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1 Mineralogical and chemical characterization of supergene copper-bearing minerals: examples 2 from Chile and Burkina Faso 3 Zia Steven Kahou^{1*}, Stéphanie Duchêne¹, Stéphanie Brichau¹, Eduardo Campos², Guillaume Estrade¹, Marc Poujol³, Janogithan Kathirgamar¹, Hugo Testa¹, Mathieu Leisen¹, Sandrine Chov¹, Philippe de 5 Parseval¹, Rodrigo Riquelme³, Sébastien Carretier¹ 6 1. Géosciences Environnement Toulouse (GET), Université de Toulouse, UPS, CNRS, 7 IRD, CNES, 14 avenue E. Belin, 31400, Toulouse, France 2. Departamento de Ciencias Geológicas, Universidad Católica del Norte, Avenida 8 9 Angamos 0610, Antofagasta, Chile 3. Univ Rennes, CNRS, Géosciences Rennes – UMR 6118, F-35000 Rennes, France 10 *Corresponding author: steven.kahou@get.omp.eu - (+33) 0782808145 11 Abstract 12 Using optical microscopy, SEM, EPMA and LA-ICP-MS, we analyzed and characterized the textural 13 features of Cenozoic supergene Cu-bearing minerals from three exotic and two in situ supergene copper 14 mineralization from the Atacama Desert in northern Chile. In addition, we analyzed their major and 15 16 rare earth elements compositions. We then compared these data to those obtained from the *in situ* supergene copper mineralization from the Gaoua Cu-Au porphyry district, emplaced during the 17 Cenozoic in a different geodynamic setting in the West African craton. In both the *in situ* and exotic 18 supergene copper mineralization, chrysocolla is the dominant supergene copper-bearing mineral, 19 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 during the crystallization of these supergene copper minerals. Our results reflect similar conditions for 26 the formation of both supergene copper minerals in all the mining districts and lead us to propose that 27

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Journal Pre-proofs

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

34 black chrysocolla; chrysocolla; pseudomalachite

35 **1. Introduction**

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

61 we present a comparison of SCM deposits in two contrasting geological and climatic settings, the62 Atacama Desert and the southwestern region of Burkina Faso.

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

72 In more details, we carried out an intensive mineralogical and mineral chemistry studies of the oxidized copper ores using optical microscopy and SEM to describe the textural features together with 73 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 processes during the SCM formation and preservation despite geodynamic differences. Our new 77 chemical study confirms and implements previous ones (Chávez, 2000; Fernández-Mort et al., 2018; 78 79 Sillitoe, 2005) by pointing out that exotic SCM deposits were formed under uninterrupted oxidizing conditions while in situ SCM deposits show changes in the redox conditions during their formation. 80

81

2. Geological Background

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

inverted normal and strike-slip faults (Scheuber and Reutter, 1992). In the Atacama Desert, the emplacement of hydrothermal alteration and hypogene mineralization was synchronous with the formation of the Precordillera (Sillitoe and Perelló, 2005) while supergene alteration occurred at least ~ 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, the second biggest Cu producer in the world. Geological, petrological and tectonic features of the 93 Chuquicamata porphyry copper as well as the Mina Sur exotic copper deposits have been discussed in 94 detail by previous authors (Dilles et al., 2011; Mortimer et al., 1977; Mpodozis and Cornejo, 2012; 95 Newberg, 1967; Ossandón et al., 2001; Rivera et al., 2012; Sillitoe and Perelló, 2005) and are only 96 briefly summarized here. In response to the uplift of the Precordillera, several forearc basins were 97 formed during the Late Tertiary (Scheuber et al., 1994) including the Calama basin, which hosts the 98 99 Mina Sur exotic copper deposit. The basement of this basin is represented by a metamorphic Paleozoic complex, extensively faulted and brecciated and by a Permian to Carboniferous Igneous complex 100 (Ossandón et al., 2001; Rivera et al., 2012). The Calama formation and the El Loa group (Tomlinson et 101 102 al., 2001), both made of continental sedimentary to volcano-sedimentary erosional gravels (May et al., 2010, 1999) lie above this basement. An ignimbrite flow deposited on top of the gravels was dated at 103 8.4 ± 0.4 Ma by K/Ar on biotite (Mortimer et al., 1977), which gives a minimum depositional age for 104 these gravels. The exotic copper mineralization, which comprises copper silicates, copper phosphates, 105 copper carbonates and copper halides is observed either filling fractures on the bedrock or the empty 106 spaces available between the gravels. 107

