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# Role of CO<sub>2</sub> in low to medium enthalpy geothermal systems in the Central Betic Cordillera (Spain)

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1 Role of CO<sub>2</sub> in low to medium enthalpy geothermal systems in the Central Betic Cordillera  
2 (Spain)

3 **Abstract**

4 There is growing interest in geothermal energy, which is considered as an efficient energy  
5 solution to mitigate rising atmospheric CO<sub>2</sub>. Besides known high enthalpy geothermal systems,  
6 increasing attention is paid to low temperature geothermal systems, as they are suitable for local  
7 use. Although geothermal production seems to be an environmentally advantageous renewable  
8 energy, it might result in significant CO<sub>2</sub> emissions. In this study, we investigate the relationship  
9 between temperature, fugacity of CO<sub>2</sub> ( $fCO_2$ ), and mineral buffers in the reservoir conditions,  
10 taking the low- to medium- enthalpy thermal waters in the Central Betic Cordillera as case  
11 study. Using geochemical modeling, three main groups of waters have been identified  
12 depending on temperature, buffering mineral assemblage, and  $fCO_2$  in their reservoir. A group  
13 of waters with a reservoir temperature ranging from 70 to 90°C and located in the intramountain  
14 sedimentary basins shows a  $fCO_2$  in depth ranging from  $\sim 6 \times 10^{-2}$  and  $6 \times 10^{-1}$ . The reservoir  
15 chemistry of this water group seems to be mainly controlled by carbonates and evaporites  
16 displaying a  $fCO_2$  variation between depth and surface ( $\Delta fCO_2$ ) of  $10^{-1}$ . Another intermediate  
17 group of waters, located in an active extension zone, displays lower temperature (50-60°C) and  
18  $fCO_2$  in the reservoir (from  $10^{-3}$  to  $10^{-2}$ ). Finally, the third group of waters, located on the  
19 metamorphic complexes contacts, show the highest estimated temperatures (130 - 140°C) and  
20  $fCO_2$  in the reservoir (1 to  $10^2$ ). The two latter groups suggest increasing buffering effect of  
21 alumino-silicates, in addition to carbonates and quartz. Therefore, we evidenced a strong  
22 relationship between temperature and  $fCO_2$  in the reservoir as well as the potential mineral  
23 buffers. We discussed the potential of geothermal systems as clean energy source based on the  
24 estimation of the CO<sub>2</sub> emissions generated by the investigated thermal systems for a practical  
25 case of household heating.

## 26 **1 Introduction**

27 Geothermal energy has been widely developed across Europe and the World for the last 50  
28 years, with main focus on the conventional high-temperature geothermal reservoirs.  
29 Nevertheless, low (30°C to 100°C) to medium (100 – 150°C) enthalpy geothermal systems have  
30 been recently subject to increasing interest (Blasco et al., 2017; Capecchiacci et al., 2015; Fusari  
31 et al., 2017) as they may be easily exploited for ground-source heat pump or greenhouses  
32 (Battistel et al., 2016). In the current context of global warming and energy transition,  
33 geothermal is generally considered to be an environmentally advantageous renewable source  
34 of energy. However, emissions of greenhouse gases, and especially CO<sub>2</sub>, might be generated  
35 by geothermal exploitation. Although CO<sub>2</sub> release from geothermal electricity production has  
36 been shown to be significantly lower than from fossil fuel (Ármansson, 2003; Hunt, 2001),  
37 the efficiency of this energy to mitigate rising atmospheric CO<sub>2</sub> is a major concern for societal  
38 acceptance. Scientific research programs have been recently dedicated to the development of  
39 cost-effective non-carbon emitting geothermal energy (e.g., “Geothermal Emission Gas  
40 Control”, Horizon 2020, European program). The studies on the CO<sub>2</sub> emissions in geothermal  
41 systems are mainly dedicated to volcanic geothermal systems (e.g., Ármansson, 2018;  
42 Chiodini et al., 1998; Harvey et al., 2017; Seward and Kerrick, 1996). However, the expansion  
43 of the geothermal sector leads to consider a broader range of geothermal resources resulting in  
44 possible large CO<sub>2</sub> emissions, even in low- and medium- enthalpy geothermal systems.

45 The CO<sub>2</sub> concentration in geothermal waters is strongly related to the geological setting,  
46 and more specifically the lithology, of the reservoir. The role of carbonates might be  
47 predominant in generation of CO<sub>2</sub> as carbonate dissolution or thermal decomposition of  
48 carbonates might be major sources of CO<sub>2</sub> in fluid whereas carbonate precipitation in the  
49 reservoir or in the ascent of the water might be a sink of geothermal CO<sub>2</sub>. The equilibrium  
50 relative to the carbonate minerals and the alumino-silicate minerals, often associated to the

51 chemical water-rock interactions, is an important parameter to consider as it “buffers” the fluid  
52 chemical composition and the CO<sub>2</sub> degassing. Therefore, understanding the relationship  
53 between the mineral buffer, the fugacity of CO<sub>2</sub> ( $f\text{CO}_2$ ) (or its partial pressure of CO<sub>2</sub>,  $p\text{CO}_2$ ),  
54 and the temperature in the reservoir, is crucial to estimate the CO<sub>2</sub> release in geothermal  
55 systems. These links between  $f\text{CO}_2$  and reservoir temperature have been subject to Chiodini  
56 and collaborators’ investigations since the early 1990’s, although they focused mainly on  
57 volcanic geothermal systems (e.g., Chiodini et al., 2007, 1998, 1995b)

58 The Central Betic Cordillera, in the South of Spain, has an interesting geothermal potential  
59 with abundant low to medium geothermal resources (Arrizabalaga et al., 2015; Sánchez  
60 Guzmán and García de la Noceda, 2010), major fault systems allowing a rapid ascent of the  
61 deep hot water (Cerón and López-Chicano, 2002), and moderate-intensity seismic activity. This  
62 region is characterized by several occurrences of thermal springs (water with temperature of  
63 more than 20°C, according to the average air temperature of this area), known as baños, which  
64 have been used, for some of them, as thermal bath since the Roman times. They are mainly  
65 exploited for balneotherapy or spa nowadays. The thermal waters in the Central Betic Cordillera  
66 are also characterized by large variability in  $f\text{CO}_2$ , and therefore in  $p\text{CO}_2$ . Low  $f\text{CO}_2$  are  
67 observed in the sulfated waters (e.g., Baños Alhama de Granada) whereas large amount of CO<sub>2</sub>  
68 degassing are known in few springs (e.g., Capuchina de Lanjaron) (Pérez del Villar, 2009). The  
69 thermal springs of Baños Alicun de la Torres have been studied as natural analogs for CO<sub>2</sub>  
70 storage (Prado-Pérez and Pérez del Villar, 2011). Nevertheless, only old Spanish studies have  
71 considered globally the thermal waters in the Central Betic Cordillera (Benavente Herrera and  
72 Sanz de Galdeano, 1985; Cruz-Sanjulián et al., 1972; Cruz Sanjulián and Granda, 1979). Recent  
73 studies (Campos, 2006; López-Chicano et al., 2001a; Prado-Pérez and Pérez del Villar, 2011)  
74 characterized the geochemical and hydrogeological properties in specific individual thermal  
75 system.

76 The aim of this study is to evaluate the suitability of the thermal waters for the geothermal  
77 exploitation in the Central Betic Cordillera with regard to CO<sub>2</sub> emissions. Geochemical and  
78 isotopic indicators and thermodynamic calculations can be applied to get insights on the fluid  
79 geochemistry, temperature, and  $f\text{CO}_2$  of the reservoir using the measured physical-chemical  
80 characteristics at the surface. The present study attempts to assess the potential mineral  
81 assemblages buffering the waters in the reservoir and the variations of  $f\text{CO}_2$  at the regional  
82 scale.

83

## 84 **2 Geological setting**

85 The sampled thermal waters (springs and wells) are located in the central region of the Betic  
86 Cordillera with a greater concentration of points in the Granada Basin (

87 Figure 1). The Central Betic Cordillera is a complex structure, resulting from the  
88 convergence of the Iberian and African plates, which can be subdivided into: (1) the non-  
89 metamorphic External Zone, (2) the metamorphic Internal Zones, (3) the Neogene basins. The  
90 External Zone is separated from the Internal Zone by a major shear zone called the Internal  
91 External Boundary Zone (IEBZ) (Sanz de Galdeano, 1990). The Granada Basin is one of the  
92 Neogene intramontainous basin in the Central Betic Cordillera, located at the junction between  
93 the Internal and External zones.

