Isotope geochemistry of Mississippi Valley Type stratabound F-Ba-(Pb-Zn) ores of Hammam Zriba (Province of Zaghouan, NE Tunisia)

Nejib Jemmali[a, ✉], Emmanuel John M. Carranza[b,c,d], Balkiss Zemmel[a]

[a] *Université de Gafsa, Faculté des Sciences, Département de Géologie, Sidi Ahmed Zarroug-2112 Gafsa, Tunisia*

[b] *Economic Geology Research Centre, Department of Earth and Oceans, James Cook University, Townsville, Queensland, Australia*

[c] *Geological Sciences, School of Agricultural, Earth and Environmental Sciences, University of KwaZulu-Natal, South Africa*

[d] *Institute of Geosciences, State University of Campinas, Campinas, São Paulo, Brazil*

ABSTRACT

The Hammam Zriba F-Ba-(Zn-Pb) ore deposit in the Province of Zaghouan in north-eastern Tunisia is hosted in the shallow dipping unconformity between green marls with chalky biomicritic limestones of Campanian age and Uppermost Jurassic carbonates. The mineralization consists mainly of fluorite and barite with minor sphalerite and galena. Calcite is the main gangue mineral. Two types of Zn-Pb sulfides can be distinguished according to the geometry of the orebodies, i.e., lenticular or stratiform ores, intra-karstic fillings. Sulfur isotope compositions ($\delta^{34}S$) of barite range from 14.7 to 17.2‰, indicating that sulfur was derived from Triassic evaporites and the higher ones (19 to 25.7‰) are due to reservoir effect associated with thermo-chemical sulfate reduction (TSR) or bacterial sulfate reduction (BSR) under conditions of restricted sulfate supply. $\delta^{34}S$ of galena and sphalerite in lenticluar and intra-karstic orebodies range from -13.8 to 2.1‰, and could be explained by multiple sources of reduced sulfur: Triassic evaporites, diagenetic primary sulfides as well as sulfur from organic matter. Both TSR and BSR as potential contributors of sulfur are needed for sulfide precipitation. Lead isotope compositions of galena exhibit very similar: $^{206}Pb/^{204}Pb$ (18.858–18.876), $^{207}Pb/^{204}Pb$ (15.667–15.684), and $^{208}Pb/^{204}Pb$ (38.680–38.747) ratios, and plot between the upper crust and orogene average growth curves, reflecting involvement of a mixing and subsequent

---

✉ Corresponding author. Faculté des Sciences de Gafsa, Sidi Ahmed Zarrouk, 2112 Gafsa, Tunisie. E-mail address: nejib.jemmali@yahoo.fr (Nejib Jemmali).

28 homogenization of Pb isotopic compositions of different source Pb reservoirs. The underlying 29 Paleozoic basement rocks were the plausible source of metals. The economic ore (fluorite F1) 30 mineralization was formed during the Eocene-Miocene compressional phase. During this deformation 31 phase, deep-seated basinal brines have been circulated as hydrothermal fluids that have interacted with 32 the Paleozoic rocks, thereby leaching metals, and have been channelized through subsidiary faults 33 associated with the major regional NE–SW-trending deep-seated Zaghouan-Ressas fault. 34 Hydrothermal fluids then migrated to the site of deposition where they got mixed with shallow, cooler, 35 metal-depleted, TSR- and BSR-derived sulfur-rich fluids, which triggered the precipitation of the ores.

36

37 **Keywords**

38 Hammam Zriba, Province of Zaghouan, Fluorite-Barite, Stratabound mineralization, Isotope 39 geochemistry

40

41 **1. Introduction**

42   The tectonic evolution of the Zaghouan-Ressas structural belt (ZRSB), which is situated in north- 43 eastern Tunisia (Fig. 1), is mainly a consequence of the following major tectonic events (Morgan et 44 al., 1998; Frizon de Lamotte et al., 2009). The Triassic-Early Jurassic period was characterized by the 45 development of N–S trending normal faults and E–W trending transfer faults, which defined the 46 eastern margin of a Jurassic carbonate platform. During the middle Jurassic – Early Cretaceous 47 extensional period, the inherited E–W trending fault, which was controlled by major faults linked to 48 the basement, continued to be active. This defined paleo-heights characterized by condensed 49 sequences and elongated basins (Bouaziz et al., 2002) and the absence of the major part of Cretaceous 50 rocks at Hammam Zriba, which are consistent with the persistence of the ZRSB at paleo-heights at 51 that time (Morgan et al., 1998). The geodynamic context during the Late Cretaceous – Early Eocene 52 was characterized by convergence, as expressed by NE–SW trending folds. The Late Eocene – Early 53 Miocene compressive event was marked by an angular unconformity at the base of the Oligocene and 54 the development of an Oligo–Miocene foreland basin. Contractional deformation of foreland basin

55 sediments in the ZRSB occurred in Early Miocene (post-Tortonian, pre-Messinian), and that 56 represented the main deformation responsible for the formation of the Atlas fold-thrust belt in Tunisia 57 (Morgan et al., 1998).

58   Several economically significant sediment-hosted F-Ba-Sr-(Zn-Pb-Cu-Hg) deposits occur along 59 the ZRSB (Fig. 1). Their mineralization is typically fluorite-rich and sulfide-poor, and shares 60 characteristics with MVT deposits such as the carbonate nature of the host rocks, the basinal brine 61 nature of fluids, the temperature of mineralizing fluids, the epigenetic character of mineralization, the 62 crustal source of metals and no magmatism associated (Souissi et al., 1997, 2010, 2013; Jemmali et al., 63 2011a). The province of Zaghouan is one of the most important fluorite-producing regions in Tunisia. 64 The deposits include the large Hammam Zriba F-Ba (Zn-Pb) deposit, Sidi Taya F-Pb (Zn-Ba-Sr) 65 deposit, Jebel Mecella F-Zn-Pb deposit, Hammam Jedidi F-Ba (Zn-Pb) deposit, Jebel Stah F deposit, 66 Jebel Oust F-Cu-Hg deposit, and the Jebel Ressas Pb-Zn (Fe) deposit (Fig. 1). Most of these deposits 67 are hosted in the Lower Liassic or Upper Jurassic massive limestones and the overlying Upper 68 Sinemurian-Carixian condensed limestones and Campanian marls. Because they have no direct 69 relationship with magmatism they are considered to have formed from basinal brines that were 70 mobilized during the Alpine orogeny (Souissi et al., 1997; Jemmali et al., 2011a).

71   Fluid inclusion measurements in fluorite from Hammam Zriba indicate that the ore-forming fluids 72 were hot (>100°± 20°C) and saline (>13 wt % NaCl equiv) basin-derived brines (Bouhlel et al., 1988). 73 These brines acquired high salinities and high molar ratios (Ca/Na, SO_4/Cl, Cl/Na), except for lower 74 Mg/Na ratio, at depth from the leaching of the Triassic evaporites by ascending hot fluids (Souissi et 75 al., 1997). The measured homogenization temperatures (110–185°C; Bouhlel et al., 1988) combined 76 with the thickness of the overburden, which never exceeded 2,100 m at the time of ore deposition, 77 imply a highly anomalous geothermal gradient that range between 50 and 70 °C/km. Consequently, 78 the reservoir of the fluids should be 3500–5000 m deep below the ore bearing layers (Souissi et al.,

79   1997).

80   In the current study, fluorite-bearing Zn-Pb ores from Hammam Zriba have been investigated for

81   their sulfur and lead isotopes composition to elucidate the source of reduced sulfur, mechanisms of ore

82   deposition and possible age of mineralization.

