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### **Geological and geochemical constrains on the genesis of the sedimentary-hosted Bou Arfa Mn(-Fe) deposit (Eastern High Atlas, Morocco)**

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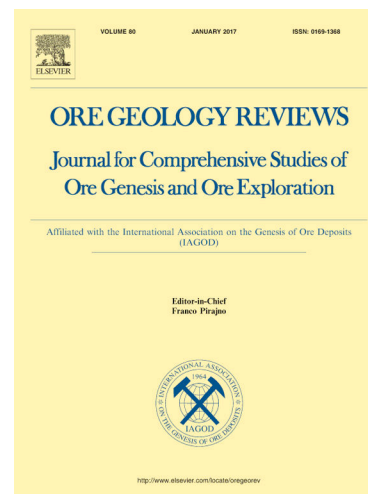
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1 **Geological and geochemical constrains on the genesis of the sedimentary-hosted Bou**  
2 **Arfa Mn(-Fe) deposit (Eastern High Atlas, Morocco)**

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21 Abstract

22 Carbonate-hosted Mn deposits are widespread in North Africa with most of the Mn ores  
23 being hosted by Mesozoic dolomitic formations of the Moroccan Atlasic system. The Bou  
24 Arfa Mn(-Fe) deposit described herein is located in the eastern High Atlas, close to the North  
25 Atlasic Front, and has accounted for the production of ~2 Mt of ore grading from 33 to 82%  
26 Mn. The mineralization occurs within Sinemurian flat-lying dolostones as stratabound and  
27 karst-filling (veins, lenses, pockets). This mineralization is characterized by the extensive  
28 presence of pyrolusite, and minor concentrations of manganite, hausmannite, goethite and  
29 hematite. Previous studies suggested that the Bou Arfa Mn-bearing mineralization has a  
30 strictly syndimentary origin, but the intense dolomitization and the occurrence of Mn oxides  
31 instead of Mn carbonates question this model. New petrographical, mineralogical and  
32 geochemical data show that three dolomitization phases accompanied the ore formation. The  
33 early syndimentary dolomitization was not responsible for strong Mn enrichments, whereas  
34 a second dolomitization took place with the formation of hausmannite and manganite during  
35 early diagenesis. The precipitation mechanism involves circulation of dissolved  $Mn^{2+}$  in pore  
36 waters, and then precipitation under diagenetic suboxic and alkaline conditions. The scarcity  
37 of Mn carbonates is likely due to competitiveness of dissolved carbonates species that have  
38 favored dolomite precipitation in the early stage. Presence of saddle dolomite in a  
39 subsequent alteration stage, crystallography of the Fe oxides, and evolution of  $\delta^{13}C$  and  $\delta^{18}O$   
40 reflect burial diagenesis and fluid mixing in the carbonate host rock. These conditions have  
41 enabled the transformation of the primary ore into pyrolusite, when diagenetically-derived  
42 hydrothermal fluids have generated vein-filling ore. The position of the Bou Arfa site above a  
43 paleohigh formed during Atlas rifting, the presence of a faulted zone and the dolomitization of  
44 the Sinemurian series have delimited the extension of this diagenetic Mn deposit, which is in  
45 some points similar to MVT deposits of North Africa. Weathering is poorly recorded in the  
46 Bou Arfa Mn ores due to the stability of the ore-forming minerals under subaerial conditions  
47 in relation to the most recent periods of exposure of the High Atlas building.

48 Keywords: manganese, Bou Arfa, diagenesis, Morocco, sedimentary-hosted

50 **1. INTRODUCTION**

51 Sedimentary-hosted Mn deposits are considered as the most significant amongst different  
52 ore deposit types, because they ensure high longevity, large tonnage, and relatively high  
53 average grades (Kuleshov, 2016; Laznicka, 1992; Maynard, 2014; Roy, 2006). The  
54 accumulation of Mn in sediments is generally triggered by the formation of (i)  
55 ferromanganese nodules above the ocean floor (Glasby, 2006; Maynard, 2014; Wang and  
56 Müller, 2009), or (ii) Mn-bearing carbonates under diagenetic conditions, either from  
57 precipitation in pore waters, or by replacement of Mn-rich oxides, oxyhydroxides and  
58 hydroxides (hereafter referred to as Mn oxides; Johnson et al. 2016). Mn sources in  
59 sediments can be either distant hydrothermal vents or hydrogenous (terrigenous) influxes  
60 (Fleet, 1983; Glasby, 2006). Formation models (Calvert and Pedersen, 1996; Cannon and  
61 Force, 1983; Force and Cannon, 1988; Force and Maynard, 1991; Maynard, 2014, 2010)  
62 involve the precipitation of primary Mn oxides at the interface between reducing and oxidizing  
63 environments. Most of these oxides are not deposited in deep sediments because they are  
64 dissolved again once they deepen in the water column, unless the seafloor is shallow  
65 enough to intercept the redox boundary. Iron is not involved in this process as Fe remains  
66 fixed in sulfide minerals at the deeper water-sediments interface (Maynard, 2014, 2010). Sea  
67 level changes may have a strong influence on the concentration and the geometry of Mn  
68 orebodies (Roy, 2006). Most of the sedimentary-diagenetic Mn deposits are hosted in C-rich  
69 shales and pelites (Kuleshov, 2016, 2011; Roy, 2006).

70 The Bou Arfa Mn deposit of the eastern High Atlas of Morocco (Fig. 1A) is located at the  
71 junction between the High Atlas and the High Plateau domain close to the North Atlasic Front  
72 (Fig. 1B). The Bou Arfa mineralization was discovered in 1912 and is the third Mn district of  
73 Morocco alongside the Imini-Tasdremt (Dekoninck et al., 2016a, 2020; Gutzmer et al., 2006)  
74 and the Ouarzazate mining districts (Choubert and Faure-Muret 1973; Pouit 1980; Fig. 1A).  
75 Previous works have shown that mineralization mainly occurs as stratabound and karst-fill  
76 within Sinemurian dolostones (Fig. 2). Their mineralogy consists exclusively of Mn oxides  
77 such as pyrolusite ( $\beta$ -MnO<sub>2</sub>; Pouit and Jouravsky 1965). Vein-related Mn mineralization is  
78 also described and displays massive Fe oxides (goethite) alongside the Mn oxides. The  
79 dolomitized host rocks are enriched up to 1–3% Mn and Pouit and Jouravsky (1965)  
80 suggested that the carbonate host rocks constitute the source of manganese.

81 These features interestingly suggest the intervention of processes different from those  
82 involved in giant sedimentary-diagenetic deposits (Johnson et al., 2016; Kuleshov, 2016;  
83 Maynard, 2014, 2010; Roy, 2006). These high-grade Mn ores occurring in a restricted area  
84 would imply epigenetic processes related to dolomitization. Pouit and Jouravsky (1965)

85 suggested a two-step model to explain the evolution of the Mn mineralization after  
86 replacement of a synsedimentary carbonate precursor and their oxidation. However, this  
87 model remains questionable (du Dresnay, 1965; Michard and Raddi, 2011; Pouit and  
88 Jouravsky, 1965). Accordingly, the genesis of Bou Arfa Mn mineralization needs an in-depth  
89 revision in order to address issues related to the syn-sedimentary, diagenetic and/or  
90 hydrothermal origin of the orebodies; the link with dolomitization of the host Sinemurian  
91 marine carbonates; the massive presence of Mn oxides instead of Mn-rich carbonates  
92 (kutnohorite, rhodochrosite or Mn-rich calcite) and the role played by supergene processes.  
93 The main objectives of this paper consist of (1) refining the mineralogy and petrography of  
94 the Mn mineralization and host carbonates, and (2) defining the relation between the ore  
95 formation and host carbonates. The final aim is to propose a robust metallogenic model for  
96 the Bou Arfa deposit and special care is devoted to the link between mineralization and  
97 dolomitization.

## 98 **2. REGIONAL AND LOCAL GEOLOGICAL SETTING**

99 The Atlasic fold and thrust belt is a complex structure resulting from the inversion of Triassic  
100 and Jurassic basins in the frame of the Africa-Europe convergence (Choubert and Faure-  
101 Muret 1962; Mattauer et al. 1977; Fig. 1A). Two main faults border the chain: the northern  
102 main thrust named the “North Atlasic Front” (NAF) and the “South Atlasic Fault” (SAF). The  
103 chronology of the Atlasic building follows two main phases: Eocene and Plio-Quaternary  
104 (Frizon de Lamotte et al., 2009, 2000). A third Miocene phase is identified due to lithosphere  
105 thinning that supports the current topography of the Anti-Atlas, the High and the Middle Atlas  
106 (Gouiza et al., 2017, 2017; Leprêtre et al., 2015; Missenard et al., 2008, 2006; Seber et al.,  
107 1996).

108 The Bou Arfa area is located in the eastern part of the High Atlas, close to the NAF.  
109 The host rocks correspond to Paleozoic schists undetermined in age unconformably overlain  
110 by a thick pre-rift Triassic succession, and Jurassic and Cretaceous syn-rift sediments. The  
111 Jbel Bou Arfa (1830m; Fig 1B) forms an E-W anticline crossed by a major E-W fault (Aïn  
112 Beida fault; du Dresnay 1965). This structure separates the Atlasic system in the south from  
113 a non-deformed domain forming the so-called “High Plateaus” in the north (Fig. 1B). Triassic  
114 to Jurassic Atlasic basins are rift basins controlled by normal faults and represent transfer  
115 zone between two opening domains, namely the Central Atlantic and Tethyan oceans (Fig.  
116 1A; Frizon de Lamotte et al. 2000). The E-W Aïn Beida fault is a main regional structure that  
117 split the Bou Arfa area in two blocks: the northern block hosts the Ain-Beida and Hamaraouet  
118 Mn mineralization, whereas the southern block hosts small Mn spots (Fig. 1B).

