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1 **Mineralogical and chemical characterization of supergene copper-bearing minerals: examples**
2 **from Chile and Burkina Faso**

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12 **Abstract**

13 Using optical microscopy, SEM, EPMA and LA-ICP-MS, we analyzed and characterized the textural
14 features of Cenozoic supergene Cu-bearing minerals from three exotic and two *in situ* supergene copper
15 mineralization from the Atacama Desert in northern Chile. In addition, we analyzed their major and
16 rare earth elements compositions. We then compared these data to those obtained from the *in situ*
17 supergene copper mineralization from the Gaoua Cu-Au porphyry district, emplaced during the
18 Cenozoic in a different geodynamic setting in the West African craton. In both the *in situ* and exotic
19 supergene copper mineralization, chrysocolla is the dominant supergene copper-bearing mineral,
20 followed by pseudomalachite with minor amount of copper wad. Chrysocolla and pseudomalachite
21 show distinct textural features. Chrysocolla appears either as black Mn-rich clasts or light-blue to green
22 masses, filling the fractures and coating the non-mineralized clasts. Pseudomalachite occurs as green
23 color bands or thin coatings filling empty spaces. All the deposits share some common features with
24 regard to their major element and REE compositions, i.e. i) same range of chemical compositions
25 suggesting similar conditions of formation and ii) strong Ce anomaly indicative of oxidant conditions
26 during the crystallization of these supergene copper minerals. Our results reflect similar conditions for
27 the formation of both supergene copper minerals in all the mining districts and lead us to propose that

28 both areas (i.e. the Atacama Desert and southwestern Burkina Faso) underwent similar geological and
29 climatic conditions in order to form and preserve supergene copper mineralization, i.e. exhumation of
30 the porphyry copper deposit and weathering of the primary copper sulfides, downward and laterally
31 moving of copper-bearing solutions to form *in situ* and exotic SCM and finally, arid to hyperarid climate
32 to prevent mechanical abrasion and leaching of the newly formed supergene copper mineralization.
33 **Keywords:** *in situ* and exotic supergene copper mineralization; Atacama Desert; Gaoua Cu-Au district;
34 black chrysocolla; chrysocolla; pseudomalachite

35 1. Introduction

36 Supergene copper mineralization (SCM) is produced by the interaction between sulfides and
37 supergene processes and was originally defined by Ransome (1912) as *sulfide oxidation and leaching*
38 *of ore deposits in the weathering environment, and any attendant secondary sulfide enrichment*. In order
39 to form supergene copper mineralization, specific tectonics, climate and geomorphologic conditions are
40 required. Tectonics controls the uplift needed to lower the groundwater table and raise the deep-seated
41 ore deposits towards more oxidizing environments where the oxidation and leaching of sulfides may
42 occur. On the other hand, climate controls water availability, and therefore the leaching of sulfides and
43 remobilization of copper-bearing solutions in the supergene environment towards the locus where
44 supergene copper-bearing minerals precipitate. Then, favorable geomorphologic conditions prevent
45 major erosion and removal of the supergene mineralized bodies (Hartley and Rice, 2005; Sillitoe, 2005).
46 Two types of SCM have been recognized: 1) *in situ* deposits, which are produced by nearly vertical
47 descending Cu-bearing aqueous solutions and precipitation of SCM within or near the leached cap
48 (Sillitoe, 2005); and 2) exotic deposits, which are originated by lateral migration of Cu-bearing solutions
49 from the parental deposit, without direct link with the original source of metal (Fig. 1, Münchmeyer,
50 1996; Sillitoe, 2005). In order to better understand the genesis of *in situ* and exotic SCM deposits and
51 the parameters controlling their formation, mineralogical and geochemical characterization are
52 required. To the best of our knowledge, apart from the work of Chavez (2000) who described in detail
53 the zoning and distribution of copper oxide minerals in SCM in general, all the previous studies have
54 been focused on the description of single SCM deposits and the characterization of the secondary K-
55 bearing minerals that are genetically linked to the precipitation of copper-bearing minerals (Alpers and
56 Brimhall, 1988; Bouzari and Clark, 2002; Cuadra and Rojas, 2001; Kahou et al., 2020; Marsh et al.,
57 1997; Mote et al., 2001a). Furthermore, most of these studies have been carried out in the Atacama
58 Desert and southwest USA. However, SCM can be observed all around the world (Fig. 2A) and were
59 therefore formed under various climatic and tectonic conditions (e.g. Atacama Desert, SW of U.S.A,
60 northern Mexico, Mongolia, Papua New Guinea, Philippines, western and central Africa, etc...). Here

61 we present a comparison of SCM deposits in two contrasting geological and climatic settings, the
62 Atacama Desert and the southwestern region of Burkina Faso.

63 For decades, the Atacama Desert represents an ideal location to study SCM because of the
64 presence of world-class examples of both *in situ* (Chuquicamata, Salvador, Cerro Colorado, Zaldivar-
65 Escondida Norte, etc.) and exotic (Mina Sur, Damiana, Tesoro, etc.) SCM formed within an active
66 continental margin under hyperarid climate resulting from the interaction between the uplift of the
67 Andean mountain and the intensification of the Humboldt Current (Garreaud et al., 2010). In this area,
68 we focused our study on Zaldivar and Gaby *in situ* SCM and Mina Sur, Damiana and El Cobre exotic
69 SCM, all formed during the Eocene to Miocene epochs. As a contrasted example, we also studied the
70 *in situ* SCM of Gaoua, in Burkina Faso, emplaced during the Cenozoic, and located in a passive tectonic
71 margin under a much wetter climate (i.e. sub-humid to Sahelian climate).

72 In more details, we carried out an intensive mineralogical and mineral chemistry studies of the
73 oxidized copper ores using optical microscopy and SEM to describe the textural features together with
74 EPMA and LA-ICPMS analyses for a chemical characterization. All the acquired data were then
75 combined in order in order to better constrain the main factors controlling the genesis of SCM. The
76 mineralogical characterizations show that Atacama Desert and SW Burkina Faso underwent similar
77 processes during the SCM formation and preservation despite geodynamic differences. Our new
78 chemical study confirms and implements previous ones (Chávez, 2000; Fernández-Mort et al., 2018;
79 Sillitoe, 2005) by pointing out that exotic SCM deposits were formed under uninterrupted oxidizing
80 conditions while *in situ* SCM deposits show changes in the redox conditions during their formation.

81 **2. Geological Background**

82 The Atacama Desert is worldwide known to host some of the world's largest porphyry copper
83 deposits, e.g. Escondida, Chuquicamata and Collahuasi. Most of these deposits are located in the
84 Precordillera, a near N-S trending pre-Andean mountain range that extends over 800 kilometers and
85 corresponds to a former magmatic arc formed during the Incaic orogeny (Fig. 2B; Mpodozis and Ramos,
86 1989; Amilibia et al., 2008; Mpodozis and Cornejo, 2012). This mountain range contains most of
87 Chile's porphyry copper deposit and is made up of Late Paleozoic to Eocene blocks, delimited by

88 inverted normal and strike-slip faults (Scheuber and Reutter, 1992). In the Atacama Desert, the
89 emplacement of hydrothermal alteration and hypogene mineralization was synchronous with the
90 formation of the Precordillera (Sillitoe and Perelló, 2005) while supergene alteration occurred at least
91 ~ 11 m.y. after the last hydrothermal event (Sillitoe and McKee, 1996).

92 The Mina Sur exotic copper deposit (Fig. 2B) is located within the Chuquicamata mining district,
93 the second biggest Cu producer in the world. Geological, petrological and tectonic features of the
94 Chuquicamata porphyry copper as well as the Mina Sur exotic copper deposits have been discussed in
95 detail by previous authors (Dilles et al., 2011; Mortimer et al., 1977; Mpodozis and Cornejo, 2012;
96 Newberg, 1967; Ossandón et al., 2001; Rivera et al., 2012; Sillitoe and Perelló, 2005) and are only
97 briefly summarized here. In response to the uplift of the Precordillera, several forearc basins were
98 formed during the Late Tertiary (Scheuber et al., 1994) including the Calama basin, which hosts the
99 Mina Sur exotic copper deposit. The basement of this basin is represented by a metamorphic Paleozoic
100 complex, extensively faulted and brecciated and by a Permian to Carboniferous Igneous complex
101 (Ossandón et al., 2001; Rivera et al., 2012). The Calama formation and the El Loa group (Tomlinson et
102 al., 2001), both made of continental sedimentary to volcano-sedimentary erosional gravels (May et al.,
103 2010, 1999) lie above this basement. An ignimbrite flow deposited on top of the gravels was dated at
104 8.4 ± 0.4 Ma by K/Ar on biotite (Mortimer et al., 1977), which gives a minimum depositional age for
105 these gravels. The exotic copper mineralization, which comprises copper silicates, copper phosphates,
106 copper carbonates and copper halides is observed either filling fractures on the bedrock or the empty
107 spaces available between the gravels.