83   **2. Hammam Zriba deposit geology**

84   The Hammam Zriba F-Ba-Zn-Pb deposit is located about 8 km SE of Zaghouan town and 60 km

85   south of Tunis. It is situated in a horst structure, with varying thickness (0.3 to 1 km) and NNW–SSE

86   strike over ~3 km (Fig. 2). This horst has formed during late Jurassic as an emerged block bounded by

87   major faults that were remobilized later during various deformation stages (Melki and Zargouni, 1991) 88

and limited mainly by two normal faults (Gharbi et al., 1981): one (F1) striking N135–145°E and 89

dipping 50–70°NE and another (F2) striking N130–150°E and dipping 50–70°SW. A N160–N180 90

trending fault in the Portlandian lithofacies has controlled the paleo-morphological framework of the 91

uppermost part of the Portlandian massive facies. The overlying Campanian unit exhibits onlap 92

structures that rest on the irregular eroded karstified and mineralized surface, which forms a screen 93

surface for the upward channelization of fluids and subsequent mineral deposit formation in karst and 94

graben (Melki and Zargouni, 1991). Rocks in the Hammam Zriba mine are intensely fractured at 95

different scales on the surface and in the subsurface (Fig. 2). The stratigraphy comprises a series of 96

sedimentary rocks from the Portlandian to the Eocene with a hiatus from the Berriasian to the middle- 97

Campanian, corresponding to an emersion period (Thibieroz, 1974, 1976) (Figs. 2 and 3). The 98

Portlandian series consists of massive, thick, biomicritic and grey limestones. The Campanian 99

comprises green marls with chalky biomicritic limestones. The bottom of the Campanian series

100   contains some thin and discontinuous black phosphatic-shale levels. The Maastrichtian and Paleocene

101   series are composed of beige limestones and interbedded grey and green marls respectively. The

102   Eocene is dominated by grey, thick, phosphate-bearing limestones beds and green marls.

103   The Hammam Zriba has been classified by Souissi et al. (1997) as a typical MVT deposit.

104   Underground mining of this deposit was operated from 1967 to 1992, when more than 4 Mt of

ore 105   grading 25% fluorite (CaF_2), 1–2% Pb+Zn has been produced (Maghreb Minerals, 2008).

4

3. Sampling and analytical methods

A total of 38 representative samples from sulfide (galena: n=10; sphalerite: n=5) and sulfate (barite: n=23) minerals were collected from mine workings and outcrops of lenticular and intra-karstic ores. Mineral separates of galena, sphalerite and barite were prepared for conventional sulfur isotope analysis by careful hand-picking under a binocular microscope, and were analyzed at the laboratory of the Institute of Mineralogy and Geochemistry of the University of Lausanne (Switzerland) using a Carlo Erba 1100 elemental analyzer (EA) connected to a Thermo Fisher Delta S isotope ratio mass spectrometer (IRMS) that was operated in the continuous He flow mode via a Conflo III split interface (EA-IRMS). The sulfur isotope compositions are reported as per mil (‰) deviations relative to the Canyon Diabolo troilite (V-CDT) standard. The overall analytical reproducibility of the EA-IRMS analyses, assessed by replicate analyses of two laboratory standards (barium sulfate, with a working $\delta^{34}S$ value of +12.5‰; pyrite E, -7.0‰) is better than ±0.2‰ (1 SD). The accuracy of the $\delta^{34}S$ analyses was checked periodically by analyses of the international reference materials IAEA-S-2 silver sulfides (+22.7 ±0.2‰, values from IAEA-Catalogue and Documents) and NBS-123 sphalerite (+17.09±0.31‰, value from NIST-Catalogue and Documents).

For Pb isotope measurements, 2–3 mg of galena sample was dissolved using ultrapure (double distilled) HCl. The Pb isotope compositions were analyzed using a multi-collector inductively coupled plasma mass spectrometer instrument within the Radiogenic Isotope facility at the University of Bern (Switzerland). Sample aliquots were subsequently mixed with ~1.5 ml of a 2% HNO_3 solution spiked with the NIST SRM 997 Thallium standard (2.5 ppb), and aspirated (~100 μl/min) into the ICP source using an Apex™ desolvating nebulizer (Nu Instruments Ltd). Simultaneous measurements of all the Pb and Tl isotopes, and ^{202}Hg ion signal were achieved by using seven Faraday collectors. The ^{205}Tl/

128 ^{203}Tl ratio was measured to correct for instrumental mass bias (exponential law; ^{205}Tl/ ^{203}Tl=2.4262).

129 Upon sample introduction, data acquisition consisted of 2 half-mass unit baseline measurements prior

130 to each integration block, and 3 blocks of 20 scans (10 s integration each) for isotope ratio analysis.

131 ^{204}Hg interference (on ^{204}Pb) was monitored and corrected using ^{202}Hg. At the beginning of the

132 analytical session, a 25 ppb solution of the NIST SRM 981 Pb standard, which was also spiked with

133   the NIST SRM 997 Tl standard (1.25 ppb), was analyzed. The external reproducibility of individual

134   analytical sessions was ca. 1×10^{-4}.

135   **4. Results**

136   *4.1. Ore petrography*

137   The mineralization is structurally- and lithologically-controlled and hosted in the shallow dipping

138   unconformity between Campanian green marls with chalky biomicritic limestones and Jurassic reef 139 limestones (Fig. 2). It consists of fluorite and barite as the dominant ore minerals associated with 140 accessory celestite and some minor sulfides, including both sphalerite and galena. Dill et al. (2014) 141 also reported the presence of minor minerals such as mimetite (zincian), pyromorphite, smithsonite, 142 and traces of hemimorphite. Calcite and quartz are the gangue minerals.

143   The synthesis of our detailed examination of hand specimens of ore samples (Fig. 4) with the

144   studies of Thibieroz (1975) and Bouhlel et al. (1988) reveals the following fluorite types:

145   -   fluorite 1, the main economic ore, is a banded ore made of coarse-grained fluorite

146   alternating with bands of spherulitic barite 1 and quartz, associated with galena 1 and sphalerite 1 in

147   the black siliceous facies (diagenetic type mineralization (Mo) according to Bouhlel et al. (1985)) and

148   bands of white fibrous barite 2, which contains galena 2 crystals;

149   -   fluorite 2, which is made of large crystals within karstic pockets cutting over the fluorite

150   1 and associated with galena 2 and sphalerite 2 and massive barite 3; and

151   -   fluorite 3 consisting of large cubic crystals within geodes in the banded ore and the

152   karstic pockets.

153   Three types of ores can be distinguished according to the geometry of the orebodies:

154   (i) lenticular or stratabound ores are the most important and widespread, in close association with

155   sub-horizontal hydraulic fractures. This type of mineralization occurs between the Portlandian (wall)

156   and the Campanian (roof) (Fig. 4A), and exhibits banded texture composed of black siliceous facies

157   (Fig. 4B) and white fibrous barite 2 (Ba2) alternating with fluorite 1 (F1). Epigenetic galena 2, with

158   cubic crystals (Gn2), was found disseminated in barite 2 (Ba2) (Fig. 4C).

159   (ii) intra-karstic ores in the Portlandian limestones correspond to fillings of cavities, which are not

160   parallel to the bedding, and consist of fluorite 2 (F2) (Fig. 4E, F, H) associated with rare, fine galena 3

161   (Gn3) and sphalerite crystals (Sp2) (Fig. 4D, E, F, H); massive white barite 3 (Ba3) (Fig. 4E, G, H, I)

162   and large rhombohedra of calcite 1 (Ca1) crystals (Fig. 4J) ;

163   (iii) vein fillings in fractures cutting the Portlandian limestones, with calcite 2 (Ca2) (Fig. 4K, L)

164   and limestone onyx (LO) (Fig. 4K, L).

165   Based on the textural, mineralogical associations observed within the deposit and based on the

166   previous works of Bouhlel et al. (1988), mineralization has been classified into three stages (Table 1):

167   (1) pre-ore stage (diagenetic period) consisting of quartz, galena 1, sphalerite 1, barite 1 and pyrite

168   associated with organic matter (Type Mo); (2) hydrothermal ore stage composed of four sub-stages:

169   sub-stage 2a disseminated galenas 2 and 3 and sphalerite 2, sub-stage 2b barites 2 and 3, sub-stage 2c

170   fluorites 1, 2 and 3, and sub-stage 2d calcites 1 and 2; and (3) post-ore stage composed of secondary

171   minerals (smithsonite, hemimorphite and pyromorphite).

172   *4.2. Sulfur isotope compositions*

173   The $\delta^{34}S$ data obtained in this study (Table 2) represent various lenticular and intra-karstic ores,

174   and sulfur-mineral assemblages of the Hammam Zriba ore deposit. The $\delta^{34}S$ data range from –13.8 to

175   –1.4‰ for galenas 1 and 2, 1.7 to 2.1‰ for sphalerite, and 14.8 to 25.7‰ for all barites (Fig. 5).

