.7		
Sulfide-rich zone	-63	7/89V2Sp	Sph	9.5		4	152
Sulfide-rich zone	-63	8/89V1Sp	Sph	9.5			
Sulfide-rich zone	-63	9/89V1Gn	Gn	5.5			
Sulfide-rich zone	-63	10/89V1Ba	Barite	23.4			
Sulfide-rich zone	-63	11/89V2Sp	Sph	9.2			
Sulfide/barite zone	-63	12/90K1Gn	Gn	3.6			
Sulfide/barite zone	-63	13/90K2Gn	Gn	5.2			
Sulfide/barite zone	-63	14/90K3Gn	Gn	5.2			
Sulfide/barite zone	-63	15/90K1Ba	Barite	20.2			
Sulfide/barite zone	-03	10/90K2Ba	Barite	22.5	22.2		
Sulfide/barite zone	-05	17/90K3Da 18/00K4Da	Darite	21.1	22.2		
Barita zono	-03	10/90 K4D a	Gn	6 27			
Barite zone	-03	20/63W/IBa	Barita	0.37	21.3		
Barite zone	-03	20/03 W4Ba 21/00CGn	Gn	58	21.5		
Sulfide_rich zone	-69	21/90COII 22/90HGSp	Sph	9.0		3.2	200
Sulfide-rich zone	-69	22/90HGp	Gn	9.2 6.0		3.2	200
Sulfide-rich zone	-69	24/41AGn1	Gn	0.0 7 1			
Sulfide-rich zone	-69	25/11AGn2	Gn	81			
Sulfide-rich zone	-69	26/8511Gn1	Gn	1.1			
Sulfide-rich zone	-69	27/8511Gn2	Gn	1.2			
Sulfide-rich zone	-69	28/8511Sp1	Sph	8.4			
Sulfide-rich zone	-69	29/8511Ba1	Barite	21.5	21.8		
Sulfide-rich zone	-69	30/15Ba	Barite	21.9			
Sulfide-rich zone	-69	31/16BGn	Gn	6.7			
Sulfide-rich zone	-69	32/69BGn1	Gn	7.1			
Sulfide-rich zone	-69	33/69BBa	Barite	23.2	23.3		
Sulfide-rich zone	-69	34/20Sp1	Sph	9.3		4.48	129
Sulfide-rich zone	-69	35/20Gn1	Gn	4.9			
Sulfide-rich zone	-69	36/20Sp2	Sph	8.6		3.77	165
Sulfide-rich zone	-69	37/20Gn2	Gn	4.8			
Sulfide-rich zone	-69	38/20Ba1	Barite	21.6			
Sulfide-rich zone	-69	39/20Ba2	Barite	22.3			
Sulfide-rich zone	-69	40/21DSp1	Sph	9.7			
Sulfide-rich zone	-69	41/21DGn	Gn	8.2			
Sulfide-rich zone	-69	42/21DBa11	Barite	22.8			
Sulfide-rich zone	-69	43/21DBa12	Barite	23.0			
Sulfide-rich zone	-69	44/25C3Gn	Gn	5.8		4.7	110
Sulfide-rich zone	-69	45/25DGn1	Gn	4./		4./	119
Sulfide-rich zone	-09	40/25DSp2	Spn	9.5			
Sulfide rich zone	-09	47/25DGff21	Gn	5.0 7.5			
Sulfide rich zone	-09	46/25D0115	Sab	7.5		25	101
Sulfide rich zone	-09	49/255p1	Spli	9.4		3.5	101
Sulfide rich zone	-09	50/255p2 51/255p3	Sph	9.5		3.4	15/
Sulfide rich zone	-09	51/255p5 52/25Cn1	Gn	5.9		4.0	194
Sulfide-rich zone	-69	53/25Gn2	Gn	5.9		5.5	101
Sulfide-rich zone	-69	54/27Sn	Sph	9.4		3.8	164
Sulfide-rich zone	-69	55/27Gn	Gn	5.6		5.0	104
Sulfide-rich zone	-69	56/48Ba1	Barite	22.0			
Sulfide-rich zone	-69	57/48Gn1	Gn	5.1			
Sulfide-rich zone	-69	58/69DSn1	Sph	8.9			
Sulfide/barite zone	-69	60/21DBa1	Barite	22.9	20.7		
Sulfide/barite zone	-69	61/21DGn2	Barite	23.4	22.5		
Sulfide/barite zone	-69	62/21G1Gn	Gn	5.3			