108 The Damiana exotic copper deposit originates from the lateral migration of copper solutions from
109 the Salvador porphyry copper deposit, within the El Salvador Mining District (Fig. 2B). This mining
110 district has been well studied by Gustafson and Hunt (1975), Cornejo et al. (1997), Gustafson et al.
111 (2001) and Mote et al. (2001b). The district is located near the Sierra Castillo fault, which represents
112 the southern segment of the Domeyko fault system. The Domeyko fault system is a near N-S trending
113 major zone of deformation in the Precordillera, related to the emplacement of some of the most
114 important porphyry copper deposits in the Atacama Desert (Mpodozis and Cornejo, 2012). The bedrock
115 of the mining district is made of a Paleocene rhyolitic dome complex, named the Cerro Indio Muerto,

116 which has been intruded by hypogene mineralized porphyries (Cornejo et al., 1997). The exotic copper
117 mineralization in the Damiana deposit is filling fractures that are present in the Early Cretaceous
118 volcanoclastic rocks *a.k.a.* the Llanta formation (Bissig and Riquelme, 2010; Rojas and Muller, 1994).
119 This mineralization is also within the gravels (i.e. Atacama Pediplain), filling paleochannels around the
120 Cerro Indio Muerto. Finally, ignimbrite flow and tuff, dated at 11.6 ± 0.5 Ma and 12.5 ± 0.5 Ma
121 respectively (Sillitoe et al., 1968), cover the Atacama pediplain and yield a minimum age for the
122 deposition of the pediment.

123 The El Cobre exotic deposit is linked to the Potrerillos porphyry copper deposit located
124 approximately 30 Km to the southeast of El Salvador deposit, in the Potrerillos mining district (Fig. 2B;
125 Bissig and Riquelme, 2009). Previous studies discussed the geology as well as the structural features of
126 the Potrerillos porphyry copper deposit (Bissig and Riquelme, 2009; Marsh et al., 1997), indicating that
127 this deposit is linked to the Sierra Castillo fault and is hosted by Jurassic to Cretaceous marine and
128 volcano-sedimentary rocks. Hypogene mineralization of the Potrerillos porphyry copper deposit were
129 emplaced during the late Eocene (~ 36 -35 Ma; Marsh et al., 1997). At El Cobre exotic deposit, copper
130 mineralization was deposited within the fractured and brecciated Paleocene andesitic and rhyolitic
131 volcanic rocks (Bissig and Riquelme, 2009), which provide therefore a maximum age for their
132 deposition.

133 The Zaldivar and Gaby *in situ* SCM are also located within the Precordillera of northern Chile
134 (Fig. 2B). Zaldivar is part of the Escondida cluster, which represents the biggest copper district in the
135 world whilst Gaby is located ~ 100 Km south of Chuquicamata and ~ 43 Km east of Spence porphyry
136 copper deposit. The formation of both deposits is linked to the compressional and transtensional
137 movements of the Domeyko fault system, related to the Incaic orogenic event (Mpodozis and Cornejo,
138 2012). Country rocks at Zaldivar is made of the La Tabla formation (Urzua, 2009), a set of Early
139 Permian rhyolite to dacite ignimbrite and volcanic rocks. The latter are intruded by granodiorite to
140 dacite porphyries, related to the Incaic magmatism (between 41 Ma and 30 Ma; Maksaevev and Zentilli,
141 1999). At Gaby, basement rocks are represented by the Carboniferous Quebrada Escondida
142 metavolcanic-sedimentary rocks and the Permian Pampa Elvira granodiorite complex. This basement
143 is intruded by two Eocene porphyries, the dike-like Gaby and Crowded porphyries. In both deposits, a

144 well-developed supergene alteration profile is observed with a 120-500 m-thick supergene copper
145 orebody at Zaldivar and a 250 m-thick copper oxide orebody at Gaby (Aguilar et al., 2003; Perelló et
146 al., 2018). Both deposits lie beneath thick gravels pediment and comprises copper silicates as
147 predominant Cu-bearing minerals, together with copper sulfates, copper phosphates and black-copper
148 oxides.

149 The Gaoua porphyry Cu-Au district in southeastern Burkina Faso (Fig. 2C), is located within the
150 West African craton (WAC) which consists of an Archean core, juxtaposed to Paleoproterozoic
151 greenstone belts also known as the Boromo-Goren greenstone belt (Baratoux et al., 2011). The
152 deposition of the Paleoproterozoic greenstone belt of the WAC took place during the Eburnean orogeny,
153 around 2.25 to 2.15 Ga ago (Baratoux et al., 2011). These Boromo-Goren greenstone belt consists of
154 volcanic to plutonic rocks affected by a greenschist facies regional metamorphism. These volcano-
155 plutonic rocks were intruded by granitoids, emplaced from ca. 2250 Ma to 2060 Ma, and deformed
156 successively by three deformation stages (Béziat et al., 2008; Baratoux et al., 2011; Baratoux et al.,
157 2015). At a local scale, the Gaoua district is located at the southwestern margin of the Boromo Belt
158 (Fig. 2C). The basement of the Gaoua porphyry copper deposit comprises a thick-sequence of mafic
159 rocks (i.e. gabbro, basalt, andesite), followed by calc-alkaline intrusive bodies (diorite, granodiorite,
160 dolerite, granite, rhyolite). All the series underwent a regional greenschist-facies metamorphism
161 (Baratoux et al., 2015). Hypogene copper mineralization is hosted by the greenschist facies volcanic
162 flows and quartz-diorite intrusions (Le Mignot et al., 2017). This mineralization appears as veins,
163 hydrothermal breccia filling or is disseminated within quartz-diorite porphyry stocks at Mont Biri,
164 Diénémara, Gongondy and Bousséra (Fig. 2D; Le Mignot et al., 2017). The supergene copper ore of
165 the Gaoua district is linked to the Tertiary history of the West African craton. During the Cenozoic, the
166 onset of a hot and wet tropical climate, in alternation with dry seasons, in this tectonically stable craton
167 and in addition to the low denudation rates in the region ($2\text{-}20\text{ m Ma}^{-1}$; Beauvais and Chardon, 2013)
168 allowed for the formation of large and flat erosion surfaces a.k.a pediplains or regolith. These
169 pediplains, which result from chemical and mechanical alteration of the bedrock (i.e. Birimian
170 greenstone belts, Gunnell, 2003), sometimes overlie supergene mineralization of various economic
171 importance, i.e. manganese at Tambao, and copper at Gaoua (Chardon et al., 2018). However, to the

172 best of our knowledge no studies have been published about the recognition and/or the characterization
173 of the *in situ* SCM from the Gaoua porphyry Cu-Au district.

174 3. Analytical Procedures

175 Samples from five Cu-deposits in northern Chile and one Cu-Au deposit in Burkina Faso have
176 been collected during a sampling campaigns in 2018 (i.e. Mina Sur, Damiana, El Cobre for exotic SCM)
177 or were provided by mining geologists (i.e. Zaldivar, Gaby and Gaoua for *in situ* SCM). Mineralogical
178 studies were carried out at the Géosciences Environnement Toulouse (GET, Université de Toulouse,
179 France) using a polarizing microscope NIKON JLV 500 on polished thin sections. Backscattered
180 electron images (BSE) as well as qualitative data were obtained using the JEOL JSM 6360 LV Scanning
181 Electron Microscope (SEM) coupled to an energy dispersive spectrometry (EDS) analysis system at the
182 GET laboratory. The analytical conditions used were 15kv for the acceleration voltage, 50 μm for the
183 beam size while a tungsten filament was used as the electron source. Quantitative analyses as well as
184 major element distribution maps were carried out at the Centre de Micro-Characterisation Raimond
185 Castaing (Université de Toulouse, France) using the CAMECA SXFive Electron Probe Micro-Analyzer
186 (EPMA) on polished thin sections. The analytical conditions for the profiles were 2 μm for the beam
187 size, 10 nA for the current intensity and an acceleration voltage of 15 keV. Data are reported in ESM
188 1. For the maps, the analytical settings were 100 nA for the current intensity, an acceleration voltage of
189 15 keV, a dwell time of 900 ms and a varying step size of 4 and 5 μm . Chemical studies, i.e. traces and
190 REE elements analyses, were carried out at the GET laboratory using a Thermo-Fisher Element-XR,
191 High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) coupled to an ESI
192 NWR213UC 213 nm laser ablation system (ns-LA). Tuning of the instrument as well as mass
193 calibration were performed on NIST SRM 610 glass reference material, i.e. $^{238}\text{U}^{+}/^{232}\text{Th}^{+}$ between 0.95
194 and 1.05, oxide production < 0.5 % and a sensitivity > 20000 cps/ppm for ^{238}U . Laser ablation were
195 carried out using a laser fluence of 3 J/cm², a repetition rate of 10 Hz and a 20 μm spot size. Ablated
196 materials were transported in helium (450 mL/min) which was used as carrier gas. Each laser spot was
197 ablated during 40s with 10s of background collection and 40s for the “wash-out”. The isotopes
198 monitored are ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb ,