176   For the lenticluar ore, the $\delta^{34}S$ values of galena 2 range from –13.8 to –11.2‰ (average = –

9

177 12.73‰). The barite 1 has $\delta^{34}S$ values ranging from 15.4 to 16.9‰ (average = 16.4‰), which are

178 close to the average $\delta^{34}S$ value of Triassic evaporates of Jebel Ressas (16.4‰; Jemmali et al., 2011a).

179 The barite 2 is more enriched in ^{34}S, with $\delta^{34}S$ values between from 19 to 25.7‰ with average of

180 22.35‰.

181 For the intra-karstic ore, the $\delta^{34}S$ values range from –2.6 to 2.1‰. Disseminated galena 3 and

182 sphalerite 2 associated with the black shales show narrow ranges of $\delta^{34}S$ values (–2.6 to –1.4‰ with

183 an average –2.17 and 1.7 to 2.1‰ with an average 1.92‰, respectively). The associated barite 3 has

184   δ^{34}S values ranging from 14.6 to 17.2‰ (average = 15.6‰). This mean δ^{34}S of barite 3 is close to the

185   average δ^{34}S a value of Triassic evaporates of Jebel Ressas (Jemmali et al., 2011a).

186   *4.3. Lead isotope compositions*

187   The results of lead isotope analyses of the Hammam Zriba galena samples are given in Table 3 and

188   plotted on Figure 6. For comparison, the lead isotopic values of galena from other Tunisian carbonate-

189   hosted deposits studied by Jemmali et al. (2011a) and Souissi et al. (2013) and from Nefza magmatic

190   rocks studied by Decrée et al. (2014) are also shown. Lead from the Hammam Zriba deposit is

191   isotopically homogeneous and show fairly uniform ^{206}Pb/^{204}Pb (18.858–18.876), ^{207}Pb/^{204}Pb (15.667–

192   15.684), and ^{208}Pb/^{204}Pb (38.680–38.747) ratios (Table 2; Fig. 6), which clearly indicate a crustal

193   source of lead.

194   **5. Discussion**

195   *5.1. urces of sulfate*

196   The δ^{34}S values of barite in Hammam Zriba are considerably variable. The δ^{34}S values of barites 1

197   and 2 from lenticular ores and barite 3 from intra-karstic ore are mostly in the range between 14.6 to

198   25.7‰ (Table 2). Two populations may be identified (Fig. 5). One population (barites 1 and 3)

199   corresponds to δ^{34}S values in the range between 14.6 and 17.2‰ with an average of 16‰; the second

200   population (barite 2) includes only six barite samples with substantially higher δ^{34}S values in the range

1

201   between 19 and 25.7‰ with an average of 22.35‰. The $\delta^{34}S$ average values of barites from the

202   population 1 overlaps with the typical composition of Triassic evaporitic rocks of Jebel Ressas

203   (Jemmali et al., 2011a), which show a well-defined and narrow range of $\delta^{34}S$ values from 15 to 17.9‰

204   (Fig. 5). This suggests that the majority of dissolved sulfate in the hydrothermal fluids that formed the

205   base metal mineralization in Hammam Zriba was derived from groundwater that had interacted with

206   Triassic evaporites. The second population includes barite samples with S isotope ratios higher than

207   the first population values and different from those of Triassic evaporates.

208   The repeated cycles of Triassic gypsum dissolution/re-precipitation by meteoric waters may have

209   generated residual brines that were slightly depleted in ^{34}S (Thode and Monster, 1965), with high Sr-

210   Ba/Ca, as necessary for Sr-Barite mineralization (Hanor, 2000). During the crystallization of sulfates

211   the residual fluid was not enriched, but was slightly depleted in ^{34}S; thus, the isotopic shift in the

212   second population of barite indicates that it did not precipitate from residual brines. Considering the

213   epigenetic character of the Hammam Zriba deposit, the formation of Ba-Sr and Pb-Zn-rich brines was

214   likely coupled to a mechanism that simultaneously led to a significant fractionation of the S isotopes

215   (Dill et al., 2009). The high δ^{34}S values can be due to reservoir effect associated with thermo-chemical

216   sulfate reduction (TSR) or bacterial sulfate reduction (BSR) under conditions of restricted sulfate

217   supply (Dill et al., 2009).

218

219   *5.2. Source (s) of sulfur*

220   The most important characteristic of the lenticular ores at Hammam Zriba is that they have

221   substantially more negative δ^{34}S values for galena in the range between −13.8 and −11.2‰ compared

222   to the intra-karstic ores, which have δ^{34}S values for galena that range between −2.6 and −1.4‰, and

223   positive δ^{34}S values for sphalerite in the range between 1.7 and 2.1‰ (Table 2; Fig. 5). The differences

224   of δ^{34}S values of galenas in lenticular and intra-karstic ores could be explained by two processes: (1)

225   multiple sources of sulfur and (2) a single source of sulfur that evolved over time.

1

226   The most likely sources of reduced sulfur for the sulfide phases is Triassic evaporites, which were

227   suggested as the likely source of sulfur in the Zaghouan district (Jemmali et al., 2011a; Souissi et al.,

228   2013) and other carbonate-hosted Pb-Zn deposits in the Nappe and Dome zones (Jemmali et al.,

229   2011b, Jemmali et al., 2013a, Jemmali et al., 2013b). The observed isotopic compositions for sulfide

230   minerals at Hammam Zriba may be explained by reduction of these sulfate sources through TSR

231   and/or BSR.

232   It is well established that BSR takes place at 60–80 °C, and may occur at temperatures as high as

233   110°C (Jørgensen et al., 1992). TSR takes place at higher temperatures (mainly 80–130°C), though it

234   becomes more active at even higher temperatures. The average temperature of fluorite precipitation of

235   100–185°C overlaps to some extent with both BSR and TSR regimes. The temperature deduced from

236   galena-sphalerite pair is ~128°C using the equation of Grootenboer and Schwarcz (1969), which rather

237   falls into the TSR regime. Moreover, TSR causes isotopic fractionation from ~0 to ~20 per mil

238   (Kiyosu and Krouse, 1990; Machel et al., 1995), whereas BSR mechanism induces isotopic

239   fractionation of ~40 per mil. The calculated isotopic fractionation range of 14.5–29‰ falls into the

240   range of both regimes. Considering the temperature range and the negative values recorded in galena

241   (up to –13.8‰), it is wise to consider both mechanisms (TSR and BSR) as potential contributors of

242   sulfur needed for sulfide precipitation.

243   Mixing of TSR- and BSR-derived sulfur may account for the bulk isotopic sulfur composition.

244   In fact, the sulfides in the Zaghouan province display negative values (up to –13.8 ‰) as well as very

245   positive values in other similar ore deposits (up to +11.4‰; cf. Souissi et al., 2013). In this context,

246   the very negative $\delta^{34}S$ values of galena 2 (average = –12.73‰) compared to that of galena 3 (average

247   = –2.17‰) recorded in Hammam Zriba may indicate an increase of light sulfur from (i) mainly BSR-

248   derived sulfur and to some extent (ii) organic sulfur, and/or diagenetic sulfides ($\delta^{34}S$ <–2.36‰;

249   Bouhlel, 1993) in the dark siliceous facies associated with organic matter. The proportion of light

250   sulfur and thus the superficial, depleted metal, bacteriologically-rich derived sulfur fluid, became more

251   pronounced in the early stage (galena 2).

252   Following the multi-sulfur source hypothesis, not only TSR- and BSR-derived sulfur but also

253   organic sulfur is considered as local source of sulfur though probably minor. The occurrence of oil

254   fluid inclusions in all type of fluorites of Hammam Zriba (cf. Bouhlel et al., 1988) could indicate the

255   contribution of organically bonded sulfur. In regard to this organically bonded sulfur and given the

256   fact that the ore is associated with black shales, thermal cracking of organic matter (e.g., presence of

257   hydrocarbon in fluid inclusion) can be considered as a possible local source of sulfur. The organic

258   sulfur and diagenetic sulfides along with BSR could have lowered the sulfur isotopic composition of

259   the epigenetic sulfides. The hydrocarbons observed in fluorite inclusions may indicate transport from a

260   deeper mature source rock.