94

### 95 2.1 Tectonic framework

96 The Central Betic Cordillera is a tectonically active region structured by several crustal  
97 faults (Bufoin et al., 2004; Sanz de Galdeano and Peláez, 2011). In the NE part of the Granada  
98 Basin, the IEBZ, mentioned above, becomes nearly coincident with the so-called Cadiz-  
99 Alicante faults system (CAFS,

100 Figure 1) extending along 550 km across the Betic Cordillera. This fault system forms a

101 corridor of dextral strike-slip faults generating crustal discontinuities of at least 7 km depth  
102 (Sanz de Galdeano, 2008 and references therein). Besides, two main sets of normal faults affect  
103 the basement and the sedimentary infilling of the Granada Basin: one set of E-W faults with  
104 low angle dip ( $< 30^\circ$ ) toward the south and the north; and a second one with NW-SE faults,  
105 which dip westward, mainly located in the NE of the basin (Figure 1) (Galindo-Zaldívar et al.,  
106 2015; Rodríguez-Fernández and Sanz de Galdeano, 2006). The thermal waters are strongly  
107 related to the faults in the Central Betic Cordillera as the thermal systems are convective  
108 fracture-controlled systems (Benavente Herrera and Sanz de Galdeano, 1985; Cruz-Sanjulián  
109 et al., 1972).

110

## 111 2.2 Lithostratigraphy

112 The material of the Internal Zone corresponds to Paleozoic to Mesozoic metasediments  
113 differentiated into three stacked metamorphic complexes, from the top to the base, by different  
114 metamorphic degree and structural position: (1) Maláguide, (2) Alpujárride, and (3) Nevado-  
115 Filábride. The Alpujárride Complex, well represented in our study area, consists in a series of  
116 nappes of Paleozoic-Mesozoic HP/LT metasediments (Azañón et al., 1998; Azañón and  
117 Crespo-Blanc, 2000). The base of the nappes consists of Paleozoic graphite mica schists, which  
118 are overlain by Permo-Triassic metapelites with layers of meta-sandstones, dolomite, and  
119 limestone. These meta-sediments are in turn overlain by middle-upper Triassic marbles with  
120 interbedded gypsum layers and Mesozoic pelagic marls forming the top of the nappes (Martín  
121 and Braga, 1987; Prado-Pérez and Pérez del Villar, 2011). The HP/LT Nevado-Filábride  
122 materials, outcropping in the Sierra Nevada and Sierra Alhamilla, comprise from the base to  
123 the top: Paleozoic graphitic schists, Permo-Triassic mica schists associated with metapelites,  
124 Triassic dolomite and marbles, and heterogeneous rocks with Jurassic metabasite inclusions  
125 (Gomez-Pugnaire et Fernandez-Soler, 1987; Gómez-Pugnaire et al., 2000).

126 The External Zone forms the northern part of the Granada Basin basement and crops out in  
127 Sierra Elvira and Alicún de las Torres. It is mainly composed of Mesozoic sedimentary rocks,  
128 with Triassic evaporitic-bearing marls, dolomitic limestones, and interbedded marls (Braga et  
129 al., 2003; Sanz de Galdeano and Vera, 1992).

130 The sedimentary infilling of the Granada Basin ranges from the Miocene to the Quaternary  
131 and is composed, from bottom to top, of clayey conglomerates, calcareous sandstones, marls  
132 and silts, gypsum/anhydrite (and locally halite), lacustrine limestones, cemented breccias and  
133 alluviums (Braga et al., 2003; Corbí et al., 2012).

134

### 135 2.3 Sample location

136 The thermal waters are mainly situated close to major tectonic and geological structures.  
137 The sampling points can be gathered into three groups depending of the nature of the geological  
138 features:

- 139 • The thermal waters related to the metamorphic complexes: Baño Salado de Lanjaron  
140 and Capuchina de Lanjaron springs (BSL and CL) are located in the Sierra Nevada along  
141 the detachment between Nevado-Filábride and Alpujárride complexes. Baños  
142 Alhamilla spring (BAA) is situated further to the east in the Sierra Alhamilla along the  
143 same tectonic contact, where it is also close to the trace of an important strike-slip fault  
144 of near N30E direction.
- 145 • The thermal waters located in the evaporitic basins (Granada Basin and Guadix-Baza  
146 Basin): Baños Santa Fe (SF), Baños de la Malahá (BM), and Sondeo Romilla de la  
147 Nueva (SRN) are wells situated in the Granada Basin. Baños Alhama de Granada  
148 (BAG), Baños Nuevo Alhama de Granada (BNAG), and Sierra Elvira (SE) are springs  
149 located in the Granada Basin. SE is also located on the trace of an active fault, belonging  
150 to the NW to NNW directed fault system. Baños de Zujar (BZ) and Baños de Alicún de

151 las Torres (AT) are springs located in the Guadix-Baza Basin, close to the above  
152 mentioned IEBZ and CAFS. The springs SE, BZ, and AT are linked by faults to small  
153 Subbetic carbonate outcrops.

154 • The thermal waters linked to the Baños Urquizar Chico (BUC) and Baños Urquizar  
155 Grande (BUG) are located within the Valle de Lecrin tectonic graben within the  
156 Alpujárride Complex along faults striking N30E, forming the western termination of the  
157 Sierra Nevada Massif.

158

### 159 **3 Material and methods**

#### 160 3.1 Water and dissolved gases sampling

161 Thirteen thermal water samples were collected in the Granada Basin and in the Betic  
162 Cordillera, from nine springs and four wells. Two wells were artesian whereas the other water  
163 samples were pumped. All water samples were filtered with 0.45 µm membrane filters and  
164 samples assigned to trace elements and Al analyses were filtered with 0.2 µm membrane filters.  
165 The water samples dedicated to cations, minor elements, and Al analyses were acidified using  
166 suprapure nitric acid (HNO<sub>3</sub>).

167 Waters were collected by filling 142 mL Pyrex glass bottles to analyze chemical composition  
168 of dissolved gases (Capasso and Inguaggiato, 1998; Inguaggiato and Rizzo, 2004; Lix et al.,  
169 2018). The glass bottles were sealed under water with silicon/rubber septa to minimize  
170 atmospheric contamination (Capasso and Inguaggiato, 1998).

171

#### 172 3.2 Water analyses

##### 173 3.2.1 Physical-chemical properties

174 Physical-chemical parameters of the waters, including temperature, pH, electrical

175 conductivity (EC), and alkalinity were measured directly on the field. The combination pH  
176 electrode was calibrated with three buffer solutions at pH 4.0, 7.0 and 10.0 (25°C) (CertiPUR®  
177 Reference material) and the EC electrode with two potassium chloride standard solutions of  
178 1.41 mS/cm and 12.8 mS/cm (25°C) (CertiPUR® Reference material). The uncertainties on the  
179 measurements of temperature, pH, and EC were of  $\pm 1^\circ\text{C}$ ,  $\pm 0.1$ , and  $\pm 0.01$  mS/cm respectively.  
180 Alkalinity was determined by titration with an 0.01M or 0.1M hydrochloric acid solution  
181 depending on the encountered alkalinity range and by following the pH evolution with the pH-  
182 meter. The equivalent volume was determined with the Gran's method (Gran, 1952) and the  
183 analytical error of the alkalinity measurements was of approximately  $\pm 5\%$ .

184

### 185 3.2.2 Laboratory chemical analyses

186 The major cations and anions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ) were analyzed by ionic  
187 chromatography. The uncertainty on  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  determination is  $\pm 5\%$  whereas that  
188 on  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  is estimated to be  $\pm 10\%$ . Minor and trace elements (Ba, Sr, Al, Fe) were  
189 analyzed by Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES. The  
190 uncertainty on Ba and Sr determination is  $\pm 10\%$  whereas that on Al is estimated to  $\pm 20\%$ . The  
191 silica concentrations were determined by a spectrophotometric method following the protocol  
192 from Centre d'Expertise en Analyse Environnementale du Québec, (2016), suitable for natural  
193 groundwater with Si concentration ranging from 0 to 20 mg/l. The total ionic balance does not  
194 exceed 8% for all water samples.

195

## 196 3.3 Gas analyses

### 197 3.3.1 Extraction and analyses of dissolved gases

198 The extraction of the dissolved gases was carried out following the method described by  
199 Capasso and Inguaggiato (1998) and Inguaggiato and Rizzo (2004). A known volume of host

200 gas was injected into the upside-down glass bottles while drawing out the equivalent water  
201 volume through needles. After equilibration for 24 hours, a variable gas volume was extracted  
202 for analyses by injecting Millipore water into the glass bottles.

203 Gas species (O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and He) were analyzed by gas chromatography (Clarus 500,  
204 Perkin Elmer instrument with Carboxen 1000 columns with a hot wire detector and a flame  
205 ionization detector) using argon as carrier gas. The composition of dissolved gases, expressed  
206 in cc.l<sup>-1</sup> STP (Standard Temperature and Pressure), was calculated taking into account the  
207 volume of gas extracted, the volume of water sample, and the solubility of each gas species  
208 (Bunsen coefficient in cc gas/l water STP). The composition of bubbling gases was expressed  
209 in either %vol or ppm vol. The accuracy to analyze dissolved gases following the method  
210 described by Capasso and Inguaggiato (1998) is within 5.0%.