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

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

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

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

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

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

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

3. Analytical Procedures

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

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

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 deposit. The copper mineralization is mainly composed of chrysocolla and atacamite that fill fractures 214 in the bedrock as well as the porosity in the overlying sedimentary cover (Mortimer et al., 1977; 215 216 Münchmeyer, 1996). Macroscopic scale observations of the samples selected for this study (Fig. 4A) show that the copper mineralization is mainly composed of chrysocolla either under the form of black 217 Mn-rich angular millimeter size clasts (a.k.a black chrysocolla or copper pitch; see Throop and Buseck, 218 1971), or as millimetric turquoise to pale green Mn-poor bands coating both the black chrysocolla and 219 the sedimentary clasts. Chrysocolla bands are intercalated with green micrometer size thin-bands of 220 221 pseudomalachite. Atacamite, a copper chloride showing an acicular texture, is also present in small proportion. Under plane polarized light, black chrysocolla appears as black clasts, showing locally a 222 223 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). Pseudomalachite has an emerald-green to dark green color (Fig. 4B) and a low pleochroism in plane-226 polarized light (Berry, 1950; Shoemaker et al., 1977). Atacamite displays thin black prismatic crystal 227 in cross-polarized light (Fig. 4C) and appears as overgrowths around the chrysocolla and 228 229 pseudomalachite bands. Backscattered electron imaging (Fig. 4D) shows a more complex textural association between these minerals as chrysocolla and pseudomalachite display intergrowth textures. 230 In some places, crystals of chrysocolla crosscut some pseudomalachite bands. Such textural 231 relationships have been interpreted as resulting from dissolution-precipitation of pseudomalachite by 232 chrysocolla (Crane et al., 2001). Finally, atacamite is present as prismatic crystals that grew on top of 233 other mineral phases or also as filling available voids. Textural observations clearly shown that 234 235 atacamite formed after chrysocolla and pseudomalachite.

236 4.1.2 The Damiana exotic SCM

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

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

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

263 4.1.3 The El Cobre exotic SCM

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

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

276 4.1.4 Zaldivar in situ SCM

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

294 4.1.5 Gaby Sur in situ SCM

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

Brochantite clearly shows the direct replacement of sulfides (Fig. 8D) displaying impregnations and
disseminations within the sulfides relicts and as coatings at the edges of the altered sulfides. Finally,
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 veins (Fig. 9A). Under the petrographic microscope, these light to dark blue masses can be identified 310 as chrysocolla, which is the most abundant oxidized Cu-bearing minerals (Fig. 9B). Under plane 311 312 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 inclusions within the chrysocolla internal texture (Fig. 9D) while copper oxides exhibit a square 315 316 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 crystals (Fig. 9D). 318

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 proportion of CuO (~ between 50-55 wt. % at Mina Sur, 35-45 wt. % at Damiana and ~ 52 wt. % at El 323 Cobre) and SiO₂ (values between ~ 40-50 wt. % at Mina Sur, 45-50 wt. % at Damiana and ~35-45 wt. 324 325 % 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 only found at Mina Sur, is distinguished from chrysocolla by a higher amount of MnO (up to 6 wt.%) 327 and H₂O (10-20 wt.%) and a lower content in SiO₂ (20-40 wt.%) and CuO (~ 45-50 wt.%). 328 329 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. % at Mina Sur, 23-27 wt. % at Damiana and 27-28 wt. % at El Cobre) and low H₂O contents (5-10 wt. %) 331 in all exotic deposits (Fig. 10C). Silica, aluminum, iron and calcium are also present as trace elements. 332 The compositional data obtained for the in situ SCM (i.e. Zaldivar, Gaby and Gaoua) are listed 333 334 in ESM 1 and displayed in Fig. 10D for chrysocolla. At Zaldivar, the chemical composition of chrysocolla is consistent with previously published analyses (Newberg, 1967; Pinget, 2016) and display 335 high SiO₂ (~43 wt. %) and CuO (~51 wt. %) contents with a low water content (~4 wt. %). Brochantite 336 contains high proportion of Cu (CuO ~ 78 wt. % and 84 wt. %), and sulfate (SO₃ ~ 11-20 wt. %) while 337 water was below the detection limits. Pseudomalachite shows CuO contents between 21-24 wt. %, P2O5 338 between 67-69 wt. % and H₂O contents between 5-8 wt. %. Chrysocolla is composed of CuO (~ 50 wt. 339 %), SiO₂ (average between 39-47 wt. %) and variable water contents (average between 0-15 wt. %). 340 At Gaby, chrysocolla presents high CuO (~ between 45-58 wt. %) and SiO₂ contents (~ between 341 28-42 wt. %) and a varying proportion of H₂O (~ between 3-12 wt. %). Low concentrations of CaO (< 342 1 wt. %) is also found in chrysocolla. Brochantite, which replaces ancient sulfides, reveals high CuO 343 (~ between 76 and 100 wt. %) and SO₃ (~ between 17-40 wt. %) contents. These wide range of values 344 does not agree with the published values for brochantite (Mrose and Reichen, 1965) but rather highlights 345

the ongoing replacement of sulfides relicts by brochantite and other Cu-phosphate minerals. EPMAanalyses carried out on atacamite show homogeneous Cl (\sim 12-15 wt. %) and CuO concentrations (74-77 wt. %) and significant quantities of SiO₂ (up to 5 wt. %), emphasizing the presence of chrysocolla or silica impurities within the atacamite.

Finally, for the Gaoua deposit, EPMA analyses reveal that chrysocolla presents chemical compositions that are similar to those of the Atacama Desert. The SiO₂ and CuO contents vary from 35 wt. % to 48 wt. % (average ~ 41 wt. %) and from 41 wt. % to 51 wt. % (average ~ 46 wt. %) respectively while the Al₂O₃ contents can reach ~ 1.5 wt. %. In Gaoua, intra-layer compositional profiles of chrysocolla show a relatively homogeneous chemical composition with SiO₂ and CuO ranging from 35 wt. % to 45 wt. % and 43 wt. % to 51 wt. %, respectively. Low K₂O, CaO and Na₂O contents have also been detected. Pseudomalachite chemical analyses show high CuO (~ 67 wt. %) and P₂O₅ (~ 21 wt. %) 357 contents with minor amounts of SiO_2 (~ up to 2 wt. %). Aluminum, calcium and magnesium are present 358 as trace elements.

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

373 *4.2.2 Rare earth elements*

Results are presented in ESM 2 for REE and in Fig. 14. Except for Damiana and El Cobre, all
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 a chondrite-normalized spider diagram (McDonough and Sun, 1995). Most of the chrysocolla from both 377 378 exotic and *in situ* deposits, show a flat pattern for all the REE with a slightly depleted spectrum for HREE, a strong negative Ce-anomaly and a small negative Eu-anomaly. Chrysocolla from the in situ 379 SCM of Zaldivar appears as an outlier, with notably lower REE contents and a strong positive Ce-380 anomaly. Chrysocolla from Gaby and Gaoua has REE contents that are ten times higher than those from 381 Zaldivar, with a strong negative Ce-anomaly. REE contents of chrysocolla from Mina Sur are ten times 382 lower than any other exotic deposits without a markedly negative Ce-anomaly. Chrysocolla from 383

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.

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

400

5. Discussion

401 5.1 Physicochemical controls for the SCM formation

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

In the *in situ* SCM deposits, the mineral parageneses are almost similar with minor copper wad at Zaldivar and Gaby, which precedes abundant chrysocolla in the three deposits, followed by lesser amount of pseudomalachite at Zaldivar. At Gaoua, cuprite is the main second stage mineral followed by pseudomalachite. This paragenetic sequence suggests that all these deposits have undergone the similar processes of *in situ* supergene oxidation. In detail, at Zaldivar and Gaby, textural and mineralogical features show that copper sulfides were replaced by oxidized sulfate-Cu minerals (Fig. 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 compared to supergene sulfides. The main thermodynamic constraints for abundant chrysocolla 412 precipitation are pH and $H_4SiO_4^0$ (aq) activity (Crane et al., 2001; Yates et al., 1998). Chrysocolla 413 precipitates when the pH exceed \sim 5 (Yates et al., 1998). Precipitation of chrysocolla is thus commonly 414 415 explained by changing conditions from acid (pH < 5) to neutral or low-alkaline (pH < 9) due to the neutralization of the acidic copper solutions during fluid-rock interaction (Newberg, 1967). It also 416 means that most of the minerals that contributes to lowers the pH (i.e. pyrite and chalcopyrite) are 417 418 leached or do not have the capacity to increase the pH. As suggested by Crane et al. (2001), when $H_4SiO_4^0$ (aq) is the dominant species in the copper solution, chrysocolla will precipitate at a pH ~ 7. 419 Inversely, when $H_2PO_4^-$ (aq) is the dominant species in the copper solutions, pseudomalachite will 420 precipitate. This can explain the precipitation of pseudomalachite at Zaldivar and Gaoua. Generally, 421 422 cuprite crystallizes as replacement of the primary sulfides (Schwartz, 1934) and is rapidly oxidized to hydrate the copper phases. In Fig. 9D, chrysocolla seems to replace cuprite which confirms the 423 424 assumption of Schwartz (1934).

In the exotic SCM (i.e. Mina Sur, Damiana, El Cobre), the same paragenetic sequence is clearly 425 observed: small amount of copper wad, followed by abundant precipitation of chrysocolla and 426 427 pseudomalachite. At Mina Sur atacamite appears as overgrowths on chrysocolla. At Damiana, apatite growth is coeval to the first phase of chrysocolla. At Damiana and El Cobre, pseudomalachite and 428 microcrystalline quartz are linked to the second crystallization stage event. Except for Mina Sur 429 characterized by the presence of reworked angular clasts of black chrysocolla linked to mechanical 430 transportation or *in situ* breaking, all three deposits show mineral textures resulting from the deposition 431 of copper transported in solution from a source (i.e. porphyry copper deposits) to a sink (i.e. the adjacent 432 basins). This requires a progressive neutralization of the mineralizing fluids originating from the 433 upstream oxidizing ore from porphyry copper deposits (Münchmeyer, 1996; Sillitoe, 2005). According 434 to Newberg (1967) and Fernández-Mort et al. (2018), chrysocolla can precipitate as soon as the pH 435 reaches value between \sim 5 and 9 with an optimum value of \sim 7. Chrysocolla is formed by the interaction 436 437 between a copper-rich fluid and SiO₂ (Yates et al., 1998). Copper comes from the porphyry while SiO₂

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

The paragenetic relationship between chrysocolla and pseudomalachite records pH variation. 441 442 Figure 7 from Crane et al. (2001) and Figure 10 from Fernández-Mort et al. (2018) have shown that a slight variation of the pH in copper-rich solutions can lead to the saturation of either chrysocolla or 443 pseudomalachite together with the H₄SiO₄⁰ (aq) activity. This could explain the alternation of 444 chrysocolla and pseudomalachite observed at Mina Sur and the presence of second stage 445 pseudomalachite at Damiana and El Cobre. The fact that, in both in situ or exotic SCM, pseudomalachite 446 has been found as thin bands or as thin coatings around chrysocolla, implies that the chemistry of 447 copper-rich solutions from the parental porphyry is not constant but has changed according to the pH 448 449 variation and the $H_4SiO_4^0$ (aq) and $H_2PO_4^-$ (aq) ions activity.

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

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

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

As observed in most of the deposits, chrysocolla and copper wad show concentric banding texture which suggests chemical variations of the mineralizing fluids as already mentioned by Nelson et al. (2007) and Campos et al. (2015). The banding textures observed within chrysocolla have also been explained by Nelson et al. (2007) as the result of biogenic processes, suggesting bacterial involvement 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

Beside the presence of oxidized copper rich minerals such as silicates, phosphates and sulfates, 480 the existence of oxidizing conditions in the studied localities is supported by the geochemical 481 characterization of the supergene copper minerals (chrysocolla and pseudomalachite) where REE 482 483 spectra (Fig. 14) are characterized by Ce-anomalies. As shown by Goldschmidt (1937) and Braun et al. (1990), Ce is the only LREE to present two oxidation states (Ce^{3+} and Ce^{4+}) in a low-T environment. 484 This makes Ce highly sensitive to redox processes. In fact, the oxidation state of Ce is mainly controlled 485 by the pH. At low pH, water could reduce Ce⁴⁺ to Ce³⁺ whereas if the pH value increases, Ce³⁺ is 486 oxidized to Ce⁴⁺ (Bouchaud et al., 2012). Bouchaud et al. (2012) have also shown, by experimental 487 studies, that Ce³⁺ and Ce⁴⁺ are soluble in meteoric water at neutral to alkaline pH values. Additionally, 488 Estrade et al. (2019 and references therein), have shown that the precipitation of Ce, either as Ce⁴⁺ or 489 Ce³⁺, within supergene environments, is linked to the depth of the supergene column. In the upper part 490 of the column, within more oxidizing and higher pH, Ce4+ precipitates in Ce-rich minerals such as 491 cerianite (CeO₂) or associated with Mn- and Fe- oxyhydroxydes. Consequently, the supergene copper 492

minerals will display negative Ce-anomaly due to the Ce4+ consumption by cerianite or Mn-Fe 493 oxyhydroxydes. This is the case for chrysocolla and pseudomalachite presented in this study who 494 recorded negative Ce-anomaly, except for chrysocolla from Zaldivar. Conversely, in the lower part of 495 the supergene column, under low pH and reduced conditions, Ce³⁺ predominates over Ce⁴⁺ and no Ce-496 rich minerals such as cerianite or Mn-Fe oxyhydroxydes can precipitate. Therefore, Ce will be available 497 in the environment and captured by Cu-rich supergene minerals that will consequently display positive 498 Ce-anomaly as seen for example for chrysocolla at Zaldivar. Similarly, Decrée et al. (2015) have shown 499 that REE spectrum in heterogenite (a supergene cobalt mineral, CoOOH) can display negative Ce-500 anomaly when this mineral co-precipitates with Mn- and Fe-oxides in the upper part of the oxidation 501 profile and positive Ce-anomaly when heterogenite forms in the deeper part of the oxidation profile. 502 The negative Ce-anomalies in exotic copper deposits will further support continuous oxidizing 503 conditions. By contrast, the REE patterns from in situ supergene copper minerals (i.e. chrysocolla and 504 pseudomalachite), which show both positive and negative Ce-anomalies, might reflect changes in the 505 506 redox conditions during the leaching process, above the porphyry, both in time (reducing to oxidizing conditions) and space, i.e. from oxidizing conditions at the top (with Ce⁴⁺ predominates) toward 507 508 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 distribution within chrysocolla and pseudomalachite are heterogenous. Pseudomalachite from El Cobre 510 and Zaldivar contains ten times more REE than those from the other deposits. Furthermore, REE 511 patterns of chrysocolla are contrasted, as the REE contents in Damiana are ten times higher compared 512 to those from Mina Sur, while the REE contents of Zaldivar are ten times lower than those from Gaby 513 and Gaoua. Indeed, in supergene environments, the REE-bearing minerals control the budget and the 514 distribution of the REE. The weathering of the primary REE-bearing minerals (i.e. zircon, monazite and 515 xenotime) will induce either the redistribution of the REE within the newly formed supergene copper 516 minerals (e.g. chrysocolla and pseudomalachite) or the consumption of the REE by secondary REE-517 bearing minerals (i.e. allanite, bastnesite, rhabdophane; Braun et al., 2018). For instance, the absence 518 of secondary REE-bearing minerals at El Cobre and Zaldivar could explain the high REE concentrations 519 520 found in pseudomalachite from both deposits whereas possible precipitation of apatite and rhabdophane

(i.e. two secondary phosphate REE-bearing minerals) in the other deposits (i.e. at Mina Sur and
Damiana) could explain the low REE contents in pseudomalachite. Similarly, the low REE content in
chrysocolla at Mina Sur and Zaldivar (Fig. 14A, B) could be explained by the precipitation of secondary
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 orogeny in Northern Chili and Eburnean orogeny in Burkina Faso) and climatic (i.e. semi-arid to arid 527 climate) settings were combined to favor supergene alteration of porphyries and the formation of thick 528 in situ supergene copper orebodies (Sillitoe, 2005; Sillitoe and McKee, 1996) and/or exotic-Cu deposits 529 530 (Fernández-Mort et al., 2018, 2018; Hartley and Rice, 2005; Münchmeyer, 1996; Riquelme et al., 2017; Sillitoe, 2005). To produce an oxidized supergene copper mineralization, three conditions are necessary. 531 First, tectonic uplift will bring the primary porphyry stock and hypogene sulfides close to the earth 532 surface where oxidizing conditions, controlled by the level of water table, prevail. Second, under 533 favorable climatic conditions, the oxidation of sulfides will produce acidic solutions which will 534 transport copper down and laterally, in the subjacent area, to form an oxidized copper ores when copper 535 solution reach saturation (Fernández-Mort et al., 2018; Reich and Vasconcelos, 2015). Finally, once the 536 supergene column is formed, favorable climatic conditions as well as moderate erosion rate can favor 537 538 SCM preservation. The fact that, although both areas have experienced different tectonic styles, the supergene copper minerals from northern Chile and SW Burkina Faso are identical and share the same 539 chemical compositions implies that they both underwent similar climatic evolutions, i.e. from semi-arid 540 to arid, during the mineralization processes. However, if Northern Chile has evolved towards a 541 542 hyperarid climate for the past ~10 m.y., responsible for the formation of atacamite, the SW Burkina Faso area has only experienced a semi-arid climate since the Eocene (Monsels, 2016). According to 543 Hartley and Rice (2005), who published a compilation of supergene copper deposits ages in the 544 Atacama Desert, the formation of *in situ* SCM took place between 36 Ma and 6 Ma. More recently, 545 Riquelme et al., (2017) and Kahou et al., (2020) have published ages between ca. 25-12 Ma and ca. 19 546 Ma for the formation of the Centinela and Mina Sur exotic copper deposits respectively, i.e. ages that 547

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

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

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

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

603 6. Conclusions

604 Supergene copper mineralization from three exotic and two in situ Cu-deposits from the Atacama Desert in Northern Chile and the Gaoua in situ Cu-Au district in Burkina Faso have been studied in 605 606 details. Mineralogical and chemical characterization of these SCM provide new insights on the genesis of these deposits. Chrysocolla, which precipitates after copper wad, is the main Cu-bearing minerals 607 and shows similar textures and chemical compositions in both in situ and exotic SCM. Precipitation of 608 chrysocolla reflects the progressive evolution of the mineralizing fluids from acidic (pH < 5) to neutral 609 or low-alkaline (pH < 9) conditions during fluid-rock interaction. Chrysocolla is then followed by the 610 611 crystallization of pseudomalachite in exotic deposits due to changes of both pH and H₂PO₄ activity of the Cu-bearings fluids (i.e.). Geochemical analyses emphasize the strong oxidizing conditions required 612 for the formation of oxidized SCM and show that REE distribution and Ce-anomaly are linked to the 613 pH evolution, the depth of the supergene column and the presence of primary and secondary REE-614 615 bearing minerals. The fact that almost the same mineralogy and geochemical patterns are observed on six different deposits, on different location and geodynamic context, point out the fact that the processes 616 617 involve in the formation of these deposits are very similar, i.e. progressive neutralization of the acidic copper solutions that lead to chrysocolla precipitation at neutral pH, high $H_2PO_4^-$ (aq) activity together 618 with low H₄SiO₄⁰ (aq) activity that permit pseudomalachite formation, and silicification process that 619 620 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 geomorphology. The formation of such deposits requires several steps with first the exhumation and 623 weathering of the primary porphyry deposit to ensure surface oxidizing processes and a preservation 624 favored by an environment characterized by moderate erosion and rain fall to prevent mechanical 625 abrasion and leaching of the newly formed deposits and finally, a possible key role played by 626 627 evaporation processes. This equilibrium has been achieved in both Northern Chile and SW Burkina Faso where similar mineralization processes have been involved to form SCM. 628

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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 hostrock. 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