261   *5.3. Sources of metals and age of mineralization*

262   On conventional uranogenic and thorogenic plots (Fig. 6), data for most of the analyzed samples

263   fall between the upper crustal and orogen model curves of Zartman and Doe (1981). The tight linear

264   clustering of Pb isotope data for the galena ores may reflect involvement of mixing and subsequent

265   homogenization of Pb isotopic composition of different source Pb reservoirs that would also explain

266   the uniform isotopic values (Fig. 6).

267   The lead isotope composition data suggest that the lead in the Hammam Zriba deposit was derived

268   from a different source than the lead in other Tunisian carbonate-hosted deposits and in the Nefza

269   magmatic rocks, and has been interpreted to probably indicate regional differences in the composition

270   of the underlying sediments, which probably include the Paleozoic basement (Jemmali et al., 2011a;

271   Souissi et al., 2010; Souissi et al., 2013). The Pb isotope ratios of galena from Jebel Ressas and Sidi

272   Taya deposits in the Zaghouan district are markedly higher and different than those from the Hammam

273   Zriba deposit (Fig. 6), and are enriched in radiogenic lead indicating that the former were derived from

274   a source enriched in both U and Th. The geographic position of the deposits was closely related to this

275   variation and the differences in lead isotopic composition may reflect the spatial dissimilarity of

276   involved crustal rocks (Jeong et al., 2012). This crustal source provenance is supported by strontium

277   isotope data from minerals associated with the ore deposits in the Zaghouan District (i.e., Sidi Taya,

278   Hammam Jedidi, Oued M'tak and Jebel Oust) (Souissi et al., 2013), which could have been sourced

279   from connate waters trapped in the Paleozoic sedimentary column. Based on the data presented above,

280   the Paleozoic seems to be the dominant source.

281   Geological field observations, textural crosscutting and paragenetic sequence, supported by fluid

282   inclusions show the existence of three chronologically distinct stages of mineralization. Mineralization

283   with fluorite types are epigenetic and formed after the lithification and dissolution of the Portlandian

284   limestone host rocks, and are structurally-controlled due to the presence of N070–090 and N160–N180

285   trending faults (Melki and Zargouni, 1991). Thus, their emplacement postdates the Upper Jurassic

286   (i.e., Portlandian). According to Melki and Zargouni (1991), the horst structure of Hammam Zriba has

287   formed during the Late Jurassic as an emerged block bounded by major fault that was re-activated

288   during various later tectonic events. The ultimate last phase in which the horst took the final form was

289   the Tortonian period, which caused the mineral deposition (Melki and Zargouni, 1991). Furthermore,

290   based on Sr isotope ages that range between 28 and 19 Ma, Dill et al. (2014) attributed the Tunisian

291   salt-related deposits to the Chattian-Burdigalian age. Moreover, in the area of Oued M'Tak, the

292   youngest rock series hosting F-(Zn-Pb) deposit is Miocene (Burdigalian) in age. All these arguments

293   strongly suggest an Upper/Late Miocene age for the mineralization of Hammam Zriba deposit. The

294   same age was suggested for other Tunisian Pb-Zn deposits (Decrée et al., 2008; Jemmali et al., 2011a,

295   b; Jemmali et al., 2013b; Souissi et al., 2013; Jemmali et al., 2014).

296   *5.4. Proposed genetic model*

297   Based on the geological, mineralogical and geochemical relationships discussed above, and

298   published literature dealing with Hammam Zriba as cited in the discussion above, a proposed genetic

299   model is postulated as follows.

300   At Hammam Zriba, anticlines are interpreted as fault-inversion folds that seem to have occurred

301   during the late Eocene – early Miocene (Frizon de Lamotte et al., 2000), formed in normal sequence

302   on the external side of the ZRSB. Flow of Triassic strata into the cores of these folds may have been

303   assisted by tectonic loading during fault inversion along the ZRSB. Subsequently, structures in the

304   ZRSB were dissected by NE–SW trending faults that propagated through the post-rift sequence during

305   post-Miocene re-activation of syn-rift extensional faults. These faults were linked to extension in NW–

306   SE trending graben that cut the ZRSB (Morgan et al., 1998). The Eocene–Miocene compressional

307   phase "Alpine orogeny" caused the development of the foreland basin (Morgan et al., 1998). The

308   generated topographic gradient induced the circulation of deep-seated basinal brines as hydrothermal

309   fluids, as indicated by fluid inclusion temperatures of fluorites which are predominantly in the 100–

310   185 ℃ range (Bouhlel et al., 1988), and the hydrothermal fluids acquired their salinity mainly from

311   Triassic evaporates. The deep-seated basinal brines probably interacted with the basement rocks,

312   thereby leaching metals, and were channelized through secondary faults associated with the ZRSB

313   major regional NE–SW-trending deep-seated fault. Alternatively, the deep-seated, hot fluids migrated

314   to the site of deposition where they got mixed with shallow, cooler, metal-depleted, TSR- and BSR-

315   derived sulfur-rich fluid, which triggered the precipitation of the ores (Fig. 7). This mixing model is

316   supported by wall-rock silicification, which indicates that hot fluids underwent conductive cooling as

317   they encountered carbonate host rocks (Fournier, 1985; Rddad and Bouhlel, 2015), as well as by the

318   temperature fluctuations recorded in fluorite. The lower part of the Campanian consists of marls and

319   black shales, which acted as an impermeable barrier of the fluid circulation.

320   The proposed ore genesis model, which involves the interaction between basement-derived ore

321   fluids and shallower H_2S-rich fluids, has similarities to numerous MVT ore deposits worldwide (e.g.,

322   Pine Point, Canada (Rhodes et al., 1984), Ozarks, USA (Leach, 1994; Souissi et al., 2007), Touissit-

323   Bou Beker district, Moroccan-Algerian confines (Bouabdellah et al., 2012), Jebel Ressas, Tunisia

324   (Jemmali et al., 2011a), and Bou Dahar, Morocco (Rddad and Bouhlel, 2015)).

325   **6. Conclusions**

326   The study of sulfur and lead isotope geochemistry of sulfide minerals allowed to constrain the

327   genesis of sulfur and metals and the timing of fluorite-bearing Zn-Pb mineralization at Hammam

328   Zriba, which occurs as lenticular (or stratiform) and intra-karstic ores in the shallow dipping

329 unconformity between Campanian and Upper Jurassic carbonates. The following conclusions are

330 reached:

331 (i) Ore mineral assemblage consists of fluorite and barite associated with minor sulfides, including

332 sphalerite and galena. Calcite and quartz are the gangue minerals.

333 (ii) The $\delta^{34}S$ values of barite are much close to the $\delta^{34}S$ of Triassic evaporates. The $\delta^{34}S$ values of

334 galena and sphalerite minerals indicate that the deposition of sulfides has resulted from mixing of

335 TSR- and BSR-derived sulfur. The most likely sources of reduced sulfur for the sulfide phases are

336 Triassic evaporites, and locally diagenetic sulfides and organic sulfur.

337   (iii) The Pb isotope compositions of galena have homogenous $^{206}Pb/^{204}Pb$ (18.858–18.876),

338    $^{207}Pb/^{204}Pb$ (15.667–15.684), and $^{208}Pb/^{204}Pb$ (38.680–38.747) ratios, which suggest mixing and

339   subsequent homogenization of Pb isotopic composition of different source Pb reservoirs: deep-sourced

340   metal-rich brines from the underlying crustal rocks, possibly the Paleozoic basement.

341   (iv) The mineralization of Hammam Zriba deposit has likely an upper or late Miocene age.

342

348

349   **References**

350   Boccaletti, M., Cello, G., Tortorici, L., 1990. First order kinematic elements in Tunisia and the Pelagian

351   block. Tectonophysics, 176(1), 215-228.