-	Sulfide/barite zone	-69	63/21G1Ba	Barite	24.5	
	Sulfide/barite zone	60	64/23GGn1	Gn	6.5	
	Sunde/Dante Zone	-09	04/2300111 (5/22CD-1	Daulta	0.5	
	Sumde/barne zone	-09	03/230Dal	Бапе	25.0	
	Sulfide/barite zone	-69	66/25BGn	Gn	4.9	
	Sulfide/barite zone	-69	67/25BBa	Barite	22.3	
	Sulfide/barite zone	-69	68/36Gn	Gn	6.0	
	Sulfide/barite zone	-69	69/36Ba2	Barite	22.2	
	Barite zone	60	70/31Ba	Barite	22.5	
	Darite zone	-09	70/31Da 71/20D-1	Danie	22.5	
	Barite zone	-69	/1/32Ba1	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	75/50Gn1	Gn	59	
	Darite Zone	60	76/60Pa	Dorito	22.5	
	Dante zone	-09	70/09Da	Dante	22.0	
	Barite zone	-69	///60Ba	Barite	23.7	
	Sulfide-rich zone	-95	78/5AGn1	Gn	5.4	
	Sulfide-rich zone	-95	79/5AGn2	Gn	5.6	
	Sulfide-rich zone	-95	805ABa	Barite	22.3	
	Sulfide-rich zone	-95	81/5 Aba	Barite	187	
	Sulfide rich zone	05	01/5110a	Cn	76	
	Sumde-ficit zone	-95	82/314gii	Gil	7.0	aa 1
	Sulfide-rich zone	-95	83/514B2	Barite	22.8	23.1
	Sulfide-rich zone	-95	84/514AGn	Gn	5.6	
	Sulfide-rich zone	-95	85/514ABa	Barite	21.2	21.8
	Sulfide-rich zone	-95	87/17AGn	Gn	7.9	
	Sulfida rich zona	05	99/17Abo	Dorito	21.2	
		-95	00/1/AUa	Dante	21.3	
	Sulfide-rich zone	-95	89/34BaG1	Barite	21.3	
	Sulfide-rich zone	-95	90/34BaG2	Barite	18.5	21.4
	Sulfide/barite zone	-95	91/34BaG2	Barite	18.6	
	Sulfide/barite zone	-95	92/33BaG2	Barite	22.8	
	Sulfide/barite.zone	-95	93/33BaG3	Barite	20.7	
	Danita zana	-95	93/33DaC3	Danie	20.7	
	Barile zone	-95	94/33DaU3	Barne	20.8	
	Barite zone	-95	95/98K3Sp	Sph	9.7	
	Barite zone	-95	96/98K3Gn	Gn	7.0	
	Barite zone	-95	97/98K3Ba	Barite	20.8	
	Barite zone	-95	98/98Ba	Barite	19.9	
	Darite zone	-)5	00/05V2Da	Darite	17.7	22.4
	Barne zone	-95	99/93K3Da	Darite	25.4	23.4
	Barite zone	-95	100/C31Ba	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
	Aptian limestone	Open pit	103*	Pvrite	15.6	
	Aption limestone	Open pit	10//*	Durito	15.0	
	Aptian linestone	Open pit	104	Domite	16.2	
	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	
	Aption limestone	Open pit	110N2*	Gn	3.2	
	Trianai ambata	Open pit	110 0 4 970*	Communi	3.2	
		Ouenza	112 SA870*	Gypsum	10.0	
	Triassic sulfate	Ouenza	113SA8729*	Gypsum	13.4	
	Triassic sulfate	Ouenza	114SA8731*	Gypsum	14.3	
	Triassic sulfate	Mesloula	115SA7982*	Gypsum	15.4	
	Triassic sulfate	Mesloula	116SA8734*	Gypsum	15.2	
	Triassic sulfate	Mesloula	117848738*	Gypsum	14.9	
		Mesioula	1100 40727*	Cypsum	14.9	
	Triassic sulfate	Mesioula	118SA8/3/*	Gypsum	15.3	
	Triassic sulfate	Mesloula	119SA873*	Gypsum	14.6	
	Triassic sulfate	Mesloula	120SA8733*	Gypsum	15.1	
	Triassic sulfate	Mesloula	121SA8739*	Gypsum	15.5	
	Triassic sulfate	Mesloula	1228A8740*	Gynsum	14 9	
	Triassic sulfate	Rou Jahar	1225110710	Gypsum	15.4	
	This said sufface	Dou Jabel	123310*	Comme	1.1.4	
	Thassic sulfate	Dou Jaber	124540*	Gypsum	14.0	
	Triassic sulfate	Bou Jaber	125S26*	Gypsum	15.3	
	Triassic sulfate	Bou Jaber	126S26*	Gypsum	13.4	
	Triassic sulfate	Bou Jaher	127S40*	Gypsum	15.3	
	Triassic sulfate	Bou Jaber	128548726*	Gynsum	15.1	
	Triaggio gulfata	Lamaimat	1205110720	Gupan	12.1	
	Thassic sullate	nameimat	1293A8/22*	Gypsum	13.4	
	Triassic sulfate	Hameimat	130SA8735*	Gypsum	14.8	
	Triassic sulfate	Fedj el Adoum	131 FH	Gypsum	16.0	15.5
	Triassic sulfate	Fedj el Adoum	132FH	Gypsum	17.1	12.9
	Triassic sulfate	Fedi el Adoum	133FH	Gypsum	16.8	16.1
				- / 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.

Ore stage	Sample	Mineral	⁸⁷ Sr/ ⁸⁶ Sr	Std dev.
Early barite	69BJP4	Barite	0.708210	0.000031
Second generation barite	6960	Barite	0.710811	0.000026
Second generation barite	6932	Barite	0.710117	0.000029
Second generation barite	6921	Barite	0.710179	0.000032
Second generation barite	9531	Barite	0.710000	0.000033
Second generation barite	9514I	Barite	0.710134	0.000017
Late stage barite	6960	Barite	0.710811	0.000026
Late stage barite	692G3	Barite	0.711408	0.000033
Late stage barite	6960G	Barite	0.711291	0.000031
Triassic sulfate	Triassic	Gypsum	0.708125	0.000044

Table 6 Lead isotope composition of galena samples from Bou Jaber collected mine levels -69m and -95m)

Samples	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
6911AGn1	18.737	15.643	38.767
6911AGn2	18.707	15.671	38.808
6921DGn	18.730	15.678	38.838
6925C3Gn	18.704	15.643	38.779
6925BGn1	18.699	15.649	38.751
6932Gn1	18.732	15.690	38.869
6936Gn1	18.707	15.670	38.806
6948Gn	18.719	15.668	38.797
6950Gn1	18.720	15.673	38.797
955ABGn1	18.783	15.762	39.100
698511G	18.733	15.664	38.816
955BGn1	18.786	15.757	39.085
9514AGn	18.755	15.664	38.821
9514BGn	18.699	15.646	38.736
9517Gn	18.729	15.686	38.838
9598K3	18.752	15.663	38.805