211

### 212 3.4 $\delta^{13}\text{C}$ of the Total Dissolved Inorganic Carbon (TDIC)

213 Analyses of  $\delta^{13}\text{C}$  of Total Dissolved Inorganic Carbon (TDIC) were carried out with the  
214 Analytical Precision 2003 (AP2003) mass spectrometer using the method outlined by Capasso  
215 et al. (2005) based on chemical and physical stripping. The results were expressed in ‰ vs. V-  
216 PDB standard and with standard deviations of <sup>13</sup>C/<sup>12</sup>C ratios of  $\pm 0.2\%$ .

217

### 218 3.5 Geochemical calculations and modeling

219 In this study, the saturation index calculations and geothermometrical modeling were  
220 performed with the (version 3-0-6) PHREEQC software (Parkhurst et al., 2013), using the  
221 phreeqc thermodynamic database distributed with the code.

222

#### 223 3.5.1 Saturation index

224 A direct thermodynamic modeling of the multi-component system equilibrium has been  
225 performed from the composition of the waters and the physical-chemical parameters. The  
226 saturation index of waters with respect to possible minerals ( $SI_m$ ) were calculated to test the  
227 equilibrium conditions or the departure from equilibrium of the system, following Equation 1:

$$SI_m = \log \Omega_m = \log \frac{\prod^i (\gamma_i [c_i])^{v_{im}}}{K_S(P, T)_m} \quad (1)$$

228 where  $[c_i]$  and  $\gamma_i$  are the concentration and the activity coefficient of the ion  $i$ ,  $v_{im}$  is the reaction  
229 coefficient for the ion  $i$  and the mineral  $m$ , and  $K_S(P, T)_m$  is the solubility constant of the mineral  
230  $m$  dependent on temperature and pressure.

231

### 232 3.5.2 Chemical geothermometers and geobarometers

233 Chemical geothermometric techniques were used to estimate the theoretical reservoir  
234 temperature of the thermal waters. The application of the chemical geothermometers needs to  
235 satisfy the basic assumptions that the waters circulating at depth are in chemical equilibrium  
236 with the minerals of the host rocks (i.e.,  $SI_m$  close to 0) and that their elemental contents have  
237 not changed significantly during the water ascent to the surface (including precipitation or  
238 dissolution of secondary mineral phases or degassing). Numerous chemical geothermometers  
239 have been described in the literature, including silica, Na/K, Na/K/Ca, K-Mg (D'Amore et al.,  
240 2000 and references therein). The silica geothermometers are the most common in geochemical  
241 investigations of geothermal systems, widely used in different contexts around the world  
242 (Verma, 2000a). However, the validity of the silica geothermometers, and especially  $SiO_2$ -  
243 quartz geothermometers, have been questioned at low temperatures ( $< 100^\circ C$ ) (Fournier, 1977;  
244 Rimstidt and Barnes, 1980; Verma, 2000a). At those temperatures, quartz precipitation rate is  
245 very slow and saturation is rarely achieved (Bjorlykke and Egeberg, 1993; Rimstidt and Barnes,  
246 1980). Nevertheless, these geothermometers might provide consistent results even at low to

247 medium temperatures (Blasco et al., 2018) and therefore they have been investigated in this  
 248 study. SiO<sub>2</sub>-quartz geothermometers from Fournier (1977), Fournier and Potter (1982),  
 249 Michard (1979) and Verma (2000b) and SiO<sub>2</sub>-chalcedony geothermometers from Arnórsson et  
 250 al. (1983) and Michard (1990) were applied for the studied thermal waters. Although cationic  
 251 (Na/K, Na/K/Ca, K-Mg) geothermometers have been proven efficient in high temperature  
 252 systems (> 180°C), they are usually considered as unsuitable in low temperature systems due  
 253 to the different mineral assemblage governing the water chemistry and equilibrium (Blasco et  
 254 al., 2017; Chiodini et al., 1995a). Due to these limitations, the Na/K, Na/K/Ca and K-Mg  
 255 geothermometers have not been applied in this study. The Ca-Mg geothermometer, developed  
 256 in the first place by Marini et al. (1986) and revised by Chiodini et al. (1995a), is more  
 257 appropriate for low temperature carbonate-evaporitic system and was therefore used here. This  
 258 geothermometer assumes equilibrium of the waters with calcite, dolomite and anhydrite in the  
 259 reservoir, which is a reasonable assumption in the investigated area where these minerals are  
 260 extensively present.

261 In order to get an estimation of the fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) at depth, the geobarometrical  
 262 relationship based on the (HCO<sub>3</sub><sup>-</sup>)<sup>2</sup>/SO<sub>4</sub><sup>2-</sup> ratio, *f*CO<sub>2</sub>, and temperature (Chiodini et al., 1995a)  
 263 was applied using the following equation:

$$\log \frac{(HCO_3^-)^2}{SO_4^{2-}} = -4.807 + 0.9871 \log pCO_2 + \frac{794.8}{T} - 0.1655 \log \Sigma_{eq} \quad (2)$$

264 where  $\Sigma_{eq}$  is the sum of equivalents in the waters.

265

### 266 3.5.3 Geothermometrical modeling

267 Another approach to estimate the reservoir temperature consists of simulating the variation  
 268 of the saturation states with respect to a group of selected minerals, potentially present in the  
 269 reservoir, to find the temperature at which the saturation indices simultaneously reach  
 270 equilibrium (Blasco et al., 2018). This method is based on the same assumption as the classical

271 chemical geothermometers: the thermal waters are in equilibrium with the mineral phases under  
272 reservoir conditions. Hence, the most realistic reservoir temperature corresponds to the  
273 temperature at which a group of minerals is at equilibrium (Asta et al., 2012; D'Amore et al.,  
274 1987; Tole et al., 1993).

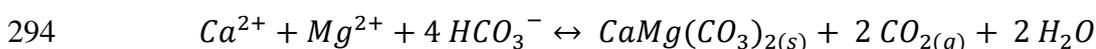
275 Saturation indices were calculated in the temperature interval between the field temperature  
276 and 150°C for the following minerals: quartz, chalcedony, anhydrite, dolomite, calcite, Ca-  
277 montmorillonite, laumontite, Mg-chlorite, albite, anorthite, K-feldspar, and kaolinite. Due to  
278 the imprecision of the thermodynamic databases, the error on the SI at which the equilibrium is  
279 reached is considered to be  $SI = 0 \pm 0.25$  (D'Amore et al., 1987). This geothermometrical  
280 modeling approach estimates the reservoir temperature within an uncertainty of  $\pm 10^\circ\text{C}$  (Tole  
281 et al., 1993).

282 An additional set of geothermometrical simulations has been performed at the end of the  
283 study including addition of  $\text{CO}_2$  to the initial solution to test the hypothesis of  $\text{CO}_2$  degassing  
284 in an open system.

285

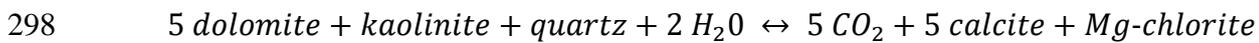
#### 286 3.5.4 Hydrogeochemical modeling between surface and depth conditions in closed 287 system

288 In order to assess the geochemistry of the waters at reservoir conditions and the variation  
289 of the  $f\text{CO}_2$  between the reservoir and the surface, we carried out hydrogeochemical simulations  
290 in closed systems. In sedimentary environments, the pH and  $f\text{CO}_2$  of the waters are highly  
291 dependent on the interaction with carbonate minerals. Dolomite is particularly important in the  
292 Central Betic Cordillera where large amount are present.  $\text{CO}_2$  generation might occurs during  
293 dolomite precipitation as shown by the following reaction:



295 The  $f\text{CO}_2$  in the system might also be controlled by reactions involving aluminosilicates

296 and carbonates such as the conversion of kaolinite to Mg-chlorite proposed by Coudrain-  
297 Ribstein et al. (1998) and Hutcheon et al. (1993):



299

300 The modeling workflow was run with the PHREEQC code and includes the following three  
301 steps:

302 (1) Saturation calculations were carried out at the outlet temperature ( $T_{\text{out}}$ ) and atmospheric  
303 pressure ( $P_{\text{out}}$ ),

304 (2) An increase in temperature was simulated up to the temperature of the quartz  
305 geothermometer ( $T_{\text{qz}}$ ) and the corresponding hydrostatic pressure of the reservoir ( $P_{\text{hydro}}$ ) using  
306 a geothermal gradient of 30°C/km,

307 (3) Waters were equilibrated with a set of minerals at  $T_{\text{qz}}$  and  $P_{\text{hydro}}$ , to test two different  
308 hypotheses:

- 309 • Equilibrium with dolomite using  $\text{CO}_{2(\text{g})}$  as an alternative phase to reach the  
310 equilibrium,  
311 • Equilibrium with carbonates and alumino-silicates using calcite, dolomite,  
312 kaolinite, quartz, Mg-chlorite as mineral assemblage. These minerals are allowed  
313 to dissolve or precipitate to reach equilibrium.