352   Bouabdellah, M., Sangster, D.F., Leach, D.L., Rown, A.C., Johnson, C.A., Emsbo, P., 2012. Genesis of the

353   Touissit-Bou Beker Mississippi Valley-Type District (Morocco–Algeria) and its relationship to the Africa

354   Europe collision. Economic Geology 107, 117–146.

355   Bouaziz, S., Barrier, E., Soussi, M., Turki, M. M., & Zouari, H., 2002. Tectonic evolution of the northern

356 African margin in Tunisia from paleostress data and sedimentary record. Tectonophysics, 357(1), 227-253.

357 Bouhlel, S., Fortuné, J.P., Guilhaumou, N., Touray, J.C., 1988. Les minéralisations stratiformes à F-Ba de

358 Hammam Zriba, Jebel Guébli (Tunisie nord orientale): l'apport des études d'inclusions fluides à la

359 modélisation génétique. Mineralium Deposita, 23(3), 166-173.

360 Bouhlel, S., 1993. Gîtologie, mineralogie et essai de modélisation des mineralisations a F-Ba-Sr-Pb-Zn-

361 (S) associees aux carbonates (Jurassiques et Cretaces) et aux diapirs triasiques: Gisements de Stah-Kohol,

362 Zriba-Guebli, Bou Jabeur et Fej lahdoum (Tunisie septentrionale). Thèse de doctorat. Faculté des Sciences

363 de Tunis. 303p.

364 Burrolet, PF., 1991. Structures and tectonics of Tunisia. Tectonophysics 195, 359–369.

365   Claypool, GE., Holser, WT., Kaplan, IR., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes

366   in marine sulfate and their mutual interpretation; Chemical Geology 28: 199-260.

367   Decrée, S., Marignac, C., De Putter, T., Deloule, E., Liégeois, JP., Demaiffe, D., 2008. Pb-Zn mineralization in a

368   Miocene regional extensional context: the case of the Sidi Driss and the Douahria ore deposits (Nefza

369   mining district, northern Tunisia). Ore Geology Reviews 34:285-303.

370   De Lamotte, D. F., Leturmy, P., Missenard, Y., Khomsi, S., Ruiz, G., Saddiqi, O., Guillocheau, F., Michard, A.

371   2009. Mesozoic and Cenozoic vertical movements in the Atlas system (Algeria, Morocco, Tunisia): an

372   overview. Tectonophysics, 475(1), 9-28.

373   Dill, H.G., Henjes-Kunst, F., Berner, Z., Stüben, D., 2009. Miocene diagenetic and epigenetic strontium

374   mineralization in calcareous series from Cyprus and the Arabian Gulf. Metallogenic perspective on sub- and

375   suprasalt redox-controlled base metal deposits. J. Asian Earth Sci. 34, 557–576.

376   Dill, H.G., Nolte, N., Hansen, BT., 2014. Lithology, mineralogy and geochemical characterizations of sediment-

377   hosted Sr–F deposits in the eastern Neo-Tethyan region–With special reference to evaporation and

378   halokinesis in Tunisia. Journal of African Earth Sciences, 92, 76-96.

379   Fournier, R.O., 1985. The behavior of silica in hydrothermal solutions. In Geology and geochemistry of

380   epithermal systems. Edited by B.R. Berger and P.M. Bethke. Reviews in Econ. Geol. 2, 45−61.

381   Frizon de Lamotte, D., Saint Bezar, B., Bracène, R., Mercier, E., 2000. The two main steps of the Atlas building

382   and geodynamics of the western Mediterranean. Tectonics, 19(4), 740-761.

383   Gharbi, M., Ben Ayed, N., Ben Said, EA., 1981. Essai d interprétation tectonique du champ filonien de Bou-

384   Jaber (Atlas tunisien central). Actes du Premier Congrès national de la terre (Tunis). Tome 1, 393-403.

385   Grootenboer, J., Schwarcz, HP., 1969. Experimentally determined sulfur isotope fractionations between sulfide

386   minerals. Earth Planet. Sci. Lett. 7, 162–166.

387   Hanor, J.S., 2000. Barite-celestine geochemistry and environments of formation. In: Alpers, C., Jambor, J.,

388   Norstrom, K. (Eds), Sulphate Minerals. Reviews in Mineralogy and Geochemistry, vol. 40, pp. 193–275.

389   Jemmali, N., Souissi, F., Vennemann, T., Carranza, EJM., 2011a. Genesis of the Jurassic carbonate-hosted Pb-

390   Zn deposits of Jebel Ressas (North-Eastern Tunisia): evidence from mineralogy, petrography and trace metal

391   contents and isotope (O, C, S, Pb) geochemistry. Resource Geology 61, 367–383.

392   Jemmali, N., Souissi, F., Villa, IM., Vennemann, T., 2011b. Ore genesis of Pb-Zn deposits in the Nappe zone of

393   Northern Tunisia: constraints from Pb-S-C-O isotopic systems. Ore Geology Reviews 40, 41-53.

394   Jemmali, N., Souissi, F., Carranza, EJM., Vennemann, TW., 2013a. Sulfur and lead isotopes of Guern Halfaya

395   and Bou Grine deposits (Dome zone, northern Tunisia): Implications for sources of metals and timing of

396   mineralization. Ore Geology Reviews, 54, 17-28.

397   Jemmali, N., Souissi, F., Carranza, E.J.M., Bouabdellah, M., 2013b. Lead and sulfur isotope constraints on the

398   genesis of the polymetallic mineralization at Oued Maden, Jebel Hallouf and Fedj Hassene carbonate-hosted

399   Pb–Zn (As–Cu–Hg–Sb) deposits, Northern Tunisia. Journal of Geochemical Exploration,132, 6-14.

400   Jemmali, N., Souissi, F., Carranza, EJM., Vennemann, TW., Bogdanov, K., 2014. Geochemical constraints on

401   the genesis of the Pb–Zn deposit of Jalta (northern Tunisia): Implications for timing of mineralization,

402   sources of metals and relationship to the Neogene volcanism. Chemie der Erde-Geochemistry, 74(4), 601-

403   613.

404   Jeong, Y. J., Cheong, C. S., Shin, D., Lee, K. S., Jo, H. J., Gautam, M. K., Lee, I., 2012. Regional variations in

405   the lead isotopic composition of galena from southern Korea with implications for the discrimination of lead

406   provenance. Journal of Asian Earth Sciences, 61, 116-127.

407   Jorgensen, B. B., Isaksen, M. F., Jannasch, H. W., 1992. Bacterial sulfate reduction above 100 degrees Celsius in

408   deep-sea hydrothermal vent sediments. Science, 258(5089), 1756-1758.

409   Kiyosu, Y., Krouse, HR., 1990. The role of organic acid in the abiogenic reduction of sulfate and the sulfur

410   isotope effect. Geochemical Journal, 24(1), 21-27.

411   Leach, D.L., 1994. Genesis of the Ozark Mississippi Valley-Type metallogenic province. In: Fontebote, L.,

412   Boni, M. (Eds.), Sediment Hosted Zn-Pb Ores, Springer–Verlag, 104−138.

413   Machel, HG., Krouse, HR., Sassen, R., 1995. Products and distinguishing criteria of bacterial and

414   thermochemical sulfate reduction: Applied Geochemistry, v. 10, p. 373−389.

415   Maghreb   Minerals   plc.,   2008.   Zinc   exploration   in   North   Africa.

416   http://equatorgold.co.uk/finex/downloads/presentations/2008/222.ppt

417   Melki, F., Zargouni, F., 1991. Tectonique cassante post jurassique de la mine de Hammam Zriba (Tunisie nord-

418   orientale). Incidences sur la karstification et les concentrations de fluorine, barytine et célestine,

419   d'environnement carbonaté. Bull. Soc. Géol. France, 162(5), 851-858.

420   Morgan, M., Grocott, J., Moody, R., 1998. The structural evolution of the Zaghouan-Ressas Structural Belt,

421   northern Tunisia. Geological Society London Special Publication, Volume 132, pp. 405-422.