119 In the Bou Arfa Mn deposit, Sinemurian series are dolostones interbedded with clays  
120 and thin gypsum-rich sandstones (Choubert and Faure-Muret 1962; du Dresnay 1965;  
121 Salahane 1978; Fig. 2). Two main dolostone units are observed (Fig. 2). The bottom  
122 dolostone called Lower “Chocolate” Unit (LCU) because of its dark brownish color is a few  
123 meters thick and displays clayey levels in the upper part (du Dresnay 1965; Fig. 2). The  
124 second unit, called the Upper “Chocolate” Unit (UCU), is a massive dolostone composed of  
125 several strata hosting evaporitic levels, with a cumulated thickness increasing from west to  
126 east (10 to 30 meters thick; du Dresnay 1965). Both are separated by an arkose level. In Bou  
127 Arfa, the Pliensbachian unit unconformably overlays the Sinemurian rocks with 180 m to  
128 200 m of arkoses, in which granitic boulders are observed (Fig. 2).

129 The Lower Cretaceous rocks are only observed north of the NAF and form a thin  
130 reddish detrital layer. Cretaceous limestones few meters thick form the Kif El Hamar relief  
131 and corresponds to an E-W syncline following the Ain Beida Fault (Fig. 1B). No Mn deposit is  
132 observed in these two reliefs but Pb-Zn-Cu-V mineralization have been described (Fig. 1B;  
133 Verhaert et al. 2017, 2018). Cenozoic conglomeratic lenses outcrop close to the Ain Beida  
134 Fault (Fig. 1B). These lenses are witnesses of the late Cenozoic activity of the Ain Beida  
135 Fault (Lafforgue, 2016).

### 136 **3. MATERIAL AND ANALYTICAL METHODS**

#### 137 **3.1. Sampling strategy and methodology**

138 The Hamaraouet cliff offers a large domain of outcrops, where most of the samples were  
139 collected (Fig. 1B). Mineralized orebodies and host rocks were sampled in the Hamaraouet  
140 area (H1 to H4, 26 samples), in the gallery 63 (HB1, 3 samples) and in the Ain Beida site (6  
141 samples; Fig. 1B; Table 1). Reference stratigraphic log and host rock samples are described  
142 in barren carbonates at Hamaraouet, where neither Fe, nor Mn oxides were observed (Fig.  
143 2).

#### 144 **3.2. Analytical methods**

145 The petrography of the samples was carried out using optical microscopy,  
146 cathodoluminescence (CL) microscopy (OPEA), scanning electron microscopy (SEM) and  
147 Raman-microspectrometry on 70 thin sections prepared in the GEOPS laboratory (Orsay,  
148 France). The description of hand specimens (Table 1) was used to select representative  
149 samples for geochemical analyses and specific mineral phases from the different stages  
150 defined in the paragenesis. ICP-AES and ICP-MS on bulk samples and EPMA on individual  
151 minerals were used for the geochemistry. Carbon and oxygen isotope geochemistry



152 performed on carbonate phases (calcite and dolomite) was undertaken to characterize the  
153 source and evolution of paleofluids.

### 154 3.2.1 Petrography

155 Thin sections were observed with an optical microscope Leica at a magnification between  
156 x25 and x100 in plane polarized light (PPL) and in cross-polarized light (CPL).  
157 Cathodoluminescence observations were made with a *Cathodyne* platine under an  
158 acceleration voltage of 10 to 15 kV and a current intensity from 250 to 400 mA. Exposure  
159 time was approximately 800 msec for dolomite and seconds for calcite. Texture and optical  
160 characteristics have been used to define the different dolomite phases in the mineralized  
161 zone. A SEM Phillips XL30 coupled with an Energy Dispersive Spectrometer (EDS) detector  
162 Synergie4 PGT was used for petrographical observations and semi-quantitative analyses  
163 under an acceleration potential from 15 to 25 kV and probe current of 1.5 nA.

### 164 3.2.2 X-ray diffraction (XRD)

165 XRD analyses were used to distinguish or correlate mineral phases, especially  
166 pyrolusite and Fe oxyhydroxide mineral species. XRD data were acquired in the GEOPS  
167 laboratory using a PANalytical X'Pert PRO diffractometer with X'Celerator detector and a  
168 copper anticathode providing Cu  $K\alpha_1$  emission ray. A Ni filter of 0.02 mm was used upon the  
169 receptor. Analyses were realized on disoriented powder. All results were treated with X'pert  
170 HighScore 3.0e in order to avoid induced  $K\alpha_2$  rays.

### 171 3.2.3 Raman microspectrometry

172 Raman microspectrometry analysis was carried out at the University of Lille 1 (France)  
173 in the CGCE laboratory. A Horiba Jobin-Yvon spectrometer equipped with an Ar<sup>+</sup> laser was  
174 used with a wavelength of 532 nm. A long acquisition time was needed for Mn oxyhydroxides  
175 (~30 sec; Julien et al. 2004; Gao et al. 2009). The Ar laser spot size was between 1–2  $\mu\text{m}$   
176 with variable power (max 92 mW). A filter (D1) was used in order to limit the power at  
177 9.2 mW and in order to avoid phase changes due to the laser power. Raman spectra were  
178 further treated with the CrystalSleuth software using the Rruff database. Peak parameters  
179 were obtained with pseudoVoigt modelisation with fityk 0.8.0 software.

### 180 3.2.4 Geochemistry

#### 181 3.2.4.1 Bulk-rock analysis

182 Twenty-five samples were analyzed as powders after crushing with an agate mortar at the  
183 SARM laboratory (Nantes, France). An ICP-AES Jobin-Yvon JY 70 Type II was used for



184 major elements (Si, Al, Fe total, Mn total, Mg, Ca, Na, K, P, Ti and LOI). Trace elements and  
185 rare earth elements were analyzed with an ICP-MS Perkin Elmer ELAN 5000 (Tables 2 and  
186 3). Samples were heated at 1000 °C (fire loss) and then treated by Li tetraborate fusion to  
187 determine the Lost On Ignition (LOI). Samples were analyzed after an acid dissolution (ICP-  
188 AES) or a dilution (ICP-MS). Standards were routinely analyzed under the same procedure.  
189 The data were compared to the Upper Continental Crust composition (Mc Donough and Sun,  
190 1995) to show up enrichment or depletion. This standard was chosen as it represents the  
191 best approximation for the types of rock involved in the mineralizing process at Bou Arfa.

#### 192 3.2.4.2 Electron Probe Microanalysis

193 An Electron Probe Microanalysis (EPMA) CAMECA SX-Five was used for quantitative  
194 analyses at the University Pierre-et-Marie-Curie of Paris (UPMC) in the Camparis Service.  
195 EPMA is equipped with a LaB<sub>6</sub> source and five Wavelengths Dispersive Spectrometers  
196 (WDS) coupled with a Bruker EDS. Acceleration potential was 15 kV and variable probe  
197 current were used for the identification of minor (low current) and major elements (high  
198 current). Standards and probe current are indicated in the data repository (DR1). Analyses  
199 were performed on the different dolomite generations (210 spots), on the Mn (217 spots;  
200 pyrolusite, hausmannite, cryptomelane, hollandite and chalcophanite) and the Fe (105 spots;  
201 hematite and goethite) oxides (Tables 4, 5 and 6).

#### 202 3.2.5 Stable Isotope geochemistry

203 The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of carbonates were obtained at the Radiometric Dating and  
204 Stable Isotope Research laboratory at the University of Kiel (Germany). Samples were  
205 formerly collected using a micro-drill tool after an in-depth cathodoluminescence  
206 characterization. Carbon and oxygen isotopic compositions were determined using 100%  
207  $\text{H}_3\text{PO}_4$  dissolution at 75 °C with a prototype Kiel 1 unit attached to a Thermo Finnigan MAT  
208 251 mass spectrometer. The results are given in the standard  $\delta$ -notation, which is expressed  
209 relative to V-PDB (Vienna Pee Dee Belemnite) for carbon isotopes and V-SMOW (Vienna  
210 Standard Mean Ocean Water) for oxygen isotopes in permil (‰; Table 7). The reproducibility  
211 of the analyses of in-house standards gave an external precision (1SD) of  $\pm 0.02\text{‰}$  for  $\delta^{18}\text{O}$   
212 and  $0.01\text{‰}$  for  $\delta^{13}\text{C}$ .

## 213 4. RESULTS

### 214 4.1 Dolomitization

215 Dolomitization is the main form of wall-rock alteration and three stages are distinguished: (i)  
216 extensive syn-sedimentary to early diagenetic replacement dolomite, (ii) epigenetic ore-stage

217 and (iii) hydrothermal dolomite superimposed on the diagenetic dolostone (Fig. 4). Regional  
218 dolomitization predates mineralization and significantly enhances porosity and permeability  
219 of the host rock. Ore-related dolomites occur as pore-filling or veins crosscutting the host  
220 dolostone.

#### 221 4.1.1 Barren Upper Chocolate Unit (UCU)

222 Three facies are recognized in the Upper Chocolate Unit (UCU; from bottom to top): (i)  
223 sandy dolostone, (ii) massive fine-grained dolostone and (iii) bedded dolostone with bird  
224 eyes (Fig. 2). (i) The UCU starts with a thin level (<50 cm thick) displaying a high proportion  
225 of detrital elements including quartz, K-feldspar, and muscovite with subordinate apatite and  
226 Ti oxides. These elements are cemented by an anhedral coarse-grained dolomite (Fig. 3A).  
227 CL exhibits a red color in the dolomite crystals. (ii) The main facies of the UCU, where most  
228 of the ore is located, is formed by a massive dolostone. The lower facies consists of a coarse  
229 dolostone where sedimentary textures (pellets, oolites and pisolites) are partly preserved  
230 (Fig. 3B), and partially replaced by well-developed cloudy microsaccharoidal to millimetric  
231 planar dolomite crystals (Fig. 3C). Pisolites have a single to multiple-nuclei structure with  
232 lightly colored columnar microbial laminations. No Mn- or Fe-rich oolites (or nodules) nor  
233 laminations are observed. (iii) In the upper facies of the UCU, bird eyes are the main feature  
234 (Fig. 3D). This level is composed of a micritic brownish dolomite, similar to the dolomite of  
235 the bottom detrital level and of the well-preserved part of the massive dolostone level. Bird  
236 eyes are filled by a clear sub-planar dolomite with a dark reddish luminescence, while  
237 dolomitic cloudy rhombs coating bird eyes have a red luminescence. A small detrital fraction  
238 (quartz, feldspar, Fe-Ti oxides, apatite, zircon) is also observed. On top of this level, a  
239 dedolomitized limestone (Figs. 3E and F) is observed beneath the unconformity with  
240 Pliensbachian arkoses (Fig. 2).