199 ^{175}Lu . The internal and external calibration procedure suggested by Longerich et al. (1996) was used.
200 The following standards were used: NIST SRM 610 reference glass as primary standard and 91500
201 zircon (as a proxy for the black chrysocolla and chrysocolla, see Wiedenbeck et al. 1995) as well as
202 Durango apatite (as a proxy for pseudomalachite, see McDowell et al., 2005) as secondary, quality
203 control standards (see Kahou et al., 2020). External measurement was carried out at the beginning and
204 the end of each analytical session and each 15 spot analyses. Data reduction was carried out using the
205 Iolite data reduction software (Paton et al., 2011). Operating conditions, traces and REE concentrations
206 obtained on black chrysocolla, chrysocolla and pseudomalachite are reported in ESM 2.

207 **4. Textural and chemical characterization of supergene copper mineralization**

208 4.1 Textural features of SCM

209 To summarize the following description of the ore samples and the mineralogical assemblages,
210 a synthetic paragenetic sequence is presented in Fig. 3.

211 4.1.1 *The Mina Sur exotic SCM*

212 The ore body at Mina Sur is ca. 2.2 km long, 1.2 km wide with a maximum thickness of about
213 110 m (Mortimer et al., 1977) and lies 2 Km south of the world-class Chuquicamata porphyry copper
214 deposit. The copper mineralization is mainly composed of chrysocolla and atacamite that fill fractures
215 in the bedrock as well as the porosity in the overlying sedimentary cover (Mortimer et al., 1977;
216 Münchmeyer, 1996). Macroscopic scale observations of the samples selected for this study (Fig. 4A)
217 show that the copper mineralization is mainly composed of chrysocolla either under the form of black
218 Mn-rich angular millimeter size clasts (*a.k.a* black chrysocolla or copper pitch; see Throop and Buseck,
219 1971), or as millimetric turquoise to pale green Mn-poor bands coating both the black chrysocolla and
220 the sedimentary clasts. Chrysocolla bands are intercalated with green micrometer size thin-bands of
221 pseudomalachite. Atacamite, a copper chloride showing an acicular texture, is also present in small
222 proportion. Under plane polarized light, black chrysocolla appears as black clasts, showing locally a
223 concentric banding texture with black to brownish color variations (Fig. 4B). The chrysocolla bands
224 (Fig. 4B) are made of microcrystalline aggregates with a strong birefringence in plane-polarized light

225 (Campos et al., 2015; Foote and Bradley, 1913; Menzies et al., 2015; Sun, 1963; Thompson, 1980).
226 Pseudomalachite has an emerald-green to dark green color (Fig. 4B) and a low pleochroism in plane-
227 polarized light (Berry, 1950; Shoemaker et al., 1977). Atacamite displays thin black prismatic crystal
228 in cross-polarized light (Fig. 4C) and appears as overgrowths around the chrysocolla and
229 pseudomalachite bands. Backscattered electron imaging (Fig. 4D) shows a more complex textural
230 association between these minerals as chrysocolla and pseudomalachite display intergrowth textures.
231 In some places, crystals of chrysocolla crosscut some pseudomalachite bands. Such textural
232 relationships have been interpreted as resulting from dissolution-precipitation of pseudomalachite by
233 chrysocolla (Crane et al., 2001). Finally, atacamite is present as prismatic crystals that grew on top of
234 other mineral phases or also as filling available voids. Textural observations clearly shown that
235 atacamite formed after chrysocolla and pseudomalachite.

236 4.1.2 *The Damiana exotic SCM*

237 At the scale of the outcrop, mineralization in both gravels (Fig. 5A) and bedrock fractures (Fig.
238 5B) appear as a homogeneous, cryptocrystalline blue-greenish mass. In hand specimens, chrysocolla is
239 the most abundant copper mineral, followed, to a lesser extent, by copper wad, a term mainly used by
240 miners to refer to a mixture of Mn, Fe, Cu oxyhydrates (Fam and Rojas, 1997; Menzies et al., 2015;
241 Mote et al., 2001a; Pincheira et al., 2003).

242 In the ore found in the Damiana bedrock, optical microscopy observations confirm that
243 chrysocolla predominates over copper wad and pseudomalachite. In the fractures, chrysocolla appears
244 as greenish and heterogenous fillings. Sometimes, chrysocolla appears as micrometric concentric bands
245 (Fig. 5C). Copper wad precedes chrysocolla and appears as thin coatings in fractures with a brown to
246 dark brown color and a low pleochroism. Pseudomalachite was the last mineral to crystallize. It shows
247 a thin coating texture under SEM, indistinguishable under the petrographic microscope and occurs as
248 overgrowths on chrysocolla (Fig. 5D). Backscattered electron imaging shows a clear paragenetic
249 sequence characterized by 1) copper wad showing colloform texture deposited as thin coatings within
250 the bedrock fractures 2) massive chrysocolla is found within fractures in the bedrock usually on top of
251 copper wad and 3) pseudomalachite filling the empty spaces left (Fig. 5D).

252 In the Damiana gravels, the SCM is deposited in the available empty spaces within the gravels
253 (Fig. 5E). Chrysocolla is the dominant copper phase with lesser amounts of copper wad,
254 pseudomalachite, microcrystalline quartz and apatite. Under plane polarized light, chrysocolla appears
255 as millimetric greenish layers coating the gravels clasts. The texture is relatively homogeneous, with a
256 low pleochroism and a strong relief (Fig. 5E). Pseudomalachite shows green to dark green color in plane
257 polarized light, strong relief with a millimeter crystal size (Fig. 5E). Finally, quartz appears as euhedral
258 micro-crystals, with low relief and birefringence (Fig. 5E). SEM-EDS analyses have shown a
259 precipitation sequence characterized by chrysocolla precipitation coeval with colloform apatite,
260 followed by the crystallization of pseudomalachite and microcrystalline quartz at a later stage (Fig. 5F).
261 BSE images of chrysocolla displays either homogeneous texture or micrometer-scale banded texture,
262 linked to variable Si/Cu ratios as shown by SEM-EDS analyses.

263 *4.1.3 The El Cobre exotic SCM*

264 At the scale of the outcrop, mineralization appears as massive cryptocrystalline light-blue to dark-
265 blue masses filling the fractures. It may also be present as thin coating on the edge of some fractures
266 (Fig. 6A, B). Chrysocolla is the most abundant Cu-bearing mineral, followed by minor copper wad and
267 traces of pseudomalachite.

268 Under a petrographic microscope, a common paragenetic sequence is easily distinguishable for
269 the filling of the fractures: first, copper wad is deposited as thin coatings covering the edges of the
270 fractures, followed by the precipitation of chrysocolla (Fig. 6C). Finally, pseudomalachite and
271 microcrystalline quartz are the last mineral phases to be deposited. At El Cobre, chrysocolla occurs
272 mostly as cluster of concentric micrometer-scale laminae (Fig. 6C). Under SEM, chrysocolla shows a
273 fairly homogeneous texture (Fig. 6D). Pseudomalachite crystallizes as concentric spherulitic and
274 mammillary texture (as shown by SEM images, Fig. 6D) filling open spaces, impregnating bedrock
275 fractures and overgrowing chrysocolla.

276 *4.1.4 Zaldivar in situ SCM*

277 The SCM at Zaldivar porphyry copper deposit extends over a thickness of about 500 m under the
278 piedmont gravels (Monroy, 2000). At a macroscopic scale, the *in situ* SCM appears as emerald green
279 to dark-green masses surrounding angular to sub-angular black clasts (Fig. 7A). The green to dark-green
280 masses are made of brochantite and pseudomalachite while the black clasts are made of dark
281 chrysocolla. Brochantite is the most abundant mineral phases whereas pseudomalachite and chrysocolla
282 are less abundant. Under plane polarized light, both types of brochantite show a weak pleochroism (Fig.
283 7B). Prismatic-crystal shaped brochantite displays zoning characterized by a silica-rich core surrounded
284 by druse crystal growth (Fig. 7B). Pseudomalachite occurs as light-green to green masses filling spaces
285 similarly to brochantite (Fig. 7B). Chrysocolla is observed, under plane polarized light, as light- to dark-
286 brown masses surrounding the clasts and filling the empty spaces or as coating the breccias (Fig. 7B).
287 Chrysocolla displays a strong relief and shows a massive texture with syneresis cracks (Fig. 7C). SEM
288 images clearly exhibit textural relationship between the copper-bearing minerals. Brochantite displays
289 a markedly druse-crystal shape with micrometer-scale size (Fig. 7C) while pseudomalachite and
290 brochantite show intergrowth textures (Fig. 7C). However, locally, brochantite seems to develop at the
291 expense of a former assemblage of chrysocolla and pseudomalachite (Fig. 7C). Occasionally,
292 pseudomalachite masses display homogeneous texture, without impurities. Copper wad forms
293 micrometer-scale thin concentric bands coating pseudomalachite crystals (Fig. 7D).