422   Ohmoto, H., Rye, RO., 1979. Isotopes of sulfur and carbon. In: Barnes, H.L. (Ed.), Geochemistry of

423   Hydrothermal Ore Deposits. Wiley, New York, pp. 509–567.

424   Ohmoto, H., 1986. Stable isotope geochemistry of ore deposits. Reviews in Mineralogy and

425   Geochemistry, 16(1), 491-559.

426   Perthuisot, V., 1978. Dynamique et pétrogenèse des extrusions triasiques en Tunisie septentrionale. Theses,

427   Doctorat d'Etat, Ecole Normale supérieure de Paris, Travaux du Laboratoire de Géologie 12, 312 pp.

428   Peter, J.M., Shanks, W.C., 1992. Sulfur, carbon and oxygen isotope variations in submarine hydrothermal

429   deposits of Guaymas Basin, Gulf of California, USA: Geochimica et Cosmochimica Acta, v. 56, no. 5, p.

430   2025–2040.

431   Rddad, L., Bouhlel, S., 2016. The Bou Dahar Jurassic carbonate-hosted Pb–Zn–Ba deposits (Oriental High

432   Atlas, Morocco): Fluid-inclusion and C–O–S–Pb isotope studies. Ore Geology Reviews, 72, 1072-1087.

433   Rhodes D., Lantos E.A., Lantos, J.A., Webb, R.J, Owens, D.C., 1984. Pine Point orebodies and their relationship

434   to the stratigraphy, structure, dolomitization and karstification of the Middle Devonian Barrier Complex.

435   Econ. Geol. 79, 991–1055.

436   Souissi, F., Dandurand, J., Fortuné, J., 1997. Thermal and chemical evolution of fluids during fluorite.

437   Mineralium Deposita, Volume 32, pp. 257-270.

438   Souissi F., Sassi R., Bouhlel S., Dandurand J-L., Ben Hamda S. (2007). – Fluid inclusion microthermometry and

439   rare earth element distribution in the celestite of the Jebel Doghra ore deposit (Dome zone, Northern

440   Tunisia) : towards a new genetic model. Bull. Soc. Géol. Fr., t. 178, n° 6, pp. 459-471.

441 Souissi, F., Souissi, R., Dandurand, J., 2010. The Mississippi Valley-type fluorite ore at Jebel Stah (Zaghouan

442 district, north-eastern Tunisia): contribution of REE and Sr isotope geochemistries to the genetic model. Ore

443 Geology Reviews, Volume 37, pp. 15-30.

444 Souissi, F., Jemmali, N., Souissi, R., Dandurand, J., 2013. REE and isotope (Sr, S, Pb) geochemistry to constrain

445 the genesis and timing of the F-(Ba-Pb-Zn). Ore Geology Reviews.

446 Thibieroz, J., 1974. Hammam Jedidi et Hammam Zriba: Etude géologique et minière de deux gisements

447 stratiformes dans le cadre de la province fluorée tunisienne; l'association des concentrations fluorées aux

448 surfaces d'émersion. 1974. Thèse de 3e cycle univ. Paris VI. 367p

449 Thibieroz, J., 1976. Reconstitution chronologique du rôle des surfaces d'émersion dans l histoire du gisement de

450 fluorine de hammam Zriba (région de Zaghouan Tunisie). Mém. H. série soc. Géol. France, 7, 33-37.

451   Thode, H.G., Monster, J., 1965. Sulphur isotope geochemistry of petroleum, evaporites and ancient seas. In:

452   Young, A., Galley, J.E. (Eds.), Fluids in Subsurface Environments, vol. 4. Am. Ass. Petrol. Geol., Tulsa,

453   Oklahoma, USA, pp. 367–377

454   Zartman, R.E., Doe, B.R., 1981. Plumbotectonics — the model. Tectonophysics 75, 135–162.

455

456 FIGURES CAPTIONS

457 Fig. 1. Tectonic and metallogenic map of Northern Tunisia (adapted from Burrolet, 1991; Perthuisot, 1978;

458 Jemmali et al., 2011; Decrée et al., 2016).

459 Fig. 2. Geologic map of the Hammam Zriba F-Ba-Sr (Zn-Pb) deposit, showing major faults and distribution of

460 ore bodies (adapted from Melki and Zargouni, 1991).

461 Fig. 3. Main lithostratigraphic column of the Hammam Zriba deposit (adapted from Melki and Zargouni, 1991).

462 Fig. 4. Appearance of representative field and hand specimens of all types of Hammam Zriba F-Ba- (Pb-Zn)

463 orebodies occurring within the unconformity between Portlandian and Upper Cretaceous rocks. A: stratabound

464 mineralization along the unconformity between Portlandian and Upper Cretaceous rocks. B: Banded ore with

465 fluorite 1 (F1), black siliceous facies "Type M0" with spherulitic barite 1 (Ba1), authigenic quartz and diagenetic

466 sulfides (galena and sphalerite) and barite 2 (Ba2) in lenticluar orebody. C: white fibrous barite 2 (Ba2) with

467 cubic crystals of galena 2 (Gn2) in lenticular orebody. D: fluorite 2 (F2) with fine-grained galena 3 (Gn3) and

468 brown sphalerite (Sp2) in intra-karstic orebody. E: Cretaceous black shales (Sh) with fluorite 2 (F2), fibrous

469 barite 3 (Ba3) associated with fine grained galena 2 (Gn2) and brown sphalerite (sp2) in intra-karstic orebody. F:

470 fluorite 2 (F2) associated with brown sphalerite (Sp2) in intra-karstic orebody. G: intra-karstic ore with fibrous

471 barite 3 (Ba3), hosted by Portlandian limestones (L). H: coarse-grained galena 3 (Gn3) associated with barite 3

472 (Ba3) and fluorite 2 (F2) in intra-karstic ore. I: calcite rhombohedra (Ca1) associated to barite 3 (Ba3) in intra-

473 karstic ore. J: veins in Portlandian limestones filled with Calcite 2 (Ca2) and limestone Onyx (LO).

23

474   Fig. 5. Frequency distribution of $\delta^{34}S$ values for mineral separates of sphalerite 2, galenas 1 and 2, all types of

475   barites from the Hammam Zriba deposit. Also shown for comparison is the sulfur isotope range for Triassic

476   evaporates at Jebel Ressas (Jemmali et al., 2011a).

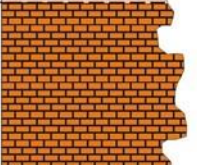477   Fig. 6. Plots of lead isotope compositions of galena from the Hammam Zriba deposit, including analyses of Jebel

478   Ressas, Sidi Taya galenas from Jemmali et al. (2011b) and Souissi et al. (2013), and analyses of Nefza

479   magmatic rocks from Decrée et al. (2014). Evolution curves for upper crust and orogene from Zartman and Doe

480   (1981) are shown for reference.

481   Fig. 7. Schematic proposed genetic model of the Hammam Zriba F-Ba- (Pb-Zn) ore deposit (adapted and

482   modified based on present-day cross section of Jebel Zaghouan-Zriba from Morgan et al. 1998).