241 At distance from the mineralized zone — ~4 km south of the Aïn Beida fault in the Jbel  
242 Bou Moktha — (Fig. 1B), the Sinemurian series display a well-exposed platform margin  
243 system with a north-south lateral facies evolution from (1) lagoonal peloidal-ooloidal  
244 dolostones to (2) bioclastic/oolitic grainstones (shoal) and finally to (3) marl/limestone  
245 alternation (upper slope). This outcrop in the Jbel Bou Moktha allows to precisely locate the  
246 bioclastic/oolitic shoal, protecting the lagoon to the open marine environment. At this  
247 location, the lateral equivalent of the UCU only displays an early generation of micritic  
248 dolomite followed by several calcite cements (Figs. 3G and H).

#### 249 4.1.2 Carbonates phases associated to the ores

250 The three ore-related dolomite phases are not observed outside the mineralized area. Table  
251 8 shows the key identification criteria for the dolomite phases.

#### 252 4.1.2.1 *Early diagenetic dolomite phase (Dol-1)*

253 The earliest dolomitic phase (labeled Dol-1a) replaces calcite precursor, here peloids  
254 or ooids. Dol-1a is micro-saccharoidal with red color in CL (Figs. 3A and B). Dol-1b  
255 precipitates around Dol-1a with a similar luminescence, unzoned in CL (Fig. 3B). Dol-1a and  
256 Dol-1b are the most common carbonate phases.

#### 257 4.1.2.2 *Ore-related epigenetic to hydrothermal dolomite phases (Dol-2 and Dol-3)*

258 Coarse grain dolomite phases (Dol-2 and Dol-3) are intimately related to the highly  
259 recrystallized part of the massive dolostone and to the mineralization (Figs. 3C). None of  
260 these dolomites occur in the unmineralized zone. Dol-2a is a cloudy dolomite related to the  
261 dissolution of sedimentary elements in the massive dolostone and forms mostly planar to  
262 sub-planar rhombs with size of ~10–20  $\mu\text{m}$ , cloudy in PPL and bright orange, unzoned in CL.  
263 Dol-2a is intrinsically associated with another phase (Dol-2b), which is likely related to the  
264 alteration of Dol-2a as shown by impregnation of Dol-2b into Dol-2a (Figs. 3C). Dol-2b is a  
265 void and vein filling dolomite, much clearer than Dol-2a in PPL, and characterized by well-  
266 developed (hundred microns) sub-planar to non-planar rhombs, bright greenish-yellowish  
267 zoned in CL. Dol-2b is a blocky cement but is also connected to veinlets (Fig. 3C).

268 The last dolomite phase (Dol-3) is observed as cement and vein- or breccia-filling. Dol-  
269 3a replaces Dol-2b and forms either a clear dolomite in PPL and dark in CL, or a dark cloudy  
270 dolomite (Fig. 3C), bright red-orange unzoned in CL (Fig. 3F). Dol-3b is a clear sub-planar to  
271 non-planar (saddle) coarse (hundred microns) rhomb dolomite. A zoned to unzoned dark  
272 reddish luminescence characterizes Dol-3b.

#### 273 4.1.2.3 *Late meteoric calcite phases*

274 Late calcite phases also occur across the whole sedimentary series filling the remaining  
275 porosity and cutting-across the host dolostone as mm-sized veins. Two generations of calcite  
276 are distinguished. The first one (Cal 1) displays yellowish color in CL with zoned  
277 scalenohedron crystals in fractures and as replacement of a former dolomite crystal  
278 (dedolomite). The second (Cal 2) postdates Dol-3 and is extinct in CL forming sparitic to  
279 anhedral crystals in fractures or in breccia (Fig. 3E and 3F).

## 280 4.2 *Ore mineralogy and petrography*

281 Crosscutting relationships and mineral assemblages indicate the presence of two  
282 distinct stages of Mn mineralization (Fig. 4). Veins systematically crosscut both the  
283 replacement and karst mineralization. Hausmannite and manganite crystals are crossed or  
284 replaced by pyrolusite and later by goethite. It suggests the existence of a prior  
285 mineralization related to the formation of Mn(II) and Mn(III) oxides and the existence of two  
286 Fe oxyhydroxide stages (Gth1 and Gth2).

#### 287 4.2.1. Macroscopic features of the Mn-Fe mineralization

288 From 1922 to 1966, the Bou Arfa manganese deposit was one of the main Mn  
289 producers in Morocco with a final production of about ~2 Mt Mn (Mouttaqi et al., 2011). The  
290 Mn ore produced metallurgic Mn (33% Mn, 17% Fe) and chemical Mn (82% Mn, <3% Fe;  
291 Pouit 1964, 1980; Pouit and Jouravsky 1965; Michard and Raddi 2011; Mouttaqi et al. 2011).  
292 The mine remains closed since the seventies. The main mining site is located at Aïn Beida  
293 with significant underground works (Figs. 1 and 3). The ore is also well exposed along the  
294 Hamaraouet cliff (Figs. 1B and 5A), which constitutes an erosion limit between the basement  
295 and the cover; minor mining activities are still in place but galleries in the Upper Chocolate  
296 Unit (UCU) are preserved (Figs. 5A and B). From Aïn Beida to Hamaraouet, the Mn  
297 mineralization occurs as: (1) a continuous 1-6 meters thick stratabound orebody (~2 km) by  
298 replacement of the UCU (Fig. 5C), and (2) veins, stockworks, breccia karst-like (pockets,  
299 lenses, cluster) mineralization filling open spaces (Figs. 5D-H; Pouit and Jouravsky 1965;  
300 Pouit 1980). This second mineralization is the most important in terms of tonnage and grade.  
301 It intensifies toward the core of the Bou Arfa anticline (Fig. 1B) and follows a NE-SW  
302 direction parallel to Atlasic directions. It can be subdivided into three sub-groups:

- 303 (i) The main sub-type is a prismatic karst-like mineralization forming vertical pipes formerly  
304 attributed to the "run-type" ore (Pouit and Jouravsky, 1965). This mineralization is ~100  
305 m long and corresponds to karst collapse structure composed by dolostone blocks  
306 embedded in the Mn-Fe mineralization (pyrolusite, manganite, psilomelane, goethite and  
307 hematite) and secondary Mn carbonates (Mn-calcite and rhodochrosite). Their main axis  
308 follows an ENE direction. According to Pouit and Jouravsky (1965), veins of various  
309 sizes (Figs. 5F and 5G) and Mn stockworks (Fig. 5H) are also connected to this  
310 mineralization.
- 311 (ii) Tabular karst-like mineralization (Fig. 5C) are ten meters long and wide with a thickness  
312 of several meters. It follows a sedimentary discontinuous/erosive surface in the upper  
313 part of the massive dolostone level of the UCU (Fig. 2) and corresponds to a network of  
314 metric channels, parallel to the Sinemurian dolostone strata.

315 (iii) Finally, local veins are described through the Upper Pliensbachian sandstone. Despite  
316 the local specificity of this poorly extended mineralization, Pouit and Jouravsky (1965)  
317 indicate that it is likely related to a main fault. Impregnation of stratabound pyrolusite is  
318 related to this vein (Figs. 5F and 5G).

319 The Bou Arfa mineralization is a mixed Mn-Fe type (25% Mn, 10-12% Fe in the bulk ore)  
320 dominantly composed of pyrolusite with manganite in the deeper zone, and locally coronadite  
321 group minerals (coronadite, hollandite and cryptomelane). Goethite and hematite are  
322 systematically present, sometimes forming massive veins (Fig. 5F). Gangue minerals are Mn  
323 carbonates, quartz, calcite and barite (Pouit, 1980).

#### 324 4.2.2 Replacement mineralization

325 The replacement mineralization is mainly composed of pyrolusite (Fig. 5C),  
326 crosscutting and replacing Dol-1b or Dol-2 (Fig. 6A). Pyrolusite occurs as elongated cleaved  
327 prismatic crystals with bipyramidal sections (Fig. 6B). Several micrometric disoriented  
328 needles of pyrolusite filling voids are present at the base of prismatic pyrolusite crystals (Fig.  
329 6C), which means at least two generations of pyrolusite. Pyrolusite grows onto sub-planar to  
330 non-planar altered crystals of Dol-2b. Dol-3b cements pyrolusite (Fig. 6B).

331 Raman peaks of pyrolusite (Julien et al., 2002, 2004) are identified with a broad shape  
332 around  $538 \pm 5 \text{ cm}^{-1}$  and  $750 \pm 5 \text{ cm}^{-1}$  (Fig. 6D). An additional peak close to  $630 \pm 5 \text{ cm}^{-1}$  is  
333 also measured. The peak broadening and the presence of an additional peak at  $630 \pm 5 \text{ cm}^{-1}$   
334 are characteristic of slight deviations of the lattice and especially to de Wolff defects  
335 corresponding to additional corner-sharing  $[\text{MnO}_6]^{8-}$  octahedra (such as in  $1 \times 2$  tunnel oxide  
336 structure; de Wolff 1959; Julien et al. 2002). Other phases are also present in the  
337 stratabound orebodies such as colloform Fe oxides (goethite) and some phyllosilicates  
338 (smectite or biotite in EDS analyses). Colloform goethite crystals are surrounded by micro-  
339 pyrolusite (Fig. 6E).