314 The concentrations of chemical species, pH,  $\text{CO}_2$  fugacity, and SI of minerals were  
315 computed during each step of modeling. By comparing the results of the geochemical modeling  
316 (Step 3) with the initial surface geochemical characteristics (Step 1), we evaluate the possible  
317 mineral assemblages in equilibrium at reservoir conditions.

318 These geochemical simulations rely on the assumption that the difference in the quartz  
319 saturation index ( $\text{SI}_{\text{quartz}}$ ) during each step of the modeling does not lead to significant change  
320 in temperature. Even if  $\text{SI}_{\text{quartz}}$  varies between -0.13 and 1.27, the  $\text{H}_4\text{SiO}_4$  concentration remains

321 quite constant for all the thermal waters resulting in a change in apparent temperature ( $\delta T$ )  
322 lower than 5°C.

323

## 324 **4 Results**

### 325 4.1 Chemical characteristics of the waters

326 The investigated thermal waters have outlet temperature ranging from 20 to 50°C,  
327 corresponding to low to medium enthalpy waters, and pH values spanning between 5.8 and 7.6  
328 (Table 1). The conductivity of the studied waters shows a large range of values, from 1 to 34  
329 mS/cm, corresponding to total dissolved solids (TDS) values from 0.67 to 18.17 g.L<sup>-1</sup>.

330 The thermal waters show a large variability in their chemical composition and a relationship  
331 can be evidenced between the water-types and their location relative to the geological structures  
332 in the Central Betic Cordillera (Figure 2).

333 The waters located in the graben formed in the Alpujarride Complex and close to the SE-  
334 NW faults have a chemical composition of Ca<sup>2+</sup>-Mg<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup> type, displaying interaction  
335 with both carbonates and sulfates.

336 The waters in the evaporitic basins are mainly Ca<sup>2+</sup>-Mg<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup> water-type resulting from  
337 clear interaction with evaporitic material and especially calcium sulfate. The samples BAG and  
338 BNAG have a higher HCO<sub>3</sub><sup>-</sup> content, with a composition close to the samples from the graben  
339 in the Alpujarride Complex. The composition of the BZ water also differs from the others with  
340 a Ca<sup>2+</sup>-Na<sup>+</sup>-K<sup>+</sup>-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup> water-type, showing significant interaction with evaporitic and detrital  
341 material.

342 The thermal waters located at contacts between metamorphic complexes display larger  
343 dispersion in their chemical composition. The samples BSL and CL are Na<sup>+</sup>-Cl<sup>-</sup> type whereas  
344 BAA is Na<sup>+</sup>-Cl<sup>-</sup>-HCO<sub>3</sub><sup>-</sup> type.

345

## 346 4.2 Saturation indices

347 The results of the saturation indices calculations at the outlet temperature are shown in  
348 Table 2. The waters are mainly close to equilibrium or slightly oversaturated with respect to  
349 calcite and dolomite whereas they are undersaturated with respect to gypsum, anhydrite, and  
350 halite. However, the thermal waters of AT and BSL display slight undersaturation to  
351 undersaturation with respect to the carbonate minerals (calcite and dolomite). Waters are  
352 oversaturated with respect to quartz and close to equilibrium with respect to chalcedony.  
353 Concerning the saturation indices with respect to alumino-silicates, the waters are oversaturated  
354 with respect to kaolinite and Ca-montmorillonite whereas they display large range of saturation  
355 with respect to K-feldspar and albite, spanning from undersaturated to highly oversaturated,  
356 independently of the relationship with the tectonic structures. The saturation indices of the  
357 waters with respect to the considered minerals are pH-dependent and therefore dependent of  
358 possible CO<sub>2</sub> degassing of the thermal waters.

## 359 4.3 CO<sub>2</sub>

360 Dissolved CO<sub>2</sub> concentrations range from 9.51 to 597.5 cc/L, corresponding to  $f\text{CO}_2$   
361 spanning from 0.02 to 0.78, i.e pCO<sub>2</sub> from 0.02 to 0.78 atm (Table 3). The water samples  
362 characterized by higher amounts of dissolved CO<sub>2</sub> display lower pH values, suggesting that  
363 CO<sub>2</sub> is the main species responsible of water acidity. The high-CO<sub>2</sub> springs of CL, BAA and  
364 BUG are also characterized by bubbling gases with similar composition as the dissolved gases  
365 (Lix et al., 2018).

366 The  $f\text{CO}_2$  values obtained from the speciation-solubility calculations at the outlet  
367 temperature range from 0.006 to 1.02 (Table 2). The total dissolved inorganic carbon content  
368 of the thermal waters and its isotopic composition ( $\delta^{13}\text{C}_{\text{TDIC}}$ ), listed in Table 3, range from 2.7  
369  $\times 10^{-3}$  to  $6.3 \times 10^{-2}$  mol.L<sup>-1</sup> and from -9.04 to -1.54‰ vs. V-PDB respectively.

370 Various carbon sources and processes control the  $\delta^{13}\text{C}$  of the TDIC including: (1) the

371 degradation of organic matter in the soil (of the recharge area), (2) carbonate dissolution, (3)  
372 degassing of mantle-derived CO<sub>2</sub>. Biological degradation processes in soils usually results in  
373 δ<sup>13</sup>C values ranging from -23‰ and -9‰ (Clark and Fritz, 1997), which is not well  
374 representative of the studied samples. Therefore, the δ<sup>13</sup>C<sub>TDIC</sub> values indicate mainly inorganic  
375 origin of CO<sub>2</sub> although possible mixing with organic carbon sources cannot be ruled out.  
376 Discriminating the carbon source between carbonate dissolution and mantle-derived CO<sub>2</sub> might  
377 be more complex as their δ<sup>13</sup>C values overlap, The isotopic composition of dissolved and  
378 bubbling gases in these thermal waters show however a dominant crustal component (Lix et al.,  
379 2018). Purely inorganic origin of CO<sub>2</sub> has been considered in these thermodynamical  
380 calculations, given the results of δ<sup>13</sup>C of the TDIC.

381

#### 382 4.4 Reservoir temperature and pressure

##### 383 4.4.1 Chemical geothermometers and geobarometers

384 The temperatures provided by the silica and Ca-Mg geothermometers are compiled in Table  
385 4. The reservoir temperatures estimated with the different SiO<sub>2</sub>-quartz geothermometers range  
386 from 42 to 146°C corresponding to a mean spanning between 51 and 143°C with a relative  
387 standard deviation lower than 6°C. The SiO<sub>2</sub>-chalcedony geothermometers yields lower  
388 temperatures ranging from 20 to 115°C. The SiO<sub>2</sub>-quartz are more reliable than the SiO<sub>2</sub>-  
389 chalcedony geothermometers since quartz might be the phase controlling the dissolved silica in  
390 the thermal waters in the Betic Cordillera. Indeed, quartz occurrences and mineralizations have  
391 been described in the Internal Zones of the Betic Cordillera as well as in the Neogene basins  
392 whereas chalcedony have not been described in mineral assemblages. Although the kinetics of  
393 quartz reaction is very slow below 100°C (Rimstidt and Barnes, 1980), the mineral equilibrium  
394 approach developed in this study might support the temperatures obtained from quartz  
395 geothermometers.

396 The thermal waters located in the evaporitic basins (Granada and Guadix-Baza Basins)  
397 show estimated reservoir temperature from SiO<sub>2</sub>-quartz ranging from 74 to 95°C. Assuming a  
398 thermal gradient of 30°C/km, which can be expected in the studied area (Fernández et al., 1998),  
399 these temperatures would correspond to depths and hydrostatic pressures varying from 2.5 to  
400 3.2 km and from 250 to 320 atm respectively. The thermal waters BUC and BUG, located close  
401 to the SE-NW faults, show the lowest estimated reservoir temperature, ranging from 51 to 58°C  
402 and corresponding to hydrostatic pressure spanning between 170 and 200 atm respectively. The  
403 thermal waters located at the contacts between metamorphic complexes (BAA, CL, and BSL)  
404 show the highest estimated reservoir temperatures ranging from 126 and 142°C, corresponding  
405 to depths of 4 - 4.5 km and a hydrostatic pressures of 400 to 450 atm.

406 The Ca-Mg geothermometer provides temperatures ranging mainly between 71 and 91°C  
407 with little variation between the different thermal waters (Table 4). The obtained temperatures  
408 are in good agreement with those of SiO<sub>2</sub>-quartz geothermometers for the waters located in the  
409 evaporitic Granada Basin. However, the Ca-Mg geothermometer give similar reservoir  
410 temperatures regardless of the geological context of the studied thermal waters, due to low  
411 variations in their Ca/Mg ratios, ranging mainly from 1.5 to 2.4. Therefore, it seems that this  
412 geothermometer might not be suitable for all investigated thermal waters in the central Betic  
413 Cordillera.

414 The results of the geobarometrical method based on the (HCO<sub>3</sub><sup>-</sup>)<sup>2</sup>/SO<sub>4</sub><sup>2-</sup> ratio (Chiodini et  
415 al., 1995a) give values of fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) in depth ranging from 0.04 to approximately  
416 23. The high values (> 5) are obtained for the thermal waters located on the contact of  
417 metamorphic complexes (CL, BSL, and BAA).

418

#### 419 4.4.2 Geothermometrical modeling

420 The first results of the geothermometrical modeling including all mineral phases (quartz,

421 chalcedony, anhydrite, dolomite, calcite, Ca-montmorillonite, laumontite, Mg-chlorite, and  
422 kaolinite) do not reach a common equilibrium temperature (Figures 3 and 4).

423 Although we can expect the carbonates as part of the buffering mineral assemblage in depth  
424 due to their ubiquity in the sedimentary basin and in the Central Betic Cordillera, they cannot  
425 reach equilibrium in the reservoir conditions. As shown in Figures 3 and 4, the waters are close  
426 to equilibrium or oversaturated with respect to calcite and dolomite in the outlet conditions and  
427 these minerals have retrograde solubility. The apparent oversaturation in the outlet conditions  
428 might result from CO<sub>2</sub> outgassing process and a corresponding increase in pH during the ascent  
429 of the waters to the surface.

430

#### 431 4.4.3 Hydrogeochemical modeling

432 The results of the simulations show that, globally,  $f\text{CO}_2$  in the outlet conditions varies  
433 between  $6 \times 10^{-3}$  and 1, i.e.  $p\text{CO}_2$  between  $\sim 6 \times 10^{-3}$  and 1 atm. The  $f\text{CO}_2$  obtained in the third  
434 step of the simulation after equilibration with dolomite show values ranging from  $\sim 2 \times 10^{-2}$  and  
435 40 (Figure 5), whereas the values of  $f\text{CO}_2$  after equilibration with alumino-silicates and  
436 carbonates vary between  $5.4 \times 10^{-3}$  and  $1.8 \times 10^2$  (Figure 6). The logarithmic relationship  
437 between  $f\text{CO}_2$  and temperature for the waters equilibrated with the both carbonates and  
438 alumino-silicates might reflect strong control by the equilibrium mineral assemblage on the  
439 chemical water composition and CO<sub>2</sub> content.

440

441 The geochemical modeling allows discriminating the three groups of waters, already  
442 distinguished by geology, regarding the  $f\text{CO}_2$  in the reservoir conditions:

- 443 • Group of waters located in the evaporitic basins

444 The results of the simulations in the evaporitic Granada Basin give a pH of the waters in  
445 equilibrium with dolomite in the reservoir conditions ( $74 < T < 95^\circ\text{C}$  and  $250 < P_{\text{hydro}} < 320$

446 atm) ranging from 6.5 to 6.8 and an estimated  $f\text{CO}_2$  spanning between  $9 \times 10^{-2}$  and  $1.6 \times 10^{-1}$   
447 (Figure 5). The simulations taking into consideration carbonates and alumino-silicates give  
448 similar ranges of pH (from 6.5 to 6.7) and  $f\text{CO}_2$  (from  $6 \times 10^{-2}$  to  $2 \times 10^{-1}$ ) to those obtained  
449 with dolomite equilibrium for the water points located in the Granada basin (Figure 6).  
450 However, the two samples BNAG and BZ show slightly higher  $f\text{CO}_2$  ranging from  $3 \times 10^{-1}$  and  
451  $6 \times 10^{-1}$ . The thermal water of Alicun de las Torres (AT), showing a lower reservoir temperature  
452 similar to BUC and BUG samples, have an estimated low  $f\text{CO}_2$  at depth for both simulations  
453 ranging from  $1 \times 10^{-2}$  to  $3 \times 10^{-2}$  (Figure 5 and 6). The variation in  $f\text{CO}_2$  between the steps 1  
454 and 3 of the simulation,  $\Delta f\text{CO}_2$ , estimated for this group of thermal waters ranges from  $3 \times 10^{-2}$   
455 to  $6 \times 10^{-1}$  (Figure 7). This corresponds to a difference in calculated  $\text{CO}_2$  concentration  
456 between the steps 1 and 3 of the simulations ranging from  $\sim 1$  to 5 mmol/L.

457

- 458 • Group of waters in the graben in the Alpujarride complex

459 The results of the equilibrium simulations with dolomite in the reservoir conditions ( $51 <$   
460  $T < 58^\circ\text{C}$  and  $170 < P_{\text{hydro}} < 200$  atm) for the waters located in the graben into the Alpujarride  
461 Complex give a pH of the waters of approximately 6.8 and an estimated  $f\text{CO}_2$  of  $6 \times 10^{-2}$   
462 (Figure 5). The simulation of these waters in equilibrium with both carbonates and alumino-  
463 silicates (calcite, dolomite, quartz, kaolinite, and Mg-chlorite) give higher values of pH ranging  
464 from 7.3 to 7.4 and lower values of  $f\text{CO}_2$  spanning between  $5 \times 10^{-3}$  and  $9 \times 10^{-3}$  (Figure 6). The  
465 estimated variation in  $f\text{CO}_2$  between the depth and the surface,  $\Delta f\text{CO}_2$ , ranges from  $\sim 0$  to  $6 \times$   
466  $10^{-2}$  (Figure 7), corresponding to maximum 1 mmol/L of  $\text{CO}_2$ .

467

- 468 • Group of waters located at contact with metamorphic complexes

469 Both geochemical simulations show high  $f\text{CO}_2$  values ( $> 7 \times 10^{-1}$ ) and low pH (ranging  
470 from 5.1 to 6.7) at reservoir conditions ( $126 < T < 142^\circ\text{C}$  and  $400 < P_{\text{hydro}} < 450$  atm) for the  
471 thermal waters located at the contact with the metamorphic complexes. The estimated  $f\text{CO}_2$  at

472 depth is lower considering the equilibrium with dolomite only (ranging from  $6 \times 10^{-1}$  to 6) than  
473 considering the equilibrium with the carbonate and alumino-silicate assemblage (ranging from  
474 25 to 180) (Figures 5 and 6). The estimated  $\Delta f_{\text{CO}_2}$  for this group of thermal waters spans from  
475  $6 \times 10^{-1}$  to  $1.8 \times 10^2$  (Figure 7), corresponding to 20 mmol/L to 0.85 mol/L of  $\text{CO}_2$ .

476

#### 477 4.4.4 Geothermometrical modeling with $\text{CO}_2$ degassing (open system)

- 478 • Group of waters located in the evaporitic basins

479 The geothermometrical simulations with the lowest estimation of  $\text{CO}_2$  addition deduced  
480 from the hydrogeochemical modeling, 1 mmol/L, result in a common reservoir temperature of  
481 75 to 90°C for the waters of the evaporitic basins (Figure 8). Waters are at potential equilibrium  
482 with the following mineral buffer: carbonates (calcite and dolomite), anhydrite, quartz, and  
483 possibly Mg-chlorite or Ca alumino-silicate (laumontite or a Ca-montmorillonite). These results  
484 show that low amounts of  $\text{CO}_2$  degassing ( $\sim 1$  mmol/L) are necessary in an open system to  
485 reach the equilibrium with dolomite and alumino-silicates. Evaporites are also part of the buffer  
486 mineral assemblage in this sedimentary environment.

487

- 488 • Group of waters in the graben in the Alpujarride Complex

489 The geothermometrical simulations in an open system with addition of 0.5 mmol/L  $\text{CO}_2$   
490 show estimated reservoir temperatures ranging from 50 to 60°C for the waters located in the  
491 graben in the Alpujarride Complex (Figure 9) with the following mineral buffer: carbonates  
492 (calcite and dolomite), quartz, and Ca alumino-silicate (Ca-montmorillonite). Higher amounts  
493 of added  $\text{CO}_2$  do not lead to a common equilibrium of mineral phases at a specific temperature.

494

- 495 • Group of waters located at contact with metamorphic complexes

496 Modeling of  $\text{CO}_2$  degassing in an open system with geothermometrical simulations shows  
497 that 7 mmol/L to 1 mol/L of added  $\text{CO}_2$  are necessary for the waters to be at equilibrium at

498 temperature ranging from 120 and 140°C with the following mineral assemblage: quartz and  
499 dolomite, and sometimes Mg-chlorite and laumontite (Figure 10).

500

## 501 **5 Discussion**

### 502 5.1 Role of the mineral buffers in CO<sub>2</sub> estimation

503 The thermal waters in the Central Betic Cordillera are characterized by large heterogeneity  
504 in their geochemistry in the outlet conditions and in their geothermal characteristics. The three  
505 groups of waters, which were defined based on water composition and geology at the thermal  
506 water locations, can be also distinguished by the temperature and  $f\text{CO}_2$  in the reservoir. The  
507 groups of thermal waters have distinct reservoir temperatures, estimated with the SiO<sub>2</sub>-quartz  
508 geothermometer, ranging from low-enthalpy (~55°C) to medium-enthalpy (~140°C)  
509 geothermal systems. Using the results of the geochemical and geothermometrical modeling we  
510 discuss in this section the mineralogical buffers and chemical properties of the reservoirs and  
511 the variations in  $f\text{CO}_2$  between depth and the surface ( $\Delta f\text{CO}_2$ ) in both closed and open system  
512 for the three groups of waters. For all groups the assessed  $\Delta f\text{CO}_2$  indicates CO<sub>2</sub> degassing during  
513 the ascent of the water to the surface. The equilibrium with respect to mineral phases in the  
514 reservoir conditions seems to have a strong control on CO<sub>2</sub> release (Figure 7).

515 The group of thermal waters located in the sedimentary basins (Granada and Guadix-Baza  
516 Basins), whose reservoir temperatures range from 74 to 95°C, seem to be buffered at depth by  
517 mainly carbonates, evaporites, quartz and a few alumino-silicates. The fact that there is a good  
518 agreement in  $\Delta f\text{CO}_2$  with both dolomite buffer and carbonate/alumino-silicate buffer shows that  
519 carbonates are the predominant mineral buffer in this environment. The values of  $f\text{CO}_2$  resulting  
520 from geochemical simulations at depth are in quite good agreement with those estimated by the  
521 geobarometer from Chiodini et al. (1995a), ranging from 0.04 to 0.16. This geobarometer,

522 specifically established for low- to medium- geothermal systems hosted in carbonates and  
523 evaporites, is certainly an efficient tool to estimate the reservoir  $f\text{CO}_2$  in this sedimentary  
524 context (similar range of temperature and  $f\text{CO}_2$ ).

525 The presence of evaporites needs to be considered for the geothermal systems in  
526 sedimentary environment as it might enhance  $\text{CO}_2$  release through a dedolomitization process.  
527 Prado-Pérez and Pérez del Villar (2011) showed that the thermal water AT may result from  
528 dedolomitization at depth followed by  $\text{CO}_2$  degassing. Dedolomitization, which is a process  
529 described in other natural systems (Auqué et al., 2009; López-Chicano et al., 2001b),  
530 corresponds to dolomite dissolution and calcite precipitation caused by the dissolution of  
531 gypsum and/or anhydrite.  $\text{CO}_2$  loss, before or after outlet of the thermal waters, might occur as  
532 evidenced by the presence of fossil and present-day massive thermogenic travertine deposits  
533 (Prado-Pérez and Pérez del Villar, 2011) in the Alicun de las Torres site. This process of  
534 dedolomitization is most probably occurring in other geothermal systems in the evaporitic  
535 Granada and Guadix-Baza basins.

536 For the thermal waters located in the graben in the Alpujárride Complex, which show the  
537 lowest estimated reservoir temperature, the buffer minerals are carbonates, quartz, and Ca  
538 alumino-silicate (Ca-montmorillonite).  $\Delta f\text{CO}_2$  is higher considering the dolomite buffer than  
539 considering the carbonate/alumino-silicate buffer. The difference in  $f\text{CO}_2$  simulated with the  
540 two types of mineral buffers (dolomite only and the carbonate/alumino-silicate association) for  
541 the thermal waters in the graben might be the signature of the basement, whereas the similar  
542  $f\text{CO}_2$  estimated for the waters in the sedimentary basin would be the signature of the  
543 sedimentary pile. Moreover, the values of  $f\text{CO}_2$  for both simulations at depth are lower than  
544 those estimated by the geobarometer from Chiodini et al. (1995a) of 0.54 and 0.66 for BUC and  
545 BUG samples respectively.

546 On the other hand, for the group of waters located at contact with the metamorphic

547 complexes, which displays the highest estimated reservoir temperature (130 – 140°C), the  
548 mineral buffer assemblage at depth is more difficult to assess due to the large CO<sub>2</sub> degassing.  
549 Indeed, these waters show the highest measured dissolved CO<sub>2</sub> concentrations (> 39 cm<sup>3</sup>/L)  
550 distinguishing them from the other thermal springs in the Central Betic Cordillera. They are at  
551 equilibrium with quartz and dolomite, and close to equilibrium with Mg-chlorite and laumontite  
552 in the reservoir conditions. The  $\Delta f\text{CO}_2$  is lower with the dolomite buffer than with the carbonate  
553 and alumino-silicate buffer (Figure 7).

554 The results of the simulations show that CO<sub>2</sub> degassing is lower in open system than in  
555 closed system, highlighting the importance to evaluate the efficiency of the system to rapidly  
556 ascend water from depth to the surface. Calcite precipitation might result from the CO<sub>2</sub>  
557 degassing process due to pH increase and kinetic constrains compared to dolomite precipitation.  
558 The amount of precipitated calcite can be evaluated during a given time range using the amount  
559 of CO<sub>2</sub> loss during the ascent of the water and the estimated flow rate of the springs found in  
560 literature and checked in the field (ranging from 0.2 to 100 L/s). Assuming a time range  
561 comprised between 1,000 and 100,000 yr, the amount of calcite precipitated is estimated to  
562 range from ~ 10<sup>2</sup> to 10<sup>6</sup> m<sup>3</sup> for the waters in the basins or their borders. This estimation is in  
563 good agreement with the volume of travertines that can be deduced from the study of Martín-  
564 Algarra et al. (2003) in the northeastern part of the Granada Basin (from 10<sup>4</sup> to 10<sup>5</sup> m<sup>3</sup> for the  
565 last 200,000 yr).

566

## 567 5.2 Relationship between $f\text{CO}_2$ and temperature

568 Using thermodynamic calculations (hydrogeochemical and geothermometrical  
569 simulations), we show the key role of the reservoir temperature and the buffer mineral  
570 assemblage on the estimation of  $f\text{CO}_2$  and therefore  $p\text{CO}_2$ . A recent study on the geochemical  
571 characterization of geothermal systems pointed out that the CO<sub>2</sub> trapping mechanism is mainly

572 controlled by reservoir temperature (Elidemir and Güleç, 2018). In our studied area, we found  
573 increasing reservoir  $f\text{CO}_2$  with increasing reservoir temperature (Figure 7). The thermal waters  
574 with intermediate reservoir temperature (70 to 90°C) show the lowest uncertainty on the  
575 variation of  $f\text{CO}_2$  between depth and the surface ( $\Delta f\text{CO}_2$ ) with the two mineral buffers (dolomite  
576 only and assemblage of carbonates and alumino-silicates). Higher uncertainty on  $\Delta f\text{CO}_2$  is  
577 observed for the thermal springs with the higher reservoir temperature (120-140°C): carbonates  
578 and alumino-silicates buffer predicts higher  $\Delta f\text{CO}_2$  than dolomite as mineral buffer. The  
579 thermal waters with the lowest reservoir temperature also show a large uncertainty in  $\Delta f\text{CO}_2$   
580 but higher  $\Delta f\text{CO}_2$  is assessed considering dolomite equilibrium in the reservoir rather than  
581 equilibrium with carbonates and alumino-silicates. The results of these highly-simplified  
582 mineralogical systems suggest that dolomite tends to equilibrate at low temperature whereas  
583 more silicates might be involved at high temperature leading respectively to higher uncertainty  
584 in  $f\text{CO}_2$ . The difference in  $\Delta f\text{CO}_2$  between low and high temperature with respect to the  
585 considered mineral buffers might also be interpreted by the large uncertainty in thermodynamic  
586 data at the system temperature conditions.

587

### 588 5.3 Implications for sustainability of geothermal energy in the Central Betic 589 Cordillera

590 In order to estimate the environmental impact associated with the  $\text{CO}_2$  degassing of the  
591 investigated thermal waters, the  $\text{CO}_2$  emissions generated by these thermal systems were  
592 estimated for potential household heating purpose and were compared to those produced by a  
593 natural gas heating system. The average household energetic consumption ( $Q$ ) for heating  
594 system of a 100 m<sup>2</sup> house in Western Europe is 11,600 kWh/yr, equivalent to  $4.18 \times 10^{10}$  J/yr  
595 (Lapillonne et al., 2014).

596 Using this average household energetic consumption, we can estimate the amount of  $\text{CO}_2$

597 ( $n_{CO_2}$ ) that would be emitted from a natural gas furnace used to heat a 100 m<sup>2</sup> house (Equation  
598 3).

$$(n_{CO_2})_{emitted} = (n_{CH_4})_{consumed} = \frac{Q}{HHV} \quad (3)$$

599 where HHV is the higher heating value of methane (891 kJ/mol). Hence, a natural gas furnace  
600 would consume  $4.69 \times 10^4$  mol of CH<sub>4</sub> and would hence produce the equal amount of CO<sub>2</sub>.

601 This value can be then compared to the amount of CO<sub>2</sub> that would be produced by the use  
602 of the geothermal energy of the thermal springs in the Betic Cordillera area. If we first consider  
603 the ideal case of a thermal water with reservoir temperature ( $T_{depth}$ ) equivalent to the maximum  
604 temperature of the heating system ( $T_{depth} = T_{max} = 60^\circ C$ ), the amount of water that has to be  
605 pumped to heat a 100 m<sup>2</sup> house,  $n_{water}$ , expressed in mol, can be estimated according to the  
606 following equation:

$$n_{water} = \frac{Q}{Cp_{water} * \Delta T} \quad (4)$$

607 where Q is the average value of household energetic consumption,  $Cp_{water}$  is the isobaric heat  
608 capacity of water and  $\Delta T$  is the temperature range of the internal heating cycle (20°C with  $T_{max}$   
609 = 60°C and  $T_{min} = 40^\circ C$ ).

610 Assuming a constant  $Cp_{water}$  of 75.4 J/mol/K and an efficiency of the heat exchanger of 100 %,  
611 the necessary quantity of water to heat a 100 m<sup>2</sup> house would therefore be  $2.77 \times 10^7$  mol.

612 We can assess the amount of water that has to be pumped for the two other groups of  
613 thermal waters considered earlier with reservoir temperature ( $T_{depth}$ ) of 90 and 140°C using to  
614 the following equation:

$$(n_{water})_{pumped} = \frac{Q}{Cp_{water} * (T_{depth} - T_{max})} \quad (5)$$

615 We found that the amount of water that has to be pumped is  $1.85 \times 10^7$  and  $6.15 \times 10^6$  mol  
616 respectively. Using the average CO<sub>2</sub> concentration estimated for each thermal water groups ( $2$   
617  $\times 10^{-4}$ ,  $5 \times 10^{-3}$ ,  $8 \times 10^{-1}$  mol/L), we can estimate the amount of natural CO<sub>2</sub> degassed during

618 household heating ranging between  $1.0 \times 10^2$  and  $8.9 \times 10^4$  mol. The estimated amount of  $\text{CO}_2$   
619 released from geothermal waters used in heating is lower by 1 to 2 orders of magnitude than  
620 the amount of  $\text{CO}_2$  generated by a natural gas furnace for the two first groups of thermal waters  
621 ( $T_{\text{depth}} < 130^\circ\text{C}$ ) (Figure 11). However, similar quantity of  $\text{CO}_2$  could be released from the  
622 thermal waters with the higher  $T_{\text{depth}}$  as those produced by a natural gas furnace.

623 These estimations of  $\text{CO}_2$  emissions in this simple practical application of heating a  $100 \text{ m}^2$   
624 house show that the geothermal energy is globally a cleaner energy than natural gas but might  
625 release as much  $\text{CO}_2$  as a natural gas furnace in certain conditions (high reservoir temperature  
626 and  $f\text{CO}_2$ ). These estimations are based on possible gas venting during the heat production,  
627 which are usually neglected in life cycle assessment of carbon intensity of geothermal system  
628 (McCay et al., 2019).

629 These estimations, giving us the order of magnitude of  $\text{CO}_2$  emissions that could be generated  
630 by the investigated geothermal systems, lead to explore possible exploitations of the geothermal  
631 resource. Direct electricity production (e.g. enhanced geothermal systems) might be considered  
632 for the thermal waters with the highest reservoir temperature ( $T_{\text{depth}} = 140^\circ\text{C}$ ) emitting large  
633 quantity of  $\text{CO}_2$ . This use would have to be coupled to  $\text{CO}_2$  capture and storage to make it a  
634 renewable and clean energy.

635

## 636 **6 Conclusions**

637 Our study provides the first characterization of the reservoir conditions (T, P, and  
638 geochemistry) for the thermal waters in the central part of the Betic Cordillera. The  $f\text{CO}_2$  at  
639 depth were tentatively assessed with both a chemical geobarometer and direct geochemical  
640 simulations. The variation of  $f\text{CO}_2$  ranges from approximately  $6 \times 10^{-3}$  to  $10^2$  at the scale of  
641 the area. Based on the geology of the thermal water locations and the results of the  
642 geothermometrical and thermodynamic geochemical simulations three groups of waters have

643 been determined.

644 The group of the thermal waters located in the sedimentary basin has estimated reservoir  
645 temperatures ranging from approximately 70 to 90°C and  $f\text{CO}_2$  varying between  $6 \times 10^{-2}$  and  
646  $6 \times 10^{-1}$ . The estimated variations in  $f\text{CO}_2$  between the depth and the surface ( $\Delta f\text{CO}_2$ ) were quite  
647 similar considering both the dolomite buffer and carbonate/alumino-silicate buffer for the  
648 thermal waters in the Granada Basin. A mineral assemblage buffering at depth mainly  
649 composed of carbonates, evaporites, and quartz characterizes this system.

650 The group of waters located in the graben in the Alpujarride Complex presents the lowest  
651 reservoir temperature of 55-60°C and  $f\text{CO}_2$  ranging from  $5 \times 10^{-3}$  to  $7 \times 10^{-2}$ , depending of the  
652 considered buffering minerals. The  $\Delta f\text{CO}_2$  between the depth and the surface is higher with the  
653 dolomite buffer than with the carbonate and alumino-silicate buffer. The buffering mineral  
654 assemblage at depth is estimated to be carbonates, quartz, and Ca alumino-silicates.

655 On the other hand, the group of waters located at contact with metamorphic complexes  
656 shows the highest reservoir temperature of 130 – 140°C and  $f\text{CO}_2$  ranging from approximately  
657 1 to 100. The  $\Delta f\text{CO}_2$  between the depth and the surface is lower with the dolomite buffer than  
658 with the carbonate and alumino-silicate buffer. The buffering mineral assemblage in the  
659 reservoir might be dolomite, quartz, Mg and Ca alumino-silicates.

660 This study highlights the importance of evaluating the mineral buffers in the reservoir  
661 conditions of the geothermal systems. The mineral assemblage at equilibrium in the reservoir  
662 conditions constrains the estimated  $\text{CO}_2$  generation and release at depth. In the case study of  
663 the Central Betic Cordillera,  $\text{CO}_2$  degassing is more constrained in the evaporitic basins thanks  
664 to a strong carbonate/evaporite/quartz buffer than in the surrounding areas of the basins where  
665 the alumino-silicates play a non-negligible role. Moreover, we pointed out the key role of the  
666 reservoir temperature on the estimation of the reactions between  $\text{CO}_2$ , water, and rocks for the  
667 geothermal systems in sedimentary basins.

668           The estimations of CO<sub>2</sub> emissions generated by the thermal systems for potential  
669 household heating purpose indicate that the geothermal energy is globally a clean energy but  
670 might release as much CO<sub>2</sub> as a natural gas furnace for the thermal waters with the highest  
671 reservoir temperature. This study points out the importance to estimate properly the amount of  
672 CO<sub>2</sub> degassing in geothermal waters depending of the reservoir conditions. Our results  
673 highlight the importance of considering geochemical estimates for heat exchanger design. In  
674 the case of thermal waters with the highest temperatures and high CO<sub>2</sub> contents, heat  
675 exchangers allowing to maintain fluids under pressure might be preferred to avoid CO<sub>2</sub> release  
676 in the atmosphere.

677

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887

888

889 List of the figures:

890 Figure 1: Location of the thermal water samples in the Central Betic Cordillera and geological  
891 map of the area modified after Sanz de Galdeano and Peláez (2011).

892 *Figure 2: Piper diagram of the thermal waters from Central Betic Cordillera. Circles and*  
893 *triangles correspond to springs and wells respectively.*

894 Figure 3: Evolution of the mineral saturation indices with temperature for the thermal waters  
895 located in the evaporitic Granada Basin by geothermometrical modeling.

896 Figure 4: Evolution of the mineral saturation indices with temperature for the thermal waters  
897 located (a) in the graben in the Alpujarride Complex and (b) on the contacts of the  
898 metamorphic complexes.

899 Figure 5: Relationship between  $f\text{CO}_2$  and temperature ( $^{\circ}\text{C}$ ), for the outlet (crosses) and  
900 reservoir (circles) conditions considering dolomite equilibrium in depth.

901 Figure 6: Relationship between  $f\text{CO}_2$  and temperature ( $^{\circ}\text{C}$ ) for the outlet (crosses) and  
902 reservoir (circles) conditions considering equilibrium with calcite, dolomite, quartz, kaolinite,  
903 and Mg-chlorite in depth.

904 Figure 7: Relationship between the variations of  $f\text{CO}_2$  calculated between steps 1 and 3 of the  
905 hydrogeochemical modeling,  $\Delta f\text{CO}_2$  and the reservoir temperature. The light gray squares  
906 correspond to equilibrium with dolomite and the dark gray squares with calcite, dolomite,  
907 quartz, kaolinite, and Mg-chlorite, both in the reservoir conditions. The variability in  $\Delta f\text{CO}_2$  is  
908 expressed for the three groups of waters with average reservoir temperature of:  $55^{\circ}\text{C}$  (blue),  
909  $85^{\circ}\text{C}$  (yellow), and  $135^{\circ}\text{C}$  (red).

910 Figure 8: Evolution of the mineral saturation indices with temperature for the thermal waters  
911 located in the evaporitic Granada Basin by geothermometrical modeling with theoretical  $\text{CO}_2$   
912 addition (1 mmol/L) to compensate possible  $\text{CO}_2$  outgassing during the ascent of the waters.

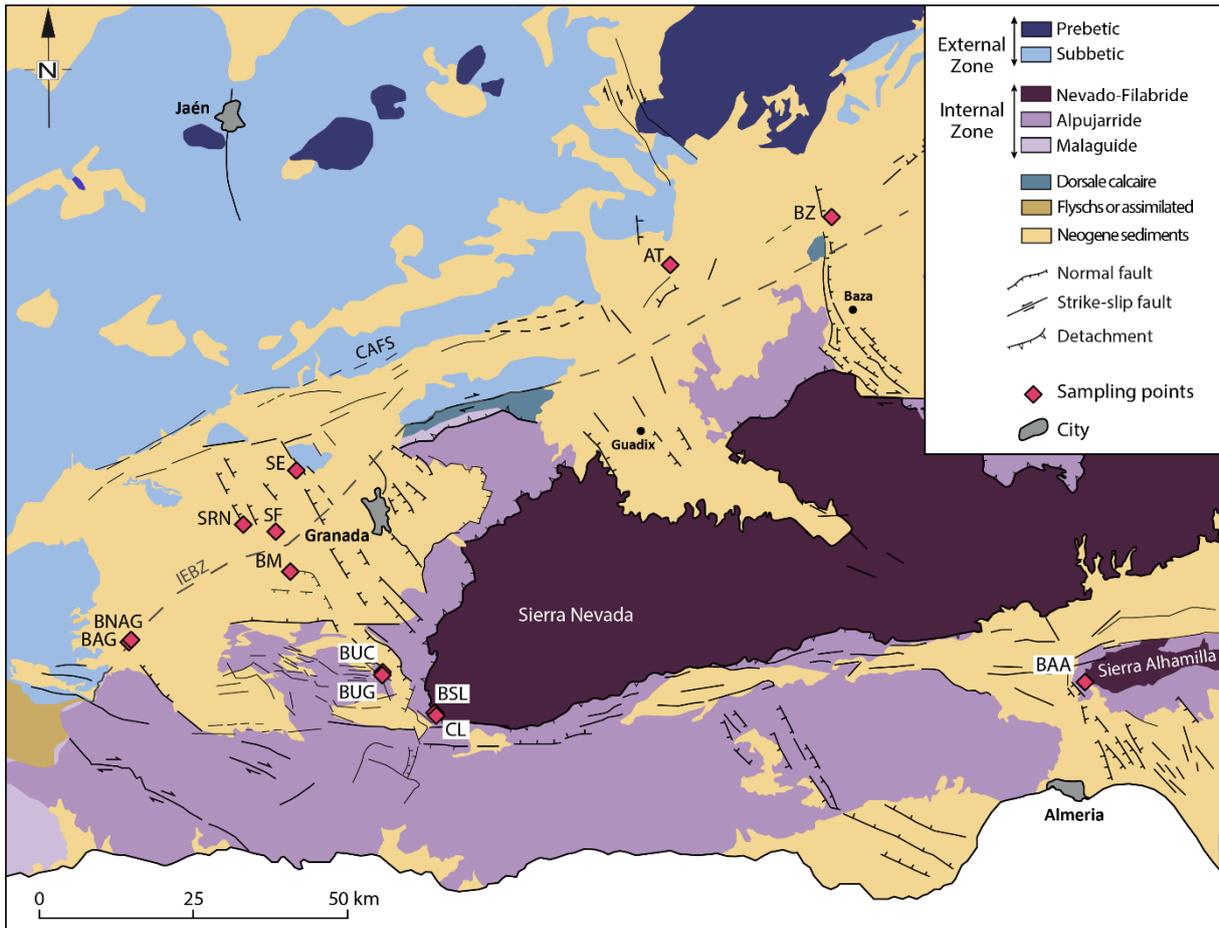
913 Figure 9: Evolution of the mineral saturation indices with temperature for the thermal waters  
914 located in the Valle de Lecrin graben by geothermometrical modeling with theoretical  $\text{CO}_2$   
915 addition (0.5 mmol/L) to compensate possible  $\text{CO}_2$  outgassing during the ascent of the waters

916 Figure 10: Evolution of the mineral saturation indices with temperature for the thermal waters  
917 located on the contacts of the metamorphic complexes. Geothermometrical modeling with  
918 theoretical  $\text{CO}_2$  addition to compensate possible  $\text{CO}_2$  outgassing during the ascent of the  
919 waters.

920 Figure 11: Comparison of  $\text{CO}_2$  emissions from heating a  $100\text{ m}^2$  house using the investigated  
921 thermal waters and a natural gas furnace.

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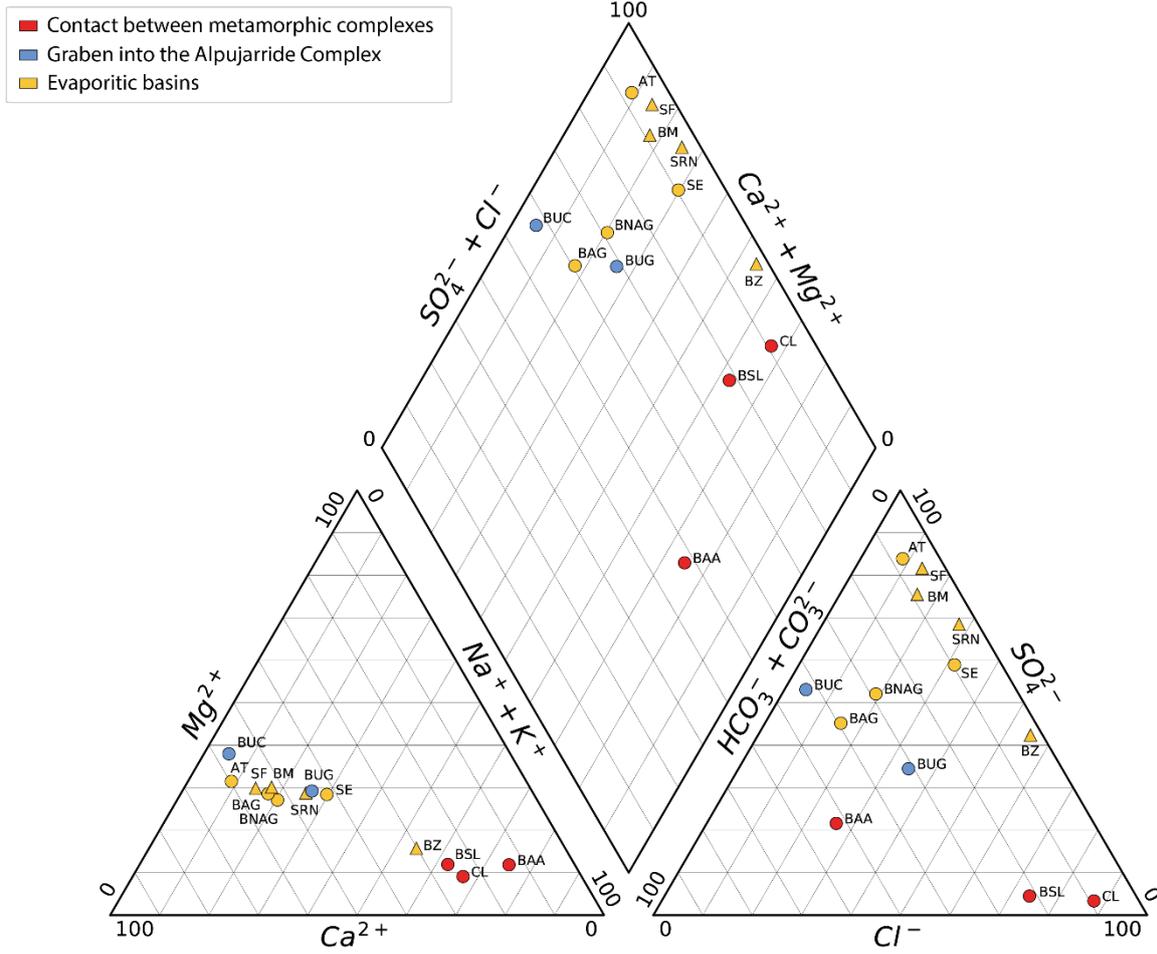
923 Figure 1



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