483

<p style="text-align:center">TABLE CAPTIONS</p>

485   Table 1. Mineral paragenetic sequence in the Hammam Zriba deposit

486   Table 2. Sulfur isotope compositions of sulfides (galena and sphalerite) and sulfate (barite) from the Hammam

487   Zriba deposit, and gypsum from Jebel Ressas (Jemmali et al., 2011a).

488   Table 3. Ratios of Pb isotope compositions in galena from the Hammam Zriba deposit.

489
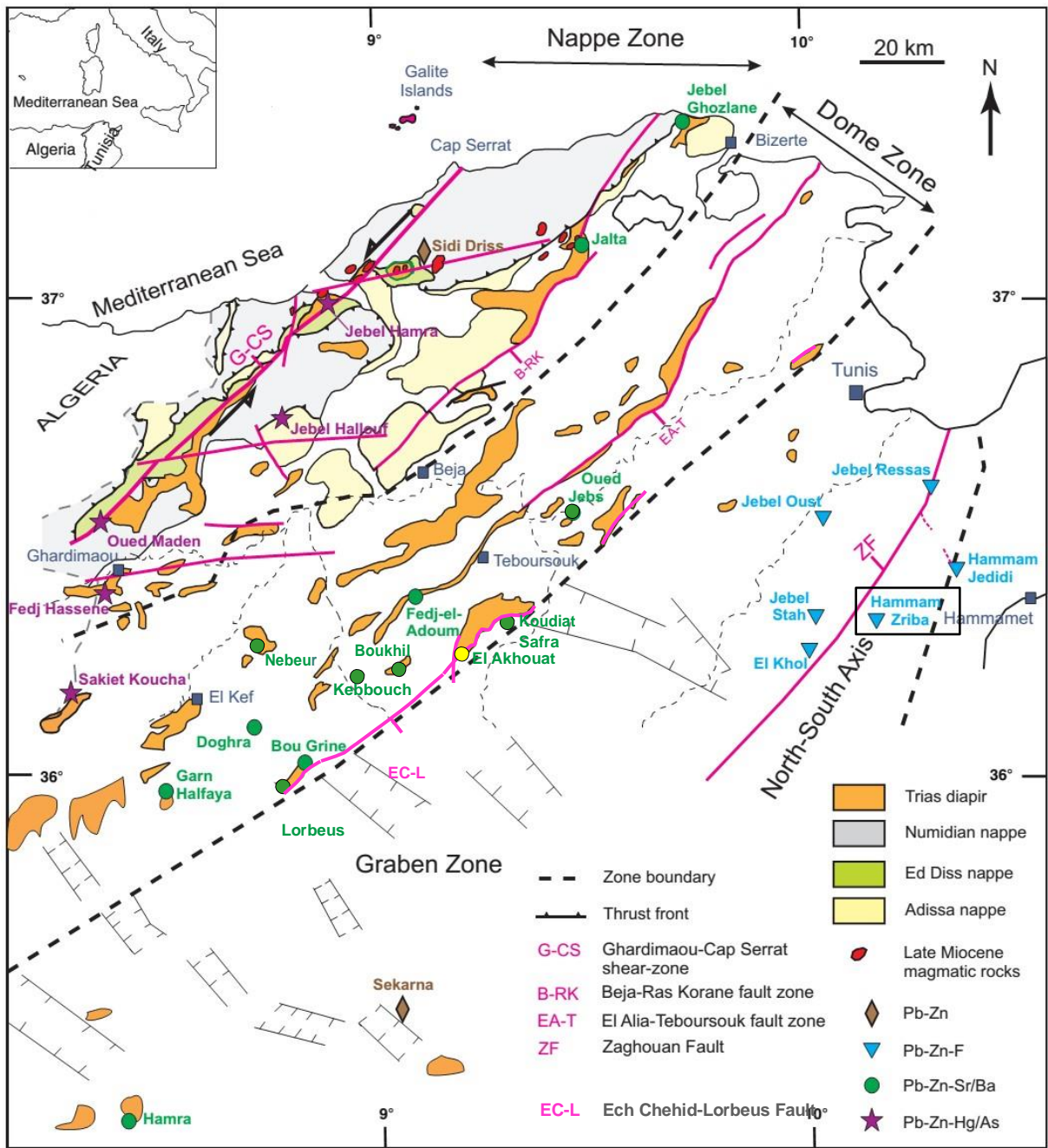
Figure 1
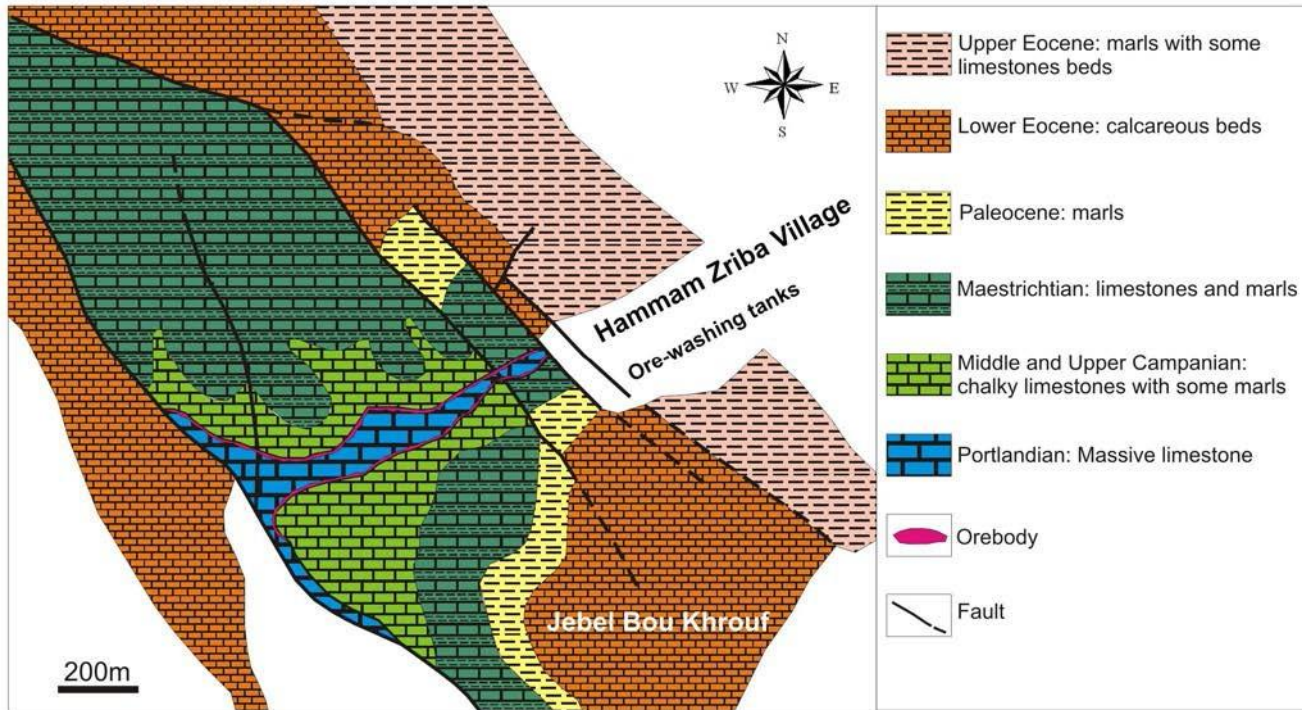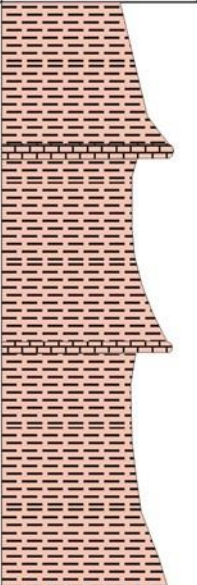
Figure 2

Age	Column	Main lithology
Upper Eocene		Yellow to green marls with some limestones beds
Lower Eocene		Grey, thick and massive phosphate-bearing calcareous beds
Paleocene		Green marls
Maaestrichtian		Beige limestones with interbedded green marls
Campanian		Chalky limestone beds
		Stratabound mineralization
Portlandian		Bioclastic and massive grey limestones beds

100m

Figure 3

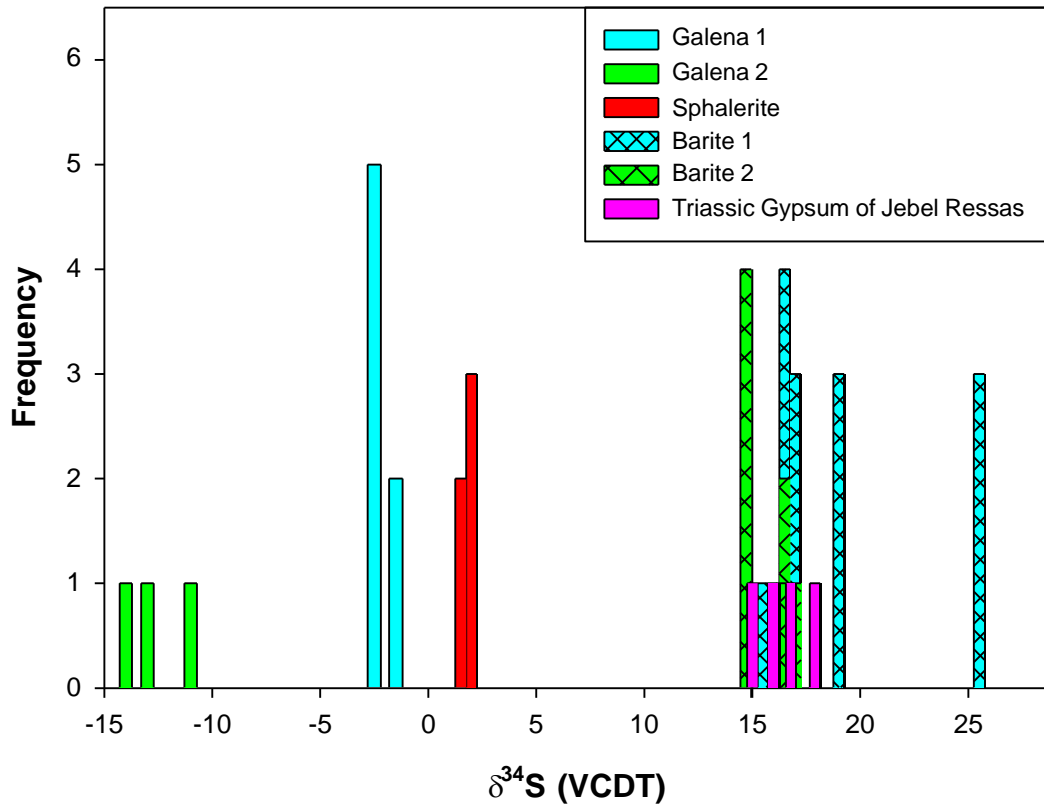A. Campanian / Stratabound mineralization / Porlandian limestones