#### 340 4.2.3 Karst and vein-related mineralization

341 The Hamarouet karst mineralization is mainly composed of Mn oxides and to a lesser  
342 extent of Fe oxyhydroxides. Hausmannite forms euhedral crystals crosscut by Dol-3 (Figs.  
343 7A and B). Hausmannite is ribbed by cleaved pyrolusite crystals that fill fissures with  
344 cryptomelane (7A and B). Hausmannite is replaced by chalcophanite or cryptomelane (Figs.  
345 7A and B). The iron mineralization is composed of centimeter rubbed dark goethite (with  
346 hematite) crosscut by calcite. This mineralization has a colloform habit and evolves to micro  
347 specular at the borders of the Mn ore (Fig. 7E). Fe oxyhydroxides also form a continuous  
348 uniform reddish level surrounding lenticular mineralization and are mostly related to the

349 prismatic karst (Fig. 5G). These reddish levels are composed of micro disoriented needles of  
350 pyrolusite replacing large Dol-2b rhombs.

351 Colloform early manganite ( $\gamma$ -MnOOH) occurs as planar crystals of ten to a hundred  
352 microns (Figs. 7C and D). These crystals form lenticular masses with rare hausmannite and  
353 barite crystals (Fig. 7D). Manganite is only observed in Aïn Beida.

354 Carbonate phases are also associated to the Mn-bearing ore minerals and are similar to  
355 those observed in the host-rock. Dol-2b, Dol-3 and late calcite phases are observable (Figs.  
356 3F, 7A and B). The late stage calcite is also associated with the precipitation of P-rich  
357 minerals (apatite) and some phyllosilicates (smectite or biotite; Fig. 3E). Dol-2b crisscrosses  
358 manganite-hausmannite phases at Aïn Beida, when Dol-3 fills voids (Fig. 7A) and surrounds  
359 hausmannite. In Aïn Beida area a late Ca-rich rhodochrosite, partially replacing manganite  
360 and Dol-2b crystals is observable (Fig. 7C and D).

#### 361 4.2.4 Crystallinity of the Fe oxides

362 According to the Scherrer formulation (Langford and Wilson, 1978; Scherrer, 1918), the  
363 average size of the crystallite populations of hematite and goethite ranges between 0.02 and  
364 0.12  $\mu\text{m}$  in the whole dataset (Fig. 8). These values were measured at the maximum width of  
365 each crystal or in the middle of the crystal and are in good agreement with different studies  
366 (Cornell and Schwertmann, 2003; Gualtieri and Venturelli, 1999; Rendon et al., 1983;  
367 Schwertmann et al., 1985). The crystallite size of hematite in the stockwork mineralization of  
368 Bou Arfa is close to a proto-hematite. This type of hematite is a non-stoichiometric phase,  
369 which is characteristic of the transformation by dehydration of goethite into hematite beyond  
370 140 °C in laboratory experiments (Gualtieri and Venturelli, 1999; Pomiès et al., 1998; Walter  
371 et al., 2001; Wolska and Schwertmann, 1989; Wolska and Szajda, 1988). This proto-  
372 hematite is not an authigenic phase and possesses two distinct groups of crystallites (Lima-  
373 de-Faria, 1963). Schwertmann et al. (1985) have shown that the dimension of the a-cell  
374 parameter is a witness of the formation temperature of goethite. A long distance  
375 ( $4.626 \pm 0.005\text{Å}$ ) refers to a low temperature of formation (4–40°C), whereas a shorter  
376 dimension ( $4.610 \pm 0.001\text{Å}$ ) corresponds to higher temperatures (50–90°C). The cell  
377 dimensions of four Bou Arfa goethites (Table 9) recovered from the reticular distance of  
378 planes (200), (040) and (111) are close to a synthetic goethite crystallized at 50 °C. It is also  
379 worth noting that a decrease in the peak intensity of 2.45Å is characteristic of goethite  
380 formed at >40 °C (Schwertmann et al., 1985), which is actually the case in Bou Arfa goethite  
381 (see DR2).

#### 382 4.3. Geochemistry



## 383 4.3.1 Mineral chemistry

## 384 4.3.1.1 Carbonates

385 EPMA results on dolomite and calcite are reported in Table 4 and plotted in Fig. 9. All  
386 the dolomitic phases show excess Ca (26.3 wt.% to 37.8 wt.%; Figs. 9A and B; Table 4). No  
387 significant variation is observed to distinguish most of the different generations of dolomites  
388 (Figs. 9A and B). Only vein-filling Dol-3 significantly differs from the others, as it contains the  
389 highest MnO content (between 1.21 and 9.03 wt.%; Table 4). MnO enrichment implies that  
390 late dolomite is close to kutnohorite. It is worth emphasizing that although FeO content (0.13  
391 to 1.11 wt.%; Table 4) is lower than MnO, the absolute FeO/MnO ratio is lower than for most  
392 of the sedimentary dolomites (Fig. 9C; Searl and Fallick 1990; Montanez and Read 1992;  
393 Gasparria et al. 2003; Fu et al. 2006). The total amount of trace elements slightly  
394 decreases from Dol-1 to Dol-3. The Sr concentration is lower than common marine  
395 carbonates (Brand and Veizer, 1980; Zenger et al., 1980). The two late calcite phases are  
396 also distinguished, one is Fe-rich, whereas the other is Mn-rich.

## 397 4.3.1.2 Manganese oxides

398 Hausmannite displays minor amounts of SiO<sub>2</sub> (0.05 to 0.30 ± 0.01 wt.%), ZnO (0.05 to  
399 2.08 ± 0.02 wt.%) and Fe<sub>2</sub>O<sub>3</sub> (0.55 to 1.55 ± 0.24wt.%). Other elements such as Na<sub>2</sub>O, MgO,  
400 Al<sub>2</sub>O<sub>3</sub> or SrO are present at very low concentrations. As hausmannite is commonly replaced  
401 by chalcophanite (Fig. 6F), some of the EPMA compositions may be affected.

402 The composition of pyrolusite is heterogeneous. All pyrolusite contain substantial  
403 amounts of Al<sub>2</sub>O<sub>3</sub> (5.75 ± 0.03 wt.%), SiO<sub>2</sub> (2.11 ± 0.03 wt.%) and CaO (2.25 ± 0.05 wt.%).  
404 Only the late-stage pyrolusite grains contain significant amounts of MgO (0.06-1.63 wt.%)  
405 and K<sub>2</sub>O (0-2.27 wt.%). Pyrolusite in stratabound ores (gallery 63) shows a low CaO content  
406 (0.20 ± 0.06%) and the highest Al<sub>2</sub>O<sub>3</sub> (0.89 ± 1.12 wt.% to 1.30 ± 0.53 wt.%). All the vein-  
407 related pyrolusite have a homogeneous composition.

408 EPMA analyzes also reveal that coronadite group minerals – here represented by  
409 hollandite and cryptomelane following the nomenclature of Biagioni et al. (2013) –,  
410 concentrate Ba, Sr, K, Ca and Mg (Table 5). K, Ba and Mg are the dominant cations and only  
411 hollandite is observed as a pure end-member. Chalcophanite sometimes displays very low  
412 Zn concentration, instead of Mg, which could be dominant (up to 4.89 wt.%).

## 413 4.3.1.3 Goethite and hematite

414 All analyzed hematite and goethite samples are from Hamaraouet (Fig. 1B). The total  
415 Fe<sub>2</sub>O<sub>3</sub> content is abnormally low for goethite and hematite (Table 6) in comparison with their



416 ideal formula. The total  $\text{Mn}_2\text{O}_3$  and  $\text{SiO}_2$  contents delimit two geochemical trends: (i) The  
417 massive colloform goethite and the Fe oxides associated with dedolomitization are enriched  
418 in  $\text{Mn}_2\text{O}_3$  (mean values from  $1.46 \pm 0.24$  to  $2.30 \pm 0.10$  wt.%; Table 6) with minor  $\text{SiO}_2$  (mean  
419 values from  $0.11 \pm 0.06$  to  $0.49 \pm 0.47$  wt.%) and; (ii) The goethite in veins are enriched in  
420  $\text{SiO}_2$  (mean values from  $1.71 \pm 0.14$  to  $3.50 \pm 0.4$  wt.%) with minor  $\text{Mn}_2\text{O}_3$  content (mean  
421 values from  $0.09 \pm 0.01$  to  $0.16 \pm 0.02$  wt.%; Table 6). Goethite and hematite also exhibit  
422 minor concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  (ranging from 0.02 to 0.75 wt. %).

#### 423 4.3.2 Bulk-rock and Mn-ore geochemistry

424 The Sinemurian dolostones display similar geochemical patterns irrespective of the  
425 dolomitizing event that affected these rocks (Fig. 10A). The presence of detrital phases such  
426 as quartz, feldspars, zircon, monazite and Ti-oxides explains some high immobile and  
427 lithophile contents. One of the striking features in all samples is the higher MnO content (0.74  
428 to 4.71 wt.%) comparative to FeO (0.26% to 1.44 wt.%; Fig. 10A; Table 2). The enrichment in  
429 As is also significant.

430 The karst Mn ores of Aïn Beida, the stratabound Mn and Fe orebodies and the fracture-  
431 filling Fe-Mn mineralization show a similar geochemical signature despite their different  
432 mineralogy (Figs. 10A and B). Geochemical patterns are close to those of the host rock but  
433 with relatively higher enrichments. Lithophile (V), chalcophile (Pb, Zn, Cu) and siderophile  
434 (Co, Ni, Mn) elements are more enriched than in the host rock (Fig. 10A). Ba, As, Zn and Fe  
435 contents differ between samples: higher Ba and As contents are recorded at Aïn Beida. The  
436 Mn/Fe ratio of samples from Aïn Beida ( $\text{Mn}/\text{Fe}_{\text{AB1}} = 66.9$ ;  $\text{Mn}/\text{Fe}_{\text{AB2}} = 1.3$ , Table 3) is also one  
437 of the lowest. The late supergene weathered ores are enriched in Sr (1316 to 2350 ppm), Zn  
438 (1446 to 2136 ppm) and  $\text{K}_2\text{O}$  (0.66 to 0.96 wt.%), likely due to the presence of hollandite,  
439 cryptomelane and chalcophanite. Concentration in lithophile, immobile elements and in REE  
440 are low compared to the host rock (Fig. 10A).

441 The enrichments of the Fe-rich ores are roughly the same as for the Mn ore with some  
442 increase in V, As and Pb in the vein-related hematite of Hamaraouet (Fig. 10B). This  
443 mineralization is also enriched in Be (6 to 114 ppm) and Ge (2 to 124 ppm). The Fe ore has  
444 also a high Mn content up to 0.14-1.07 wt.%  $\text{Fe}_2\text{O}_{3\text{t}}$  (Table 3).

445 Overall, As and Mn are enriched in both the host dolostone and in the mineralization  
446 (Tables 2 and 3). Paleozoic schists are depleted in Mn (0.02 wt.% MnO). Chalcophile  
447 elements (As, Pb, Zn, Cu) are abundant in the Mn ores and in most of the Fe ores (Fig. 10A  
448 and B; Table 3).

#### 449 4.3.3 Carbon and oxygen isotopic compositions of carbonates

450 The analyzed carbonates show a wide range of carbon and oxygen isotopic  
451 compositions with  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  ratios ranging from -8.6 to 2.2‰ and 17.3 to  
452 29.8‰, respectively (Fig. 11; Table 7).  $\delta^{18}\text{O}_{\text{VSMOW}}$  and  $\delta^{13}\text{C}_{\text{PDB}}$  ratios for the primary Dol-1  
453 phase are rather homogenous clustering around 29.2‰ and 29.8‰ for  $\delta^{18}\text{O}_{\text{VSMOW}}$  and 0.1‰  
454 to 2.2‰ for  $\delta^{13}\text{C}_{\text{VPDB}}$ . Later dolomite phases (Dol-2 and Dol-3) display  $\delta^{18}\text{O}$  values from  
455 17.3‰ to 28.6‰ VSMOW and  $\delta^{13}\text{C}$  values ranging from -7.8‰ to 2.1‰ VPDB. Based on  
456  $\delta^{13}\text{C}$  values, there is a slight distinction between the Dol-2 cement in the host rock (average  
457 value:  $-0.04 \pm 0.40\%$  VPDB) and the heavier  $\delta^{13}\text{C}$  values of the vein filling Dol-2 (mainly  
458 represented by Dol-2b; average value:  $1.01 \pm 0.95\%$  VPDB; Fig. 11). Vein-filling Dol-3 shows  
459 the lightest  $\delta^{13}\text{C}$  values (Fig. 11). Some values are heavier, but this may likely be due to  
460 impurities in Dol-2 during the analysis. For Dol-2 and Dol-3, both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values  
461 evolve simultaneously towards lighter isotopic values. Late calcite cements display values  
462 ranging from 19.5 to 23.1‰ for  $\delta^{18}\text{O}$  and from -8.5 to -6.1‰ for  $\delta^{13}\text{C}$  (Fig. 11).

## 463 5. DISCUSSION

### 464 5.1. Paragenetic sequence

465 The formation of the Mn(-Fe) ores of Bou Arfa can be summarized in three main  
466 stages: (i) Mn-Fe protore, (ii) main Mn-Fe ore and (iii) post ore (Fig. 4). The second stage is  
467 economically the most important accounting for most of the extracted Mn ore in the Bou Arfa  
468 district, which is mainly expressed by the occurrence of massive pyrolusite. The multistage  
469 deposition of Mn-bearing minerals was accompanied by several dolomitization synchronous  
470 with the first two stages of Mn deposition (Fig. 4).

#### 471 5.1.1 Mn-Fe protore

472 Manganite and hausmannite (Figs. 6F, 7A, B, C) accompany Dol-2, along with colloform to  
473 specular Mn-rich Fe oxyhydroxides (goethite and hematite) and barite (Fig. 4). This early  
474 Mn(-Fe) mineralization is mainly observed in the Ain Beida site (Fig. 1B), but the occurrence  
475 of hausmannite in the Hamaraouet area also indicates that early stage of mineralization has  
476 a larger extension.

#### 477 5.1.2 Main Mn ore

478 Fracture-filling and karst mineralization are later than Dol-2. Pyrolusite is the only Mn oxide  
479 (Figs. 3E, 6A, B, F, G and H) and occurs alongside Si-rich goethite, hematite and Mn-  
480 dolomite to Ca-rhodochrosite (Fig. 4). The massive pyrolusite shows a wide range of textures  
481 from tiny micrometric needles to large prismatic millimetric crystals (Figs. 3E, 6B and F).  
482 Variation of pyrolusite bands in Raman spectra (Fig. 6D) are interpreted as replacement of

483 manganite (Gaudefroy, 1960; Hewett, 1972; Pasero, 2005; Post, 1999; Yoshino et al., 1993,  
484 1992). Prismatic pyrolusite is frequently related to manganite replacement (Fleischer et al.,  
485 1962). The replacement of Mn<sup>2+</sup>- or Mn<sup>3+</sup>-bearing minerals by pyrolusite enhances the Jahn  
486 Teller deformation pattern by including a c-axis elongated Mn<sup>3+</sup>-octahedra in the pyrolusite  
487 structure (Julien et al., 2004; Post, 1999; Post et al., 2003; Zwicker et al., 1962). These  
488 textures indicate that this mineralization stage impregnates the host rock dolostone and  
489 support that pyrolusite partly replaced manganite. Also important is that pyrolusite remains  
490 stable and does not accommodate any supplementary cation other than Mn in its structure,  
491 unlike manganite, for which substitutions are facilitated by its layer structure (Post, 1999;  
492 Post et al., 2003). Conversion from manganite to pyrolusite explains Si, Al and Ca (>2 wt.%)  
493 enrichment in pyrolusite (Tables 3 and 5). Mn-Fe oxides precipitated from a similar  
494 mineralizing fluid, although Si-rich Fe oxides formed later than pyrolusite (Fig. 7E). This  
495 means that this second ore formation stage partly reworks the early mineralization episode.  
496 Although, pyrolusite by replacement of manganite is well documented in the Bou Arfa ore,  
497 the main ore consists of open-space filling of pyrolusite (Figs. 6A and F). Botryoidal-hematite,  
498 proto-hematite and goethite formed later than Dol-2 and destabilized some dolomitic phases  
499 (Fig. 4).

### 500 5.1.3 Late stage supergene enrichment

501 The post-ore supergene stage is poorly expressed in the Bou Arfa ores (Fig. 4). This  
502 feature is due to the stability of the main ore-forming minerals under surface or near-surface  
503 conditions (Post, 1999), such as pyrolusite and Fe oxides. Some typical supergene minerals  
504 have unevenly precipitated as chalcophanite or hollandite-cryptomelane (Figs. 6F, 7A and B)  
505 in partial replacement of hausmannite. Chalcophanite is a common weathering product in Mn  
506 and Zn deposits (Decrée et al., 2010, 2008; Ostwald, 1992; Post, 1999), and its relation with  
507 hausmannite is due to little amounts of Zn (0.3 wt.%; Table 5). Pyrolusite is also partially  
508 destabilized and transformed into coronadite group minerals (here hollandite and  
509 cryptomelane) as it is often the case in the weathering zone of Mn deposits (Ostwald, 1992;  
510 Varentsov, 1996). Late calcite cement (Figs. 3E and F) is also associated with the Mn  
511 supergene assemblage and extensively develops in the host rock and mineralization (Fig. 4).  
512 The meteoric origin of calcite is supported by partial dedolomitisation (Fig. 3E; Ayora et al.  
513 1998; Dewaide et al. 2014) and light isotopic values (Fig. 11).

## 514 **5.2 Metallogenic model**

### 515 5.2.1 Metal source(s) in seawater

516 All mineralization, whatever their stage, display similar geochemical patterns (Fig.  
517 10B), close to the signal of the host rock dolostone (Figs. 10A and B). It implies that the three  
518 ore stages have a similar origin and that the later stages rework an early stock. Chalcophile  
519 (As, Zn, Pb, Cu, Ni, Co, V) and some mobile elements (Sr, Ba, Be; Table 3; Figs. 10A and B)  
520 are particularly enriched in the orebodies. However, a Principal Component Analysis (PCA)  
521 also links As, V, Mo, Co, Ni, Ba, Zn, Sr, Pb, U to the Mn orebodies, unlike immobile and  
522 lithophile, which characterize the host Sinemurian dolostone and the Pliensbachian arkoses  
523 (Fig. 12A). This indicates that the Mn ore involves external inputs of Mn and associated  
524 metals, i.e. from basement rocks. Therefore, it is likely that upward (hot?) mineralizing fluids  
525 additionally participated to the ore formation, for example by mixing with shallower  
526 oxygenated ground waters, which might explain the karst-like mineralization (Varentsov,  
527 1996). This is materialized in Nicholson's diagnostic plots by a clear hydrothermal trend of  
528 the Bou Arfa ores (Figs. 12B; Fig. 12C). In addition, this highlights the difference between the  
529 Bou Arfa Mn ores from other carbonate-hosted Mn deposits in Morocco (Fig. 12C; Gutzmer  
530 et al. 2006; Dekoninck et al. 2016b, a, 2020).

### 531 5.2.2 Syn-sedimentary and early diagenetic (pre)concentration

532 The occurrence of evaporitic levels, pisoids, oncoids, bird eyes and micro-saccharoidal  
533 dolomite (Dol-1; Fig. 3) supports a restricted lagoonal environment, part of the platform  
534 interior. This restricted lagoon is protected from open marine environments by an ooid and  
535 bioclastic sand shoal, probably forming the platform margin 4-5 km south of the Mn ore  
536 deposit of Aïn Beida, in the Jbel Bou Mokhta (Fig. 1B). These restricted lagoonal  
537 environments are particularly suitable for early dolomitization (Fig. 4; Land 1985; Jones and  
538 Renault 1994; Machel 2004; Arenas-Abad et al. 2010). The oxygen composition of Dol-1 are  
539 higher than most common lagoonal dolomite (Blaise et al., 2014; Brigaud et al., 2018;  
540 Mauger and Compton, 2011; Ren and Jones, 2017), but they are consistent with shallow  
541 depth Mn-rich dolomite (Burns and Baker 1987; Fig. 11). Dolomite (Dol-1) is less abundant in  
542 shoal and upper slope facies outside the Bou Arfa (Jbel Bou Mokhta; Figs. 1B, 3G and H).

543 In these shallow marine to lagoonal environments, anoxic to suboxic basins or microbial  
544 activity are the most suitable trap for Mn (Folk and Chafetz, 2000; Jones and Renault, 1994;  
545 Mandernack et al., 1995b, 1995a; Ostwald, 1990). Microbial activity is usually observed  
546 through the coalescence of Mn-Fe-rich pisoid laminae in sedimentary Mn deposits (Groote  
547 Eylandt, Chinese, Brazil deposits; Force and Cannon 1988; Frakes and Bolton 1992;  
548 Ostwald 1992; Fan and Yang 1999; Fan et al. 1999; Biondi et al. 2020). The absence of Mn-  
549 rich or Fe-rich laminae and  $\delta^{13}\text{C}$  isotopic values of Dol-1 greater than 0‰ VPDB (Fig. 11) are  
550 not consistent with Mn and Fe enrichment by bacteria-mediated organic matter degradation

551 (i.e., black shales; Okita et al. 1988; Polgári et al. 1991, 2012; Fan et al. 1999; Maynard  
552 2014; Johnson et al. 2016). Alternatively, the C-O evolutionary trend shown in Figure 11  
553 could be interpreted as resulting from fluid mixing between deep upward migrating warm  
554 basinal brines and downward infiltration of later cooler meteoric fluid. However, C-rich layers  
555 (i.e., coal, lignite) are not present in the sedimentary series. A second dolomitization episode  
556 is recorded by Dol-2, although no textural argument clearly establishes if this second event  
557 belongs to an early diagenesis or epigenesis (Fig. 5).

558 The high Mn contents of Dol-1 (up to  $1.58 \pm 0.51$  wt.% MnO in Dol-1; Table 4) suggests  
559 an early Mn enrichment (Fig. 9C) under suboxic conditions with the absence Fe sulfides or  
560 Fe carbonates (Maynard 2014). Without any contribution of organic matter in the Mn fixation,  
561 an extremely high alkaline and anoxic to dysoxic environment (0-0.4 Eh) would prevail.  
562 Anoxic-suboxic events related to the closure of a narrow and shallow Bou Arfa basin (Piqué  
563 et al., 2000; Yelles-Chaouche et al., 2001) may trap the dissolved  $Mn^{2+}$  in pore waters. The  
564 porosity increased thanks to the early dolomitization and transformation of the earliest  
565 carbonates into dolomite. The high Mg:Mn ratio favors precipitation of dolomite with little  
566 amounts of Mn, the major part staying in the pore fluid (Table 2). Burial of the Sinemurian  
567 sediments would reinforce suboxic conditions that precipitate  $Mn^{2+}$  from pore waters into  
568 “reduced” Mn oxides ( $Mn^{2+}$  and  $Mn^{3+}$ ), when alkaline conditions are maintained. The high As  
569 content in goethite (Table 6) is also consistent with a precipitation under alkaline and suboxic  
570 conditions (Campbell and Nordstrom, 2014; Pierce and Moore, 1982). At the same time,  
571 dolomitization continued, increasing the porosity of the host rock, and helped to  
572 accommodate  $CO_3^{2-}$  from pore waters into dolomite phase. The extensive pseudomorphosis  
573 between dolomite generations during the ore formation (Figs. 3 and 4) may have limited  
574 massive release of  $CO_3^{2-}$  in pore waters, and have prevented the formation of Mn-rich  
575 carbonates (i.e., Ca-rhodochrosite or kutnohorite; Fig. 4). Only alteration of this primary ore  
576 assemblage led to Ca-rhodochrosite (Figs. 4 and 7C; Maynard 2014; Manceau et al. 2014).  
577 Consequently, hausmannite and manganite precipitated instead of Mn carbonates. The  
578 presence of Mn-rich Fe oxides in the primary stage also indicates a local separation of Fe  
579 from Mn at macro/microscopic scale. However, the high Mn content in goethite shows that  
580 Fe and Mn probably came with the same mineralizing fluid, but have precipitated separate  
581 phases, in different proportions. It likely suggests that the mineralizing fluids carried Mn and  
582 Fe with a very low Fe/Mn ratio (Table 6; Fig. 9C).

### 583 5.2.3 Late diagenetic evolution and hydrothermal circulation during burial

584 The synchronous precipitation of manganite, hausmannite and barite in Mn deposits  
585 are commonly attributed to thermal conditions with temperatures much higher (250-350°C)



586 than at the surface (Fan et al., 1999; Gutzmer and Beukes, 1996; Hewett, 1972). Dol-2b and  
587 Dol-3 display sub-planar to saddle texture (Figs. 3C and F) due to an increase of  
588 temperature (Blaise et al., 2014; Radke and Mathis, 1980; Searl, 1989). Decrease of the  
589  $\delta^{18}\text{O}$  values and slight decrease of  $\delta^{13}\text{C}$  values from Dol-1 to Dol-2 (Fig. 9) is characteristic of  
590 an isotopic re-equilibration triggered by a temperature increase (Brand and Veizer, 1981; Lee  
591 and Friedman, 1987; Nader et al., 2007, 2006; Warren, 2000). Moreover,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$   
592 values of the saddle dolomite (Dol-3) are among the lightest (Fig. 9) and support a  
593 continuous increase in temperature along the formation of the dolomite generations, and  
594 consequently along the formation of the Bou Arfa Mn(-Fe) ores. The saddle dolomite (Dol-3b)  
595 originates from a thermal effect instead of oversaturation of Mg (Searl, 1989; Warren, 2000).  
596 The temperature allowing non-planar dolomite (Dol-2b) is close to 50°C and a temperature of  
597 60°C to 80°C is needed for the saddle dolomite formation (Dol-3b; Radke and Mathis 1980;  
598 Machel 2000; Warren 2000). This thermal effect is also shown through the crystallography of  
599 Fe oxides (Fig. 8; Table 9). In experiments, the formation of proto-hematite occurs beyond  
600 ~140°C (Wolska and Schwertmann, 1989) and the short a axis of the goethite cell at Bou  
601 Arfa (Table 9) testifies to the higher formation temperatures (>50°C; Schwertmann et al.  
602 1985). This interpretation is further supported by the evolutionary trend shown by the  
603 distribution of C and O isotopic data (Fig. 11) and an important change in  $\delta^{13}\text{C}$  from the  
604 classical burial diagenesis in Dol 3. This involves warm basinal brines and their subsequent  
605 mixing with downward percolating cooler meteoric fluids. The E-W-trending Aïn Beida fault  
606 zone would have enhanced the widespread infiltration of meteoric fluids. These observations  
607 indicate that burial and additional hot fluids are the driver for late dolomitization (Dol-2 and  
608 Dol-3) and Fe oxide stages (Fig. 5). It is materialized by karst and vein mineralization (Fig.  
609 6A, F, 6A, B and C) and by mineralogical transformations of the primary ore (Fig. 5). The  
610 successive dolomite generations are similar to the burial model of Cu-Co deposits described  
611 in the Central Africa Copper Belt (Dewaele et al., 2006; El Desouky et al., 2009; Hoy and  
612 Ohmoto, 1989). The formation of Mn-rich dolomite and Ca-rhodochrosite are also indicators  
613 of burial diagenesis in the Bou Arfa deposit (Fig. 4). Actually, the reductive conditions related  
614 to burial and the loss of oxygen renewal is suitable for the partial manganite degradation into  
615 Ca-rhodochrosite (Fig. 7C; Roy 2006; Johnson et al. 2016).

616 Consequently, the genesis of the remobilized ore (Fig. 5) might be due to (i)  
617 remobilization of the primary ore and (ii) migration of Mn by diagenetically-driven  
618 hydrothermal fluids. The Aïn Beida fault (Fig. 1B) played an important role by facilitating  
619 fracturation of the host rock and enhancing Mn-bearing fluid circulation. It is not excluded that  
620 hausmannite and manganite resulted from the transformation of former Mn oxides. Such  
621 mineral evolution is common in hypogene and metamorphic Mn deposits (Hewett 1972;

622 Nicholson 1992; Gutzmer et al. 1995; Post 1999). There are few petrographical arguments  
623 pleading for the presence of an early Mn carbonate precursor as formerly presented by Pouit  
624 and Jouravsky (1965).

#### 625 5.2.4. The Cenozoic Atlas exhumation: supergene enrichment

626 Hollandite, cryptomelane and chalcophanite (Figs. 6F and G) were accompanied by  
627 dedolomitisation (Fig. 4E). These late meteoric fluids have not substantially enriched the Bou  
628 Arfa ore, except maybe for Zn that was concentrated in chalcophanite, and Sr in hollandite-  
629 cryptomelane (Table 3). The supergene origin of the Fe oxides is unlikely with their  
630 crystallographic features (Fig. 8; Table 9) and explains why these minerals have precipitated  
631 later than manganite, hausmannite and pyrolusite. This relatively poor weathering is quite  
632 contrasting with the numerous Cu-Zn-Pb-V hypogene deposits of the eastern High Atlas and  
633 Anti-Atlas, where an oxidation zone systematically occurs (Bouabdellah et al., 2012; Choulet  
634 et al., 2014; Poot et al., 2020; Rddad and Bouhleb, 2016; Verhaert et al., 2018, 2017). The  
635 weathering phase recorded in the Bou Arfa ores is probably connected to the repeated  
636 exhumation of the Atlas since late Cretaceous times (Dekoninck et al., 2020; Frizon de  
637 Lamotte et al., 2000; Froitzheim, 1984; Leprêtre et al., 2018, 2015).

#### 638 **5.3 Place of the Mn Bou Arfa deposit in the Mesozoic evolution of the Atlas**

639 Without geochronological constraints, the absolute timing of the Bou Arfa Mn(-Fe)  
640 mineralization is difficult to establish, but has seemingly occurred after the deposition of the  
641 Sinemurian carbonates. Sinemurian dolostones were deposited in the context of rifting and  
642 deepening of several sedimentary basins along the Atlas belt (Frizon de Lamotte et al., 2009;  
643 Nottvedt et al., 1995; Teixell et al., 2009; White and McKenzie, 1988). This setting would  
644 explain the position of the Bou Arfa Mn deposit, as the basin could act as a threshold, given  
645 its location above a paleohigh. The strong variation in the thickness of the sedimentary series  
646 in the Bou Arfa basin indicates an important variation of the geometry and/or significant  
647 lateral variation of the sedimentary facies that would have delimited the extension of the Mn  
648 mineralization (Torres-Ruiz, 1983). This sharp transition of sedimentary facies is well  
649 demonstrated in the Jbel Bou Moktha (Fig. 1B), where the Sinemurian carbonate facies  
650 evolves from a lagoonal (dolomitic-peloidal facies) to an offshore environment  
651 (marls/limestones alternations). Transgression events during the Sinemurian interval  
652 repeatedly supplied dissolved  $Mn^{2+}$ , and when the Bou Arfa area was isolated from seawater  
653 influxes, was trapped in pore waters. The situation of the Bou Arfa deposit in a narrow basin  
654 pinched to the north by the Tendirara rift shoulder and to the south by a narrow ditch (Tamlet  
655 plain; Piqué et al. 2000; Yelles-Chaouche et al. 2001) was an efficient trap for dolomitization  
656 and Mn pre-concentration. The position of the deposit above paleohigh basement rocks and



657 close to a major tectonic thrust (Fig. 1B) have provided suitable conditions for brecciation  
658 and fracturing enhancing diagenetically-driven hydrothermal circulation in porous Sinemurian  
659 dolostones.

660 The metallogenesis of the Bou Arfa ores is different from the high-grade Imini-Tasdremt Mn  
661 deposits (Figs. 12B and C). Accordingly, the Imini-Tasdremt Mn ores postdate the latest  
662 meteoric dolomite generation and do not show any Mn precursor (Dekoninck et al., 2016a)  
663 nor saddle dolomite (Force et al., 1986). Moreover, the host dolostone is intensely karstified  
664 with dissolution and collapse breccia filled by sands (Gutzmer et al., 2006) and the age of the  
665 Mn ore span over a period of ~25 Ma during the late Cretaceous (Dekoninck et al., 2020).  
666 The accepted formation model of the Imini-Tasdremt ores involves mixing of O<sub>2</sub>-rich meteoric  
667 waters and acidic O<sub>2</sub>-free ground waters (Gutzmer et al., 2006). For these reasons, the  
668 comparison between these two carbonate-hosted Mn deposits is unfaithful although the  
669 dolomitic trap has some similarities, i.e. the isotopic composition (Fig. 11) and Fe:Mn ratios  
670 (Fig. 9C) of the host dolostones.

#### 671 **5.4. Relation of the Bou Arfa Mn(-Fe) ores with Mississippi Valley Type deposits in** 672 **North Africa**

673 Mississippi Valley Type (MVT) deposits are widespread along Meso-Cenozoic shallow-water  
674 carbonate platforms forming the Atlas system (Bouabdellah and Sangster, 2016; Decrée et  
675 al., 2016). The occurrence of numerous Pb-Zn MVT and Cu mineralization in Jurassic series  
676 of the Bou Arfa region (Fig. 1; e.g., Chefchaouni et al. 1963; Verhaert et al. 2017, 2018) also  
677 supports the predominant role of dolostone in trapping various metals. The Bou Arfa deposit  
678 is comparable with major Zn-Pb MVT deposits of Morocco (Bouabdellah et al., 2015, 2012;  
679 Bouabdellah and Sangster, 2016; Jébrak et al., 1998; Rddad, 2021; Rddad et al., 2018;  
680 Rddad and Bouhleb, 2016) at several levels: (1) they are hosted in Lower to Middle Jurassic  
681 unmetamorphosed platform carbonate rocks; (2) the mineralization fills open spaces (veins,  
682 interconnected cavities, solution-collapse breccias) and replaces carbonate; (3) the  
683 mineralization is accompanied by different generations of saddle dolomite or calcite; (4) the  
684 deposits are located above basement paleohighs where Triassic to Jurassic rocks are  
685 pinched out; and (5) the ENE-WSW and E-W faults have facilitated fluid circulation in  
686 permeable rocks hosting the ore. The genesis of Pb-Zn MVT mineralization in Morocco is  
687 explained by ascending diagenetically-derived hydrothermal solutions due to compaction  
688 and/or gravity-driven systems mixing with surficial cooler fluids. The mineralizing fluids were  
689 forced to spread laterally along the porous Lower and Middle Jurassic aquifer due to Upper  
690 Jurassic cap rock (Bouabdellah and Sangster, 2016). MVT deposits are likely formed before  
691 the onset of the non-sulphide supergene ores supposed at ~20 Ma (Choulet et al., 2014;

692 Verhaert et al., 2017). The heat source for MVT deposits in the Atlas range may derived from  
693 the Alpine orogenesis itself that caused large-scale fluid circulation of deep-seated fluids  
694 rather than direct volcanic activities (Rddad, 2021). The High Atlas has indeed a thin  
695 lithosphere supported by a thermal anomaly since the Miocene (Leprêtre et al., 2018 and  
696 reference therein), which has provided proper thermal conditions for various mineralization  
697 types in the High Atlas. Such interpretation can be applied to the Bou Arfa Mn(-Fe) deposit.

## 698 **6. CONCLUSIONS**

699 This study emphasizes the role of dolomitization in the formation of the Bou Arfa Mn(-  
700 Fe) deposit. The accumulation of the Bou Arfa Mn ores follows a multistage genesis in close  
701 association with three dolomite events. Early diagenesis (Dol-1 and Dol-2) and epigenesis  
702 (Dol-3) are associated with the mineralization process by providing suitable conditions for Mn  
703 oxides precipitation instead of Mn carbonates. The porosity, depletion in dissolved carbonate  
704 species in pore waters and suboxic conditions are responsible for the primary hausmannite,  
705 manganite, barite and (Mn-)goethite assemblage. The subsequent burial of the host  
706 Sinemurian dolostone is clearly observed through (i) a textural evolution from non-planar  
707 (Dol-2b) to saddle dolomite (Dol-3), (ii) a decrease in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic values and  
708 (iii) crystallographic changes of the Fe oxides. This increase in temperature and pressure  
709 triggered mineralogical transformations of the primary manganite into massive pyrolusite with  
710 (Si-)goethite, hematite and (Mn-)dolomite to Ca-rhodochrosite, whereas hausmannite  
711 remained stable. Diagenetically-driven hydrothermal circulation, enhanced by the vicinity of  
712 the Aïn Beida fault, is responsible for the formation of deep karst and vein-type Mn and then  
713 Fe ores. A mixing fluid model is also suitable for the late evolution of the Mn mineralization. It  
714 emphasizes that goethite and some of the Mn oxides, commonly attributed to strictly  
715 supergene conditions, were formed under higher temperatures ( $>50^\circ\text{C}$ ). The supergene  
716 contribution is very low given the stability of the ore-forming minerals under supergene  
717 conditions. Weathering only proceeded through partial replacement of hausmannite (and  
718 rarely pyrolusite) into chalcophanite and coronadite group minerals.

719 The Bou Arfa deposit can be considered as a diagenetic deposit showing similarities  
720 with MVT deposits of North Africa, where a predominant role is played by dolomitization. In  
721 the context of global extension (opening of Tethys) forming several Jurassic basins along the  
722 High Atlas, the Bou Arfa area played differently due to local settings. This narrow basin lying  
723 above a paleohigh basement in a heavily faulted zone probably facilitated circulation of  
724 diagenetic fluids and strictly delimited the geometry of the Mn ores. Transgression-regression  
725 intervals determined the input of dissolved Mn into the basin.

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1172

## 1173 Figures

1174 **Fig. 1 (color).** **A.** Simplified structural map of Morocco showing the location of Mn  
1175 mineralization. MA= Middle Atlas, EHA=Eastern High Atlas, HA= High Atlas, WHA=Western  
1176 High Atlas, SAF=South Atlas Front, NAF=North Atlas Front. **B.** Local geological map of the  
1177 Bou Arfa cliff and the Mn mineralization (modified after Pouit and Jouravsky 1965). H1-  
1178 4=Hamaraouet, HB=Hamarouet and Aïn Beida, 63= Gallery 63.

1179 **Fig. 2 (black and white).** Stratigraphic column of the Tamlet area (left) and in the  
1180 Hamaraouet sector (right).

1181 **Fig. 3 (color).** Petrographic views of carbonate generations in the host rock. **A.** CL view of a  
1182 sandstone level at the base of the UCU cemented by Dol-1a (sample J2-2). **B.** Oolith  
1183 replaced by Dol-1a and cemented by Dol-1b under CL at the bottom of the UCU. **C.**  
1184 Successive generations of dolomite crystals filling fractures and void in H2 (sample H2 – Dol  
1185 – Min). **D.** Bird eyes facies in the UCU dolostone at Hamaraouet (H1) crisscrossed by  
1186 several calcite veins. **E.** Dedolomitization of Dol-2A in the Mn ore at Hamaraouet (H3) with  
1187 pyrolusite crystals. **F.** Late calcite filling void at Hamaraouet (sample H2-Br-Dol). **G.** Early  
1188 dolomite generation with ferrous (Cal-1a) and non-ferrous (Cal-1b) calcites in the UCU of the  
1189 Jbel Bou Moktha under PPL prepared with a mix of alizarine-red and K-ferricyanide. **H.** Late  
1190 calcite generations in the UCU of Jbel Bou Moktha under CL. Dol=dolomite, Py=pyrolusite,  
1191 Ca=calcite.

1192 **Fig. 4 (color).** Tentative paragenetic sequence of the Bou Arfa deposit. Schematic  
1193 petrographic reconstruction of dolomite generations is given for cement and veins (see Table  
1194 6 for key features of dolomite generations).



1195 **Fig. 5 (color).** Field observations of the Mn and Fe ores. See location on Fig. 1B. **A.**  
 1196 Galleries in the Hamaraouet area (H1) in the Upper “Chocolate” Unit. **B.** View of the Aïn  
 1197 Beida mining site and the Bou Arfa cliff. **C.** Stratabound orebody in gallery 63. **D.** Stockwork  
 1198 in the host UCU dolostone between Aïn Beida and Hamaraouet (HB). **E.** Mn and Fe oxides in  
 1199 the Hamaraouet area (H1). **F.** Massive goethite vein in the Hamaraouet area (H3). **G.** Fe  
 1200 oxide vein crossing the stratabound Mn ore in gallery 63. **H.** Stockwork of pyrolusite in the  
 1201 UCU in Hamaraouet (H3).

1202 **Fig. 6 (color).** Petrographic views of main mineralization types. **A.** Cluster mineralization  
 1203 showing pyrolusite veins crossing early dolomite generation (Dol-1 and 2) filled by calcite  
 1204 under SEM-BSE view at Hamaraouet. **B.** Disseminated bipyramidal pyrolusite growing onto  
 1205 altered Dol-2B and cemented by coarse Dol-3B under SEM-BSE view at H2 (sample H2-Dol-  
 1206 Min). **C.** Cluster mineralization showing needles and fusiform pyrolusite in gallery 63 under  
 1207 NAPL. **D.** Raman spectra for pyrolusite in gallery 63 (63-01\_3D1, 63-01\_2D1) and between  
 1208 Hamaraouet and Aïn Beida (HA; HAB\_1D1). **E.** Pyrolusite growing onto early botryoidal  
 1209 goethite generation in gallery 63 under NAPL. **F.** Pyrolusite and cryptomelane crossing  
 1210 hausmannite crystals and Dol-3 under SEM-BSE view at Hamaraouet (H1-Min2).  
 1211 Hausmannite is partly weathered into chalcophanite. Note that pyrolusite, in turn, seems to  
 1212 partly weathers into cryptomelane. **G.** Late botryoidal goethite brecciated by Dol-3A  
 1213 generation under SEM-BSE view at Hamaraouet. Note that late goethite grows onto the  
 1214 pyrolusite-calcite matrix. **H.** SEM-BSE view of hausmannite filled by Dol-3b and pyrolusite.  
 1215 Hollandite partly replaces pyrolusite. Dol=dolomite, Cal=calcite, Py=pyrolusite,  
 1216 Cph=chalcophanite, Hs=hausmannite, Cry=cryptomelane, Gth=goethite, Hol=hollandite.

1217 **Fig. 7 (color).** Petrographic views of main mineralization types. **A.** Mixing of different Mn  
 1218 oxides (hausmannite, pyrolusite, cryptomelane, chalcophanite) within the host dolostone in  
 1219 Hamaraouet (H1) under PPL. **B.** Zoom of Fig. 6A under SEM-BSE showing hausmannite  
 1220 replaced by chalcophanite and cryptomelane. Pyrolusite occurs between hausmannite  
 1221 crystals. Note that Dol-3 is broken by cryptomelane. **C.** SEM-BSE view showing phase  
 1222 relation between hausmannite and manganite crossed by Mn carbonate (Ca-rhodochrosite)  
 1223 at Aïn Beida (AB). **D.** SEM-BSE view of crest-like barite associated with manganite and late  
 1224 Mn carbonate at Aïn Beida (AB). **E.** Massive late goethite generation growing onto  
 1225 hummocky pyrolusite in Hamaraouet (H4). Dol=dolomite, Cal=calcite, Py=pyrolusite,  
 1226 Cph=chalcophanite, Hs=hausmannite, Cry=cryptomelane, Gth=goethite, Mnt=manganite,  
 1227 Ba=barite, Rh=rhodochrosite.

1228 **Fig. 8 (black and white).** Average integral crystallites of goethite (A) and hematite (B)  
 1229 samples.

1230 **Fig. 9 (color).** Geochemistry of dolomite generations (Table 4). **A.** Composition of cement  
1231 dolomite in the host rock. **B.** Composition of vein-filling dolomite. **C.** Distribution of MnO and  
1232 FeO of dolomite in various geological settings. The Bou Arfa dolomite generations display an  
1233 individual trend toward low FeO/MnO ratio.

1234 **Fig. 10 (color).** Trace element pattern of whole rock analyses in the Mn (A) and Fe (B) ores  
1235 (Tables 2 and 3).

1236 **Fig. 11 (color).** Stable isotope (Table 7) plot to show the trend of progressive dolomitization  
1237 in the Bou Arfa Mn deposit. Data from MVT deposits (Bouabdellah et al., 2012; Rddad, 2021;  
1238 Rddad et al., 2018; Rddad and Bouhlel, 2016), Mn Imini deposit (Force et al., 1986) and  
1239 shallow Mn-rich dolomite (Burns and Baker, 1987) are included.

1240 **Fig. 12 (black and white).** **A.** PCA statistical distribution of chemical elements in the Bou  
1241 Arfa deposit. **B-C.** Discrimination plot (Nicholson, 1992) between hydrothermal, supergene  
1242 and dubhite Mn accumulation.

#### 1243 TABLES

1244 **Table 1.** Description and location (Fig. 1B) of the studied samples. The mineralogy is  
1245 referred as Qz=quartz, Fds=feldspars, Zr=zircon, Ap=apatite, Musc=muscovite,  
1246 Dol=dolomite, Bt=biotite, Fe-Ti Ox.= Fe-Ti oxides, Py=pyrolusite, Hs=hausmannite, Fe-ox=  
1247 Fe oxyhydroxides, Cph=chalcophanite, Cpm=cryptomelane, Cal=calcite, Hem=hematite,  
1248 Goe=goethite, Hol=hollandite, Ba=barite. The main minerals are in bolt. WRA is the whole  
1249 rock analysis.

1250 **Table 2.** Whole rock geochemistry (major and trace elements) of the host and basement  
1251 rocks given in wt.% (major oxides and LOI) and ppm (traces). <D.L. is under detection limit.  
1252 LOI is the lost on ignition.

1253 **Table 3.** Whole rock geochemistry (major and trace elements) of the Mn and Fe ores rocks  
1254 given in wt.% (major oxides and LOI) and ppm (traces). <D.L. is under detection limit. LOI is  
1255 the lost on ignition.

1256 **Table 4.** EPMA analyses of different carbonate phases. The average values are given with  
1257 their minimum (min) and maximum (max) values. The number of analyses is mentioned (=n).  
1258 Standard deviation is also indicated for each batch and for the instrument ( $\sigma$ ). D.L. is the  
1259 detection limit. Standard list can be found in the data repository.

1260 **Table 5.** EPMA analyses of Mn oxides: hausmannite and pyrolusite in Hamaraouet, and  
1261 supergene cryptomelane, hollandite and chalcophanite. The number of analyses is

1262 mentioned (=n). The average values are given. Standard deviation is also indicated for each  
1263 batch and for the instrument ( $\sigma$ ). D.L. is the detection limit. Standard list can be found in the  
1264 data repository. Standard list can be found in the data repository.

1265 **Table 6.** EPMA analyses of different Fe oxides. The number of analyses is mentioned (=n).  
1266 The average values are given. Standard deviation is also indicated for each batch and for the  
1267 instrument ( $\sigma$ ). D.L. is the detection limit. Standard list can be found in the data repository.

1268 **Table 7.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of dolomite in the Bou Arfa deposit. See Fig. 1B for the  
1269 location of the studied samples.

1270 **Table 8.** Key identification criteria of the dolomite generations under cathodoluminescence  
1271 (CL) and light microscopy (LM).

1272 **Table 9.** Cell dimensions of four goethite in Hamaraouet (Fig. 2) following the three main cell  
1273 orthorhombic axis. The error is calculated according to the deviation of the experimental  
1274 peak from the standard value.



1276 **Supplementary data repository**1277 **DR1.** Analytical conditions standards of the EPMA CAMECA SX-five analyses.1278 **DR2.** Peak features in the XRD patterns of botryoidal hematite (H3\_Hem) and across the  
1279 massive goethite vein (H3\_Gth6-9).

## 1280 Highlights

- 1281 • The Bou Arfa Mn(-Fe) mineralization (High Atlas, Morocco) is formed by post-  
1282 sedimentary processes
- 1283 • Dolomitization is considered as the main driver for Mn and Fe concentration
- 1284 • The stability of the Mn(-Fe)-bearing minerals disabled strong post-ore weathering
- 1285 • The proposed metallogenic model is similar to the genesis of Atlasic MVT deposits

1286