294 4.1.5 Gaby Sur *in situ* SCM

295 In hand and core-logging samples, copper oxide mineralization appears either as veins (filling
296 fractures) or disseminated within the porphyry (Fig. 8A). Chrysocolla is the most common mineral
297 phases, followed by minor amounts of black copper oxides, brochantite and atacamite. Under the
298 petrographic microscope, chrysocolla appears as light- to dark- green masses filling empty spaces (Fig.
299 8B). Under plane polarized light, chrysocolla shows a strong relief without cleavage. Chrysocolla
300 presents no outward crystal form, although sometimes crystalline in internal structure (Fig. 8B). Copper
301 wad is observed, under plane polarized light, as dark brown to black amorphous masses. Under SEM,
302 chrysocolla displays a relative homogeneous texture with a lot of internal cracks and/or fractures (Fig.
303 8C). Copper wad is filling fractures and empty spaces and exhibits a colloform texture (Fig. 8C).

304 Brochantite clearly shows the direct replacement of sulfides (Fig. 8D) displaying impregnations and
305 disseminations within the sulfides relicts and as coatings at the edges of the altered sulfides. Finally,
306 atacamite coats both chrysocolla and brochantite as highlighted by SEM images (Fig. 8D).

307 4.1.6 Gaoua *in situ* SCM

308 SCM is disseminated inside the porphyries or fills some veins in association with primary
309 sulfides. In hand samples, oxidized copper ore displays homogeneous light- to dark- blue masses filling
310 veins (Fig. 9A). Under the petrographic microscope, these light to dark blue masses can be identified
311 as chrysocolla, which is the most abundant oxidized Cu-bearing minerals (Fig. 9B). Under plane
312 polarized light, chrysocolla appears as green to dark-green heterogeneous masses mainly found within
313 fractures or as coating (Fig. 9B). Pseudomalachite and copper oxides (i.e. cuprite) are present in lesser
314 amounts while no copper wad and atacamite have been found (Fig. 9C). Pseudomalachite is found as
315 inclusions within the chrysocolla internal texture (Fig. 9D) while copper oxides exhibit a square
316 granular shape due to corrosion and occurs as thin coatings as well as impregnating silica clasts as
317 illustrated in Fig. 9D. Chrysocolla seems to replace cuprite and fills the empty spaces between the quartz
318 crystals (Fig. 9D).

319 4.2 Chemical compositions of the main Cu-bearing minerals

320 4.2.1 Mineral chemistry

321 Quantitative major and minor element distributions of the studied SCM are reported in ESM 1.

322 In the exotic deposits (i.e. Mina Sur, Damiana or El Cobre), chrysocolla shows slightly variable
323 proportion of CuO (~ between 50-55 wt. % at Mina Sur, 35-45 wt. % at Damiana and ~ 52 wt. % at El
324 Cobre) and SiO₂ (values between ~ 40-50 wt. % at Mina Sur, 45-50 wt. % at Damiana and ~35-45 wt.
325 % at El Cobre) as well as a variable proportion of H₂O (average between 0-10 wt. %). Al₂O₃, CaO,
326 K₂O, MgO, FeO are also found as trace elements (Fig. 10A). Black chrysocolla (Fig. 10B), which is
327 only found at Mina Sur, is distinguished from chrysocolla by a higher amount of MnO (up to 6 wt.%)
328 and H₂O (10-20 wt.%) and a lower content in SiO₂ (20-40 wt.%) and CuO (~ 45-50 wt.%).
329 Pseudomalachite displays more homogeneous composition with high CuO (~ 68.4 wt. % at Mina Sur,

330 between 63-70 wt. % at Damiana and ~ 67 wt. % at El Cobre) and P_2O_5 contents (average 24.2 wt. %
331 at Mina Sur, 23-27 wt. % at Damiana and 27-28 wt. % at El Cobre) and low H_2O contents (5-10 wt. %)
332 in all exotic deposits (Fig. 10C). Silica, aluminum, iron and calcium are also present as trace elements.

333 The compositional data obtained for the *in situ* SCM (i.e. Zaldivar, Gaby and Gaoua) are listed
334 in ESM 1 and displayed in Fig. 10D for chrysocolla. At Zaldivar, the chemical composition of
335 chrysocolla is consistent with previously published analyses (Newberg, 1967; Pinget, 2016) and display
336 high SiO_2 (~ 43 wt. %) and CuO (~ 51 wt. %) contents with a low water content (~ 4 wt. %). Brochantite
337 contains high proportion of Cu (CuO ~ 78 wt. % and 84 wt. %), and sulfate (SO_3 ~ 11-20 wt. %) while
338 water was below the detection limits. Pseudomalachite shows CuO contents between 21-24 wt. %, P_2O_5
339 between 67-69 wt. % and H_2O contents between 5-8 wt. %. Chrysocolla is composed of CuO (~ 50 wt.
340 %), SiO_2 (average between 39-47 wt. %) and variable water contents (average between 0-15 wt. %).

341 At Gaby, chrysocolla presents high CuO (~ between 45-58 wt. %) and SiO_2 contents (~ between
342 28-42 wt. %) and a varying proportion of H_2O (~ between 3-12 wt. %). Low concentrations of CaO (<
343 1 wt. %) is also found in chrysocolla. Brochantite, which replaces ancient sulfides, reveals high CuO
344 (~ between 76 and 100 wt. %) and SO_3 (~ between 17-40 wt. %) contents. These wide range of values
345 does not agree with the published values for brochantite (Mrose and Reichen, 1965) but rather highlights
346 the ongoing replacement of sulfides relicts by brochantite and other Cu -phosphate minerals. EPMA-
347 analyses carried out on atacamite show homogeneous Cl (~ 12-15 wt. %) and CuO concentrations (74-
348 77 wt. %) and significant quantities of SiO_2 (up to 5 wt. %), emphasizing the presence of chrysocolla
349 or silica impurities within the atacamite.

350 Finally, for the Gaoua deposit, EPMA analyses reveal that chrysocolla presents chemical
351 compositions that are similar to those of the Atacama Desert. The SiO_2 and CuO contents vary from 35
352 wt. % to 48 wt. % (average ~ 41 wt. %) and from 41 wt. % to 51 wt. % (average ~ 46 wt. %) respectively
353 while the Al_2O_3 contents can reach ~ 1.5 wt. %. In Gaoua, intra-layer compositional profiles of
354 chrysocolla show a relatively homogeneous chemical composition with SiO_2 and CuO ranging from 35
355 wt. % to 45 wt. % and 43 wt. % to 51 wt. %, respectively. Low K_2O , CaO and Na_2O contents have also
356 been detected. Pseudomalachite chemical analyses show high CuO (~ 67 wt. %) and P_2O_5 (~ 21 wt. %)

357 contents with minor amounts of SiO₂ (~ up to 2 wt. %). Aluminum, calcium and magnesium are present
358 as trace elements.

359 In order to better characterize the chemical homogeneity of the Cu-bearing minerals (i.e.
360 chrysocolla and pseudomalachite), distribution maps of Si, Cu and P were built for both type of deposits
361 (i.e. exotic and *in situ*). At Mina Sur, silica, copper and phosphorous show a fairly homogeneous
362 distribution in both minerals (Fig. 11A, B, C) although low-Cu and high-Si spots demonstrate the
363 presence of impurities and/or mineral inclusions. At Damiana and El Cobre, elemental distribution maps
364 show that the distribution of Si, Cu and P are rather homogenous in both chrysocolla and
365 pseudomalachite with the exception of the micro-cracks as seen in Fig. 12A-F. Nevertheless, a faint
366 concentric zoning can be observed in pseudomalachite at El Cobre (as shown in Fig. 12B, D, F), which
367 underlines concentric mineral layering and reveals the crosscutting relationship between chrysocolla
368 and pseudomalachite. For chrysocolla and pseudomalachite from Zaldivar, elemental distribution maps
369 are homogeneous for P, Si and Cu and show a faint zoning for Si, Cu and P in the copper wad (Fig.
370 13A, C, E). Finally, for the Gaby deposit, distribution maps for Si and Cu at the boundaries between
371 chrysocolla and copper wad, show growth bands within the copper wad contrasting with the
372 homogenous distributions within the chrysocolla (Fig. 13B, D).

373 4.2.2 Rare earth elements

374 Results are presented in ESM 2 for REE and in Fig. 14. Except for Damiana and El Cobre, all
375 the chrysocolla and pseudomalachite samples have REE concentrations above the detection limits.

376 REE data of chrysocolla from exotic (Fig. 14A) and *in situ* (Fig. 14B) SCM have been plotted in
377 a chondrite-normalized spider diagram (McDonough and Sun, 1995). Most of the chrysocolla from both
378 exotic and *in situ* deposits, show a flat pattern for all the REE with a slightly depleted spectrum for
379 HREE, a strong negative Ce-anomaly and a small negative Eu-anomaly. Chrysocolla from the *in situ*
380 SCM of Zaldivar appears as an outlier, with notably lower REE contents and a strong positive Ce-
381 anomaly. Chrysocolla from Gaby and Gaoua has REE contents that are ten times higher than those from
382 Zaldivar, with a strong negative Ce-anomaly. REE contents of chrysocolla from Mina Sur are ten times
383 lower than any other exotic deposits without a markedly negative Ce-anomaly. Chrysocolla from

384 Damiana displays LREE contents ten times higher than those from Mina Sur and El Cobre. Black
385 chrysocolla from Mina Sur show a strong negative Ce-anomaly, a flat HREE spectrum with HREE
386 contents that are ten times higher than chrysocolla from the same deposit.

387 With the exception of Damiana, the REE patterns for pseudomalachite found in the exotic and *in*
388 *situ* SCM show high LREE and HREE concentrations when compared to REE contents of chrysocolla
389 and black chrysocolla (Fig. 14C, D). The REE spectrum at El Cobre shows concentrations up to ten
390 times higher than those obtained at Damiana and Mina Sur, especially for LREE. For Mina Sur and El
391 Cobre, LREE spectrum show a strong negative Ce-anomaly while LREE data at Damiana show an
392 almost flat spectrum without any noticeable negative Ce-anomaly. In spite of their distinct, negative
393 Ce-anomaly, REE contents from El Cobre are more Ce-rich than those from Damiana and Mina Sur.
394 Compared to the LREE spectrum, the HREE spectrum from Mina Sur and Damiana shows a slight
395 enrichment while at El Cobre, the HREE displays a slight depleted spectrum (Fig. 4C). The notable
396 exception is the pseudomalachite REE pattern from the Zaldivar deposit (Fig. 14D), which shows a
397 HREE depleted spectra compared to LREE and a weak negative Eu-anomaly. We also note that the
398 LREE contents in pseudomalachite from Zaldivar are systematically an order of magnitude higher than
399 pseudomalachite from Mina Sur and Damiana.

400 5. Discussion

401 5.1 Physicochemical controls for the SCM formation

402 In all the studied *in situ* and exotic SCM, chrysocolla is by far the most abundant copper-bearing
403 mineral and predominates over copper wad, atacamite and pseudomalachite.

404 In the *in situ* SCM deposits, the mineral parageneses are almost similar with minor copper wad
405 at Zaldivar and Gaby, which precedes abundant chrysocolla in the three deposits, followed by lesser
406 amount of pseudomalachite at Zaldivar. At Gaoua, cuprite is the main second stage mineral followed
407 by pseudomalachite. This paragenetic sequence suggests that all these deposits have undergone the
408 similar processes of *in situ* supergene oxidation. In detail, at Zaldivar and Gaby, textural and
409 mineralogical features show that copper sulfides were replaced by oxidized sulfate-Cu minerals (Fig.
410 7C and Fig. 8C). The oxidation process is accompanied by a lower pH (Anderson, 1982) and a loss of

411 copper (i.e. by downward or lateral migration) as shown by the lower copper contents in sulfate minerals
412 compared to supergene sulfides. The main thermodynamic constraints for abundant chrysocolla
413 precipitation are pH and H_4SiO_4^0 (aq) activity (Crane et al., 2001; Yates et al., 1998). Chrysocolla
414 precipitates when the pH exceed ~ 5 (Yates et al., 1998). Precipitation of chrysocolla is thus commonly
415 explained by changing conditions from acid ($\text{pH} < 5$) to neutral or low-alkaline ($\text{pH} < 9$) due to the
416 neutralization of the acidic copper solutions during fluid-rock interaction (Newberg, 1967). It also
417 means that most of the minerals that contributes to lowers the pH (i.e. pyrite and chalcopyrite) are
418 leached or do not have the capacity to increase the pH. As suggested by Crane et al. (2001), when
419 H_4SiO_4^0 (aq) is the dominant species in the copper solution, chrysocolla will precipitate at a pH ~ 7 .
420 Inversely, when H_2PO_4^- (aq) is the dominant species in the copper solutions, pseudomalachite will
421 precipitate. This can explain the precipitation of pseudomalachite at Zaldivar and Gaoua. Generally,
422 cuprite crystallizes as replacement of the primary sulfides (Schwartz, 1934) and is rapidly oxidized to
423 hydrate the copper phases. In Fig. 9D, chrysocolla seems to replace cuprite which confirms the
424 assumption of Schwartz (1934).

425 In the exotic SCM (i.e. Mina Sur, Damiana, El Cobre), the same paragenetic sequence is clearly
426 observed: small amount of copper wad, followed by abundant precipitation of chrysocolla and
427 pseudomalachite. At Mina Sur atacamite appears as overgrowths on chrysocolla. At Damiana, apatite
428 growth is coeval to the first phase of chrysocolla. At Damiana and El Cobre, pseudomalachite and
429 microcrystalline quartz are linked to the second crystallization stage event. Except for Mina Sur
430 characterized by the presence of reworked angular clasts of black chrysocolla linked to mechanical
431 transportation or *in situ* breaking, all three deposits show mineral textures resulting from the deposition
432 of copper transported in solution from a source (i.e. porphyry copper deposits) to a sink (i.e. the adjacent
433 basins). This requires a progressive neutralization of the mineralizing fluids originating from the
434 upstream oxidizing ore from porphyry copper deposits (Münchmeyer, 1996; Sillitoe, 2005). According
435 to Newberg (1967) and Fernández-Mort et al. (2018), chrysocolla can precipitate as soon as the pH
436 reaches value between ~ 5 and 9 with an optimum value of ~ 7 . Chrysocolla is formed by the interaction
437 between a copper-rich fluid and SiO_2 (Yates et al., 1998). Copper comes from the porphyry while SiO_2

438 can come from either the porphyry host rocks or from the gravels present in the basins (e.g. altered
439 feldspars). Finally, the good porosity and permeability of the host gravels will favor the precipitation
440 of chrysocolla.

441 The paragenetic relationship between chrysocolla and pseudomalachite records pH variation.
442 Figure 7 from Crane et al. (2001) and Figure 10 from Fernández-Mort et al. (2018) have shown that a
443 slight variation of the pH in copper-rich solutions can lead to the saturation of either chrysocolla or
444 pseudomalachite together with the H_4SiO_4^0 (aq) activity. This could explain the alternation of
445 chrysocolla and pseudomalachite observed at Mina Sur and the presence of second stage
446 pseudomalachite at Damiana and El Cobre. The fact that, in both *in situ* or exotic SCM, pseudomalachite
447 has been found as thin bands or as thin coatings around chrysocolla, implies that the chemistry of
448 copper-rich solutions from the parental porphyry is not constant but has changed according to the pH
449 variation and the H_4SiO_4^0 (aq) and H_2PO_4^- (aq) ions activity.

450 At Damiana and El Cobre, the last mineral to precipitate was the microcrystalline quartz. Bustillo
451 (2010) has shown that microcrystalline quartz is stable at $\text{pH} < 9$ whereas at $\text{pH} > 9$, calcite is broadly
452 stable. At pH between 5 and 9, chrysocolla and pseudomalachite tend to co-precipitate. When the
453 mineralizing fluids is depleted in copper, microcrystalline quartz can precipitate (Dold, 2006). The
454 meaning of microcrystalline quartz precipitation can be discussed in terms of a silicification process
455 (Bustillo, 2010), favored by the silica content, temperature, host-rock permeability and pH. Highly
456 silica oversaturated solutions will lead to poorly-ordered silica phases (e.g. opal and amorphous silica)
457 while slightly saturated solutions conduct to more ordinated forms (i.e. quartz and chalcedony). This
458 transition may reflect a dilution of the silicification process as shown by Thiry et al. (2006) and
459 highlighted by Fernández-Mort et al. (2018) at Tesoro Central exotic copper deposit. Indeed, the
460 transition from chrysocolla to microcrystalline quartz, observed in our samples, could be a proof of a
461 silicification process.

462 The fact that no copper carbonates were observed in both type of deposits could be explained by
463 either the combination of high H_4SiO_4^0 (aq) activity and a pH maximum value of ~ 9 for the copper-
464 rich solutions or by the fact that the fluid was too depleted in copper after chrysocolla and
465 pseudomalachite formation to promote copper carbonates precipitation.

466 Ultimately, when the climate become more arid (or hyperarid), atacamite, a copper salt highly
467 soluble in fresh water, started to crystallize. This is well exemplified by the atacamite needles
468 overgrowing pseudomalachite at Mina Sur (Fig.5D) linked to salt-rich water circulation in the hyperarid
469 conditions of the Atacama Desert (Reich et al., 2008). The fact that atacamite was not found at Gaoua
470 can be explained either by the absence of saline fluids which could have promoted the formation of
471 atacamite or salt minerals (e.g. gypsum, anhydrite), or by their late destabilization in the context of
472 modern semi-arid climatic conditions (the West African Craton never experienced a hyperarid climate;
473 Séranne, 1999).

474 As observed in most of the deposits, chrysocolla and copper wad show concentric banding texture
475 which suggests chemical variations of the mineralizing fluids as already mentioned by Nelson et al.
476 (2007) and Campos et al. (2015). The banding textures observed within chrysocolla have also been
477 explained by Nelson et al. (2007) as the result of biogenic processes, suggesting bacterial involvement
478 in the formation of *in situ* (i.e. at Gaby) and exotic (i.e. at Mina Sur, Damiana and El Cobre) SCM.

479 5.2 REE concentration in supergene copper minerals

480 Beside the presence of oxidized copper rich minerals such as silicates, phosphates and sulfates,
481 the existence of oxidizing conditions in the studied localities is supported by the geochemical
482 characterization of the supergene copper minerals (chrysocolla and pseudomalachite) where REE
483 spectra (Fig. 14) are characterized by Ce-anomalies. As shown by Goldschmidt (1937) and Braun et al.
484 (1990), Ce is the only LREE to present two oxidation states (Ce^{3+} and Ce^{4+}) in a low-T environment.
485 This makes Ce highly sensitive to redox processes. In fact, the oxidation state of Ce is mainly controlled
486 by the pH. At low pH, water could reduce Ce^{4+} to Ce^{3+} whereas if the pH value increases, Ce^{3+} is
487 oxidized to Ce^{4+} (Bouchaud et al., 2012). Bouchaud et al. (2012) have also shown, by experimental
488 studies, that Ce^{3+} and Ce^{4+} are soluble in meteoric water at neutral to alkaline pH values. Additionally,
489 Estrade et al. (2019 and references therein), have shown that the precipitation of Ce, either as Ce^{4+} or
490 Ce^{3+} , within supergene environments, is linked to the depth of the supergene column. In the upper part
491 of the column, within more oxidizing and higher pH, Ce^{4+} precipitates in Ce-rich minerals such as
492 cerianite (CeO_2) or associated with Mn- and Fe- oxyhydroxydes. Consequently, the supergene copper

493 minerals will display negative Ce-anomaly due to the Ce^{4+} consumption by cerianite or Mn-Fe
494 oxyhydroxydes. This is the case for chrysocolla and pseudomalachite presented in this study who
495 recorded negative Ce-anomaly, except for chrysocolla from Zaldivar. Conversely, in the lower part of
496 the supergene column, under low pH and reduced conditions, Ce^{3+} predominates over Ce^{4+} and no Ce-
497 rich minerals such as cerianite or Mn-Fe oxyhydroxydes can precipitate. Therefore, Ce will be available
498 in the environment and captured by Cu-rich supergene minerals that will consequently display positive
499 Ce-anomaly as seen for example for chrysocolla at Zaldivar. Similarly, Decrée et al. (2015) have shown
500 that REE spectrum in heterogenite (a supergene cobalt mineral, $CoOOH$) can display negative Ce-
501 anomaly when this mineral co-precipitates with Mn- and Fe-oxides in the upper part of the oxidation
502 profile and positive Ce-anomaly when heterogenite forms in the deeper part of the oxidation profile.
503 The negative Ce-anomalies in exotic copper deposits will further support continuous oxidizing
504 conditions. By contrast, the REE patterns from *in situ* supergene copper minerals (i.e. chrysocolla and
505 pseudomalachite), which show both positive and negative Ce-anomalies, might reflect changes in the
506 redox conditions during the leaching process, above the porphyry, both in time (reducing to oxidizing
507 conditions) and space, i.e. from oxidizing conditions at the top (with Ce^{4+} predominates) toward
508 reducing conditions at depth (with Ce^{3+} predominates).

509 If we focus on the REE concentration processes for both *in situ* and exotic deposits, the REE
510 distribution within chrysocolla and pseudomalachite are heterogenous. Pseudomalachite from El Cobre
511 and Zaldivar contains ten times more REE than those from the other deposits. Furthermore, REE
512 patterns of chrysocolla are contrasted, as the REE contents in Damiana are ten times higher compared
513 to those from Mina Sur, while the REE contents of Zaldivar are ten times lower than those from Gaby
514 and Gaoua. Indeed, in supergene environments, the REE-bearing minerals control the budget and the
515 distribution of the REE. The weathering of the primary REE-bearing minerals (i.e. zircon, monazite and
516 xenotime) will induce either the redistribution of the REE within the newly formed supergene copper
517 minerals (e.g. chrysocolla and pseudomalachite) or the consumption of the REE by secondary REE-
518 bearing minerals (i.e. allanite, bastnesite, rhabdophane; Braun et al., 2018). For instance, the absence
519 of secondary REE-bearing minerals at El Cobre and Zaldivar could explain the high REE concentrations
520 found in pseudomalachite from both deposits whereas possible precipitation of apatite and rhabdophane

521 (i.e. two secondary phosphate REE-bearing minerals) in the other deposits (i.e. at Mina Sur and
522 Damiana) could explain the low REE contents in pseudomalachite. Similarly, the low REE content in
523 chrysocolla at Mina Sur and Zaldivar (Fig. 14A, B) could be explained by the precipitation of secondary
524 REE-bearing silicates minerals (e.g. allanite, bastnesite) that trapped the REE.

525 5.3 Necessary conditions for the genesis and preservation of oxidized SCM

526 In the Atacama Desert of northern Chile and in southwestern Burkina Faso, tectonics (i.e. Incaic
527 orogeny in Northern Chili and Eburnean orogeny in Burkina Faso) and climatic (i.e. semi-arid to arid
528 climate) settings were combined to favor supergene alteration of porphyries and the formation of thick
529 *in situ* supergene copper orebodies (Sillitoe, 2005; Sillitoe and McKee, 1996) and/or exotic-Cu deposits
530 (Fernández-Mort et al., 2018, 2018; Hartley and Rice, 2005; Münchmeyer, 1996; Riquelme et al., 2017;
531 Sillitoe, 2005). To produce an oxidized supergene copper mineralization, three conditions are necessary.
532 First, tectonic uplift will bring the primary porphyry stock and hypogene sulfides close to the earth
533 surface where oxidizing conditions, controlled by the level of water table, prevail. Second, under
534 favorable climatic conditions, the oxidation of sulfides will produce acidic solutions which will
535 transport copper down and laterally, in the subjacent area, to form an oxidized copper ores when copper
536 solution reach saturation (Fernández-Mort et al., 2018; Reich and Vasconcelos, 2015). Finally, once the
537 supergene column is formed, favorable climatic conditions as well as moderate erosion rate can favor
538 SCM preservation. The fact that, although both areas have experienced different tectonic styles, the
539 supergene copper minerals from northern Chile and SW Burkina Faso are identical and share the same
540 chemical compositions implies that they both underwent similar climatic evolutions, i.e. from semi-arid
541 to arid, during the mineralization processes. However, if Northern Chile has evolved towards a
542 hyperarid climate for the past ~10 m.y., responsible for the formation of atacamite, the SW Burkina
543 Faso area has only experienced a semi-arid climate since the Eocene (Monsels, 2016). According to
544 Hartley and Rice (2005), who published a compilation of supergene copper deposits ages in the
545 Atacama Desert, the formation of *in situ* SCM took place between 36 Ma and 6 Ma. More recently,
546 Riquelme et al., (2017) and Kahou et al., (2020) have published ages between ca. 25-12 Ma and ca. 19
547 Ma for the formation of the Centinela and Mina Sur exotic copper deposits respectively, i.e. ages that

548 are within the range found for the *in situ* SCM. As stated by Sillitoe (2005) and Sanchez et al. (2018),
549 in Chile, the processes necessary for the formation of well-developed oxidized SCM profile can take
550 anything from a million to ten millions of years and ceased at the onset of hyperaridity. In SW Burkina
551 Faso, the age of the SCM deposit is unknown but the phases responsible for the exhumation of the
552 porphyry towards oxidizing conditions were contemporaneous with lateritization/bauxitisation
553 processes, i.e. between 59 Ma and 3 Ma (Beauvais and Chardon, 2013; Gunnell, 2003). These
554 exhumation phases were controlled by evolving weathering conditions and took place at rates lower
555 than 20 m/m.y. (Beauvais and Chardon, 2013). The comparison between Chilean and African SCM
556 suggest that the preservation of the supergene deposits is due to a favorable combination of slow erosion
557 rates and aridity.

558 Another necessary factor for the genesis of oxidized SCM can be related to evaporation process.
559 In the southern part of the Atacama Desert, a stable isotope study by Bissig and Riquelme (2010) has
560 shown that meteoric waters were affected by high evaporation rates to favor the deposition of supergene
561 alunite. In the same manner, Fernández-Mort et al. (2018) also highlighted that evapoconcentration was
562 the main parameter to form the exotic SCM of Tesoro Central. Although no isotope studies have been
563 carried out in this study, this evaporation process can be involved in the formation of both *in situ* and
564 exotic SCM deposits from Chile but also in the *in situ* SCM from Burkina Faso.

565 5.4 Oxidized SCM characterization: key for an exploration success

566 Oxidized SCM are the result of supergene alteration of hypogene sulfides, namely pyrite and
567 chalcopyrite from any sulfide-rich deposit. This supergene alteration produces a vertical zonation
568 consisting on a Fe- and Al-rich leached cap depleted in Cu, followed by an oxidized horizon moderately
569 enriched in copper (up to 1 wt. % of Cu) and at the bottom a secondary sulfide enrichment zone, highly
570 enriched in copper (up to 2 wt. % of Cu) formed below the paleo water table (Chávez, 2000; Sillitoe,
571 2005). As stated by Chavez (2000), the distribution of oxidized copper minerals can be used as
572 exploration keys. For example, as shown by our study, the broad distribution of chrysocolla within *in*
573 *situ* SCM are interpreted as characteristic of a geochemically mature supergene system and the
574 formation of a well-developed *in situ* oxidized SCM. In fact, both types of oxidized SCM represent an

575 important target for numerous exploration and mining companies as their exploitation is
576 environmentally friendly compare to process required for the recovery of copper from sulfide ore. As a
577 result, mineralogical characterization of SCM can provides some useful keys to better improve the
578 metallurgical treatment.

579 To date, mapping exploration program combined with geophysical and geochemical studies,
580 successfully located oxidized and enriched porphyry copper deposits buried beneath piedmonts gravels.
581 Moreover, geomorphological and sedimentological studies are powerful tools to discover new *in situ*
582 and exotic SCM. As proposed by Riquelme et al. (2017), the exploration of these deposits, buried under
583 gravels and ignimbrite, needs to take into consideration both the landscape evolution and the
584 depositional history of the piedmont gravels. The study of the landscape and the piedmont evolution
585 has also been presented as a major guide for the exploration of supergene ore by Chardon et al. (2018)
586 in Burkina Faso. When the conditions are favorable, supergene alteration of porphyry copper deposit
587 also leads to the deposition of exotic SCM, hosted within piedmont gravels or underlying bedrock
588 fractures. The presence of exotic copper deposits is indicative of the existence of primary copper
589 porphyry deposits somewhere upstream and can be used as exploration tool. Although in some cases,
590 the source of these deposits are known (e.g. Chuquicamata porphyry for Mina Sur and Salvador
591 porphyry for Damiana, see Munchmeyer, 1996), the sources of some exotic-Cu deposits remain
592 unknown (e.g. Tesoro and Lagarto exotic-Cu deposits; Munchmeyer, 1996; Sillitoe, 2005). Therefore,
593 the mineralogical and geochemical characterization of the supergene copper minerals should be
594 implemented during exploration strategies. For instance, the predominance of chrysocolla over copper
595 wad in an exotic-Cu deposit is indicative of a lateral migration of copper-rich solutions within a radius
596 of 2 to 6 km around the primary porphyry copper deposit. When combined with mass-balance
597 calculation model and geomorphology, mineralogical studies can assess the geochemical maturity of
598 the oxidized ore of the porphyry copper deposit and the directions followed by the copper solutions
599 from the primary copper deposits to the sink (Alpers and Brimhall, 1989; Mote et al., 2001b).
600 Consequently, an integrated study involving geomorphology, sedimentology and geochronological
601 together with a mineralogical and geochemical characterization of the oxidized SCM must be taken into
602 account for enhanced exploration success.

603 **6. Conclusions**

604 Supergene copper mineralization from three exotic and two *in situ* Cu-deposits from the Atacama
605 Desert in Northern Chile and the Gaoua *in situ* Cu-Au district in Burkina Faso have been studied in
606 details. Mineralogical and chemical characterization of these SCM provide new insights on the genesis
607 of these deposits. Chrysocolla, which precipitates after copper wad, is the main Cu-bearing minerals
608 and shows similar textures and chemical compositions in both *in situ* and exotic SCM. Precipitation of
609 chrysocolla reflects the progressive evolution of the mineralizing fluids from acidic ($\text{pH} < 5$) to neutral
610 or low-alkaline ($\text{pH} < 9$) conditions during fluid-rock interaction. Chrysocolla is then followed by the
611 crystallization of pseudomalachite in exotic deposits due to changes of both pH and H_2PO_4 activity of
612 the Cu-bearings fluids (i.e.). Geochemical analyses emphasize the strong oxidizing conditions required
613 for the formation of oxidized SCM and show that REE distribution and Ce-anomaly are linked to the
614 pH evolution, the depth of the supergene column and the presence of primary and secondary REE-
615 bearing minerals. The fact that almost the same mineralogy and geochemical patterns are observed on
616 six different deposits, on different location and geodynamic context, point out the fact that the processes
617 involve in the formation of these deposits are very similar, i.e. progressive neutralization of the acidic
618 copper solutions that lead to chrysocolla precipitation at neutral pH, high H_2PO_4^- (aq) activity together
619 with low H_4SiO_4^0 (aq) activity that permit pseudomalachite formation, and silicification process that
620 lead to the late crystallization of microcrystalline quartz.

621 The role of regional and local controls on the formation and preservation of supergene
622 mineralization is now well-understood and requires a subtle balance between tectonics, climate and
623 geomorphology. The formation of such deposits requires several steps with first the exhumation and
624 weathering of the primary porphyry deposit to ensure surface oxidizing processes and a preservation
625 favored by an environment characterized by moderate erosion and rain fall to prevent mechanical
626 abrasion and leaching of the newly formed deposits and finally, a possible key role played by
627 evaporation processes. This equilibrium has been achieved in both Northern Chile and SW Burkina
628 Faso where similar mineralization processes have been involved to form SCM.

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Captions

Fig. 1 Schematic representation of the relationships between hypogene porphyry copper mineralization and supergene copper mineralization (SCM) forming *in situ* and exotic copper deposits (modified after Sillitoe, 2005)

Fig. 2 Location and geological map of the studied areas. a) location of major SCM in the world map, including Atacama Desert of northern Chile and Gaoua Cu-Au district (after Sillitoe, 2010). b) Structural map of the Precordillera of northern Chile (after Mpodozis and Cornejo, 2012) showing the location of the *in situ* and exotic SCM deposit studied. Black squares mark the location of the Chuquicamata, Salvador and Potrerillos mining districts in which the Mina Sur, Damiana and El Cobre exotic SCM deposits are located, respectively c) Location (black square) of the Gaoua Cu-Au district within the simplified geological map of Burkina Faso (BGB: Boromo Greenstone Belt; HGB: Houndé Greenstone Belt after Béziat et al., 2008). d) Detailed geological map of the Gaoua Cu-Au district showing the location of the Mont Biri, Diénémara, Gongondy and Bousséra *in situ* supergene Cu-Au occurrences (Baratoux et al., 2015; Le Mignot et al., 2017)

Fig. 3 Synthetic paragenetic sequence for the studied exotic and *in situ* SCM deposits. Stage 1 corresponds to the main supergene oxidation while Stage 2 corresponds to the late filling empty spaces

Fig. 4 Sample and thin sections photographs showing the relationships between Mina Sur copper minerals. a) Black chrysocolla (B-Ccl) is coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. b) Plane-polarized light photograph showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) and pseudomalachite (Psm) bands. c) Cross-polarized light and d) SEM photomicrographs showing black chrysocolla clast (B-Ccl) coated by chrysocolla (Ccl) laminae and pseudomalachite (Psm) bands and an overgrowth of atacamite needles (Ata) on chrysocolla and pseudomalachite

Fig. 5 Sample and thin sections photographs showing the relationships between Damiana copper minerals. Chrysocolla (Ccl) filling empty spaces and porosity of the gravels at a) Damiana gravels and fractures at b) Damiana bedrock. c) Cross-polarized light photograph showing chrysocolla (Ccl) and copper wad (Cwad) filling fractures at Damiana bedrock. d) SEM photomicrographs showing copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl), and pseudomalachite (Psm) coating chrysocolla. e) Plane-polarized light photograph of chrysocolla (Ccl) filling porosity of the gravels at

Damiana gravels and pseudomalachite and microcrystalline quartz filling empty spaces. f) SEM photomicrographs showing chrysocolla (Ccl) coeval with apatite (Apa) filling porosity of the gravels and pseudomalachite (Psm) crystallizing in empty spaces

Fig. 6 Sample and thin sections photographs showing the relationships between El Cobre copper minerals. a, b) Chrysocolla (Ccl) filling fractures of the altered andesite bedrock. c) Plane-polarized light photograph showing copper wad (Cwad), chrysocolla (Ccl) and pseudomalachite filling fractures of the andesite bedrock. d) SEM photomicrograph showing chrysocolla (Ccl) coating on copper wad (Cwad) banding mammillary texture and chrysocolla (Ccl) and pseudomalachite (Psm) and amorphous quartz filling empty spaces

Fig. 7 Sample and thin sections photographs showing the relationships between Zaldivar copper minerals. a) Hand-samples of Zaldivar supergene copper minerals. b) Plane-polarized light photograph showing relicts of altered sulfides replaced by brochantite and brown chrysocolla and pseudomalachite gradually replacing brochantite. c, d) SEM photomicrographs showing a complex textural relationship between brochantite, copper wad (Cwad) thin band, chrysocolla and pseudomalachite

Fig. 8 Sample and thin sections photographs showing the relationships between Gaby copper minerals. a) Hand-samples of Gaby showing chrysocolla (Ccl) filling fractures in the Gaby micro-diorite host-rock. b) Plane-polarized light photograph showing copper wad (Cwad) and chrysocolla filling fractures of the host-rock. c, d) SEM photomicrographs showing c) copper wad thin band and fractured and homogeneous texture of chrysocolla, crystallizing within host-rock veins and d) an altered sulfide replaced by brochantite and chrysocolla, and atacamite (Ata) overgrowing on brochantite

Fig. 9 Sample and thin sections photographs showing the relationships between Gaoua copper minerals. a) Hand-samples of Gaoua showing chrysocolla (Ccl) filling fractures in the Gaoua quartz-andesite host-rock. b) Plane-polarized light photograph showing chrysocolla (Ccl) filling fractures of the host-rock. c) Plane-polarized light and d) SEM photographs showing thin green crystals of cuprite (Cup) and pseudomalachite (Psm) coating on quartz crystals and chrysocolla filling empty spaces and corrodes cuprite

Fig. 10 Representative diagrams of oxidized supergene copper mineralization chemical analyses showing in Triplot diagrams. a) chrysocolla chemical analyses from Mina Sur, Damiana and El Cobre

exotic SCM deposits. b) black chrysocolla chemical analyses from Mina Sur exotic SCM deposit. c) Pseudomalachite chemical analyses from Mina Sur, Damiana and El Cobre exotic SCM deposits. d) Chrysocolla chemical analyses from Zaldivar, Gaby and Gaoua *in situ* SCM deposits

Fig. 11 EPMA chemical characterization of supergene copper minerals from Mina Sur exotic SCM deposit. a) Si map b) Cu map and c) P map at the transition between black chrysocolla (B-Ccl), chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the homogeneity/heterogeneity distribution of silicon, copper and phosphorus. Dotted square represents the area analyzed

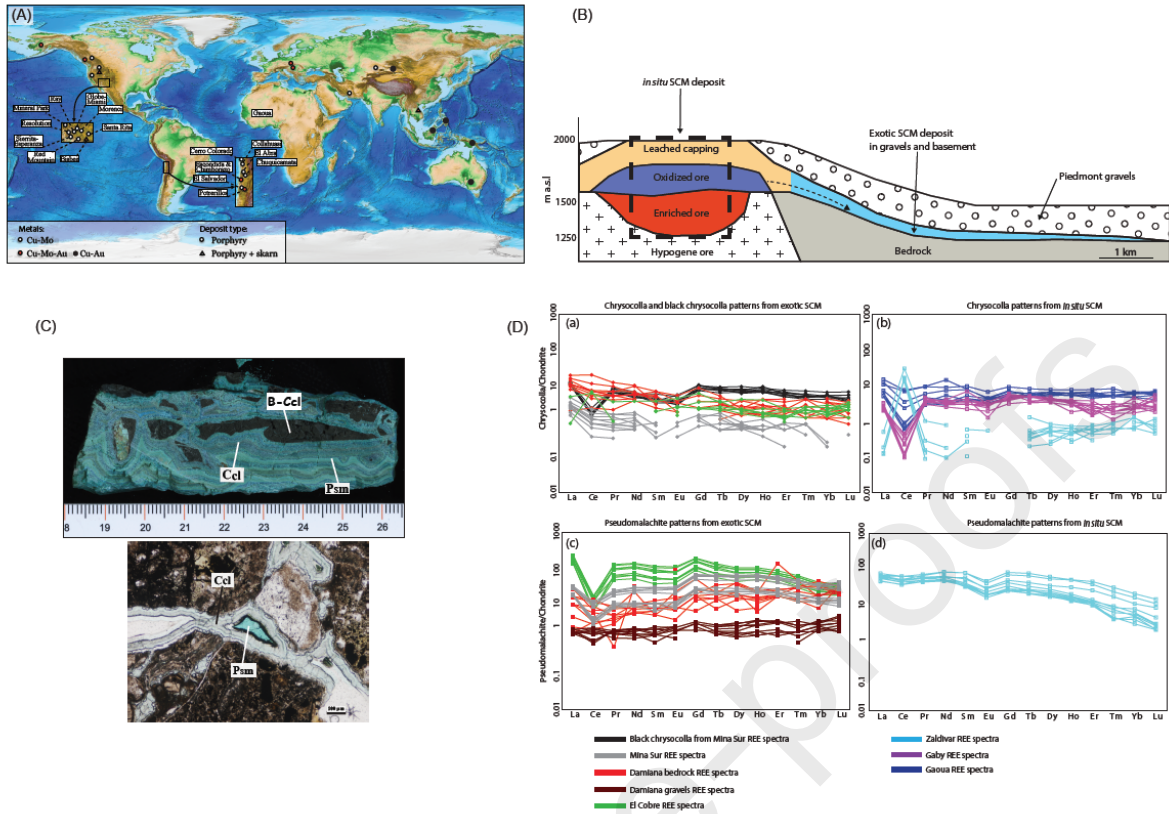
Fig. 12 EPMA chemical characterization of supergene copper minerals from a, c, e) Damiana and b, d, f) El Cobre exotic SCM deposits. a, b) Si map c, d) Cu map and e, f) P map at the transition between chrysocolla (Ccl) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analyzed

Fig. 13 EPMA chemical characterization of supergene copper minerals from Zaldivar and Gaby *in situ* SCM deposit. a, b) Si c, d) Cu and e) P maps at the transition between chrysocolla (Ccl), copper wad (Cwad) and pseudomalachite (Psm) to highlight the distribution of silicon, copper and phosphorus within these minerals. Dotted square represents the area analyzed

Fig. 14 Chondrite normalized REE patterns for oxidized supergene copper minerals. a, b) REE patterns of chrysocolla and black chrysocolla from exotic and *in situ* SCM deposits. c, d) REE patterns of pseudomalachite from exotic and *in situ* SCM deposits. Chondrite normalizing values are taken from McDonough and Sun (1995)

ESM 1 Summary of supergene copper minerals EPMA analyses from exotic and *in situ* SCM deposits

ESM 2 Summary of LA-ICP-MS analyses carried out on supergene copper minerals from exotic and *in situ* SCM deposits. Operating conditions and data obtained on standards are also listed



Highlights

- Supergene copper mineralization (SCM) from Atacama Desert and SW of Burkina Faso
- Paragenesis and chemical characterization of SCM from different geodynamic context
- The same mineralogy and geochemical patterns are observed in both areas
- REE study suggests oxidizing conditions to form supergene copper mineralization
- Geological and climatic controls involve in the genesis of these SCM are similar