B. F1 / Qz / Ba1

C. Gn 1 / Sp / F1

D. Sh / Sp / Gn 1 / OM

E. Sp / Sh / F1 / Ba1

F. Sp / F1

G. L / Ba2 / L

H. Ba2 / Gn2 / Gn2
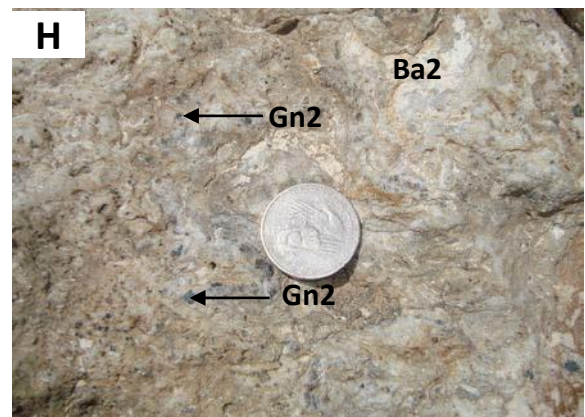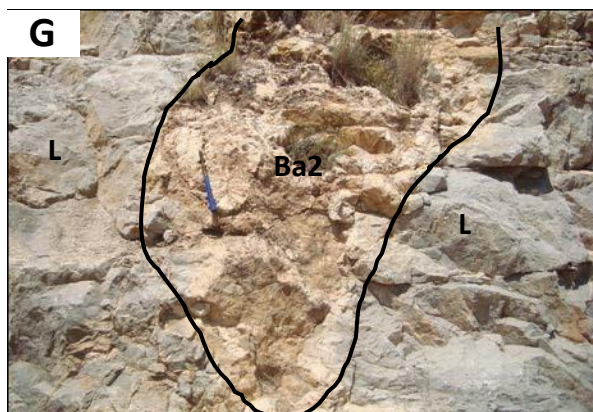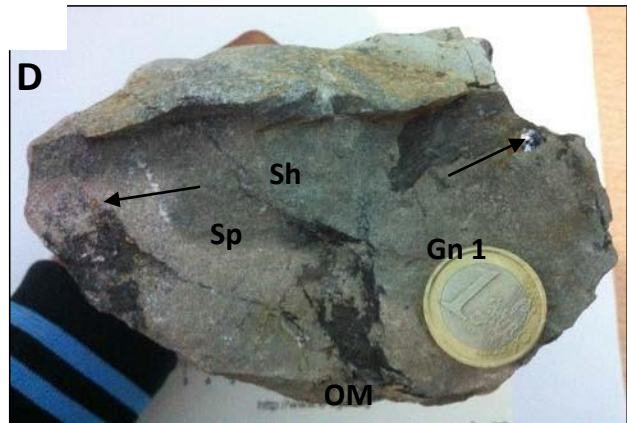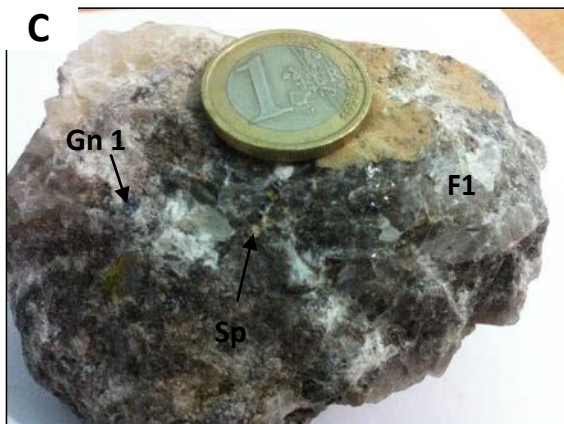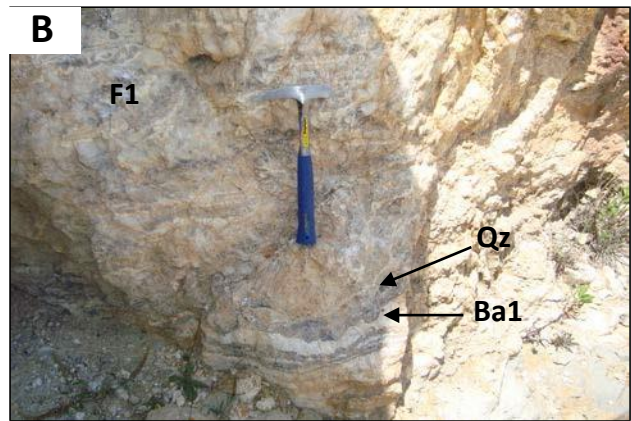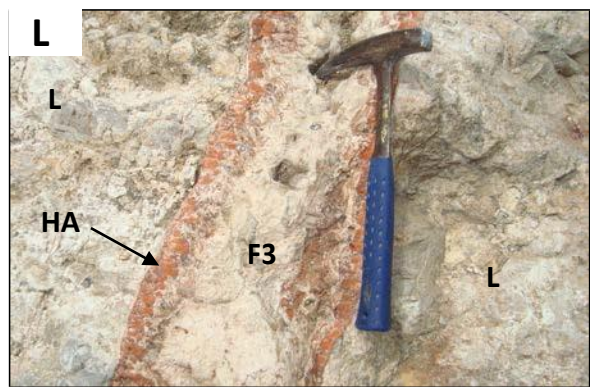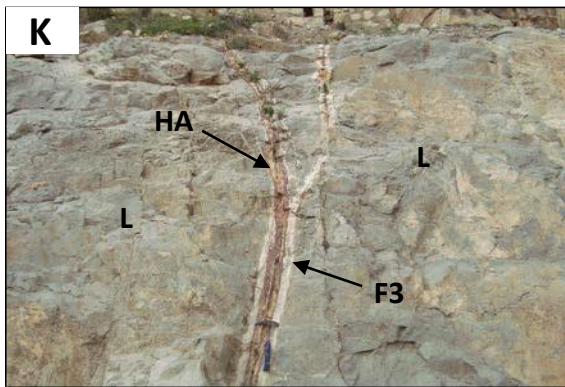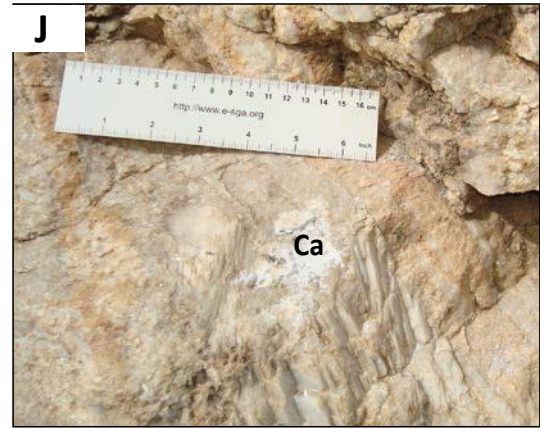
Figure 4

Figure 5

Figure 6

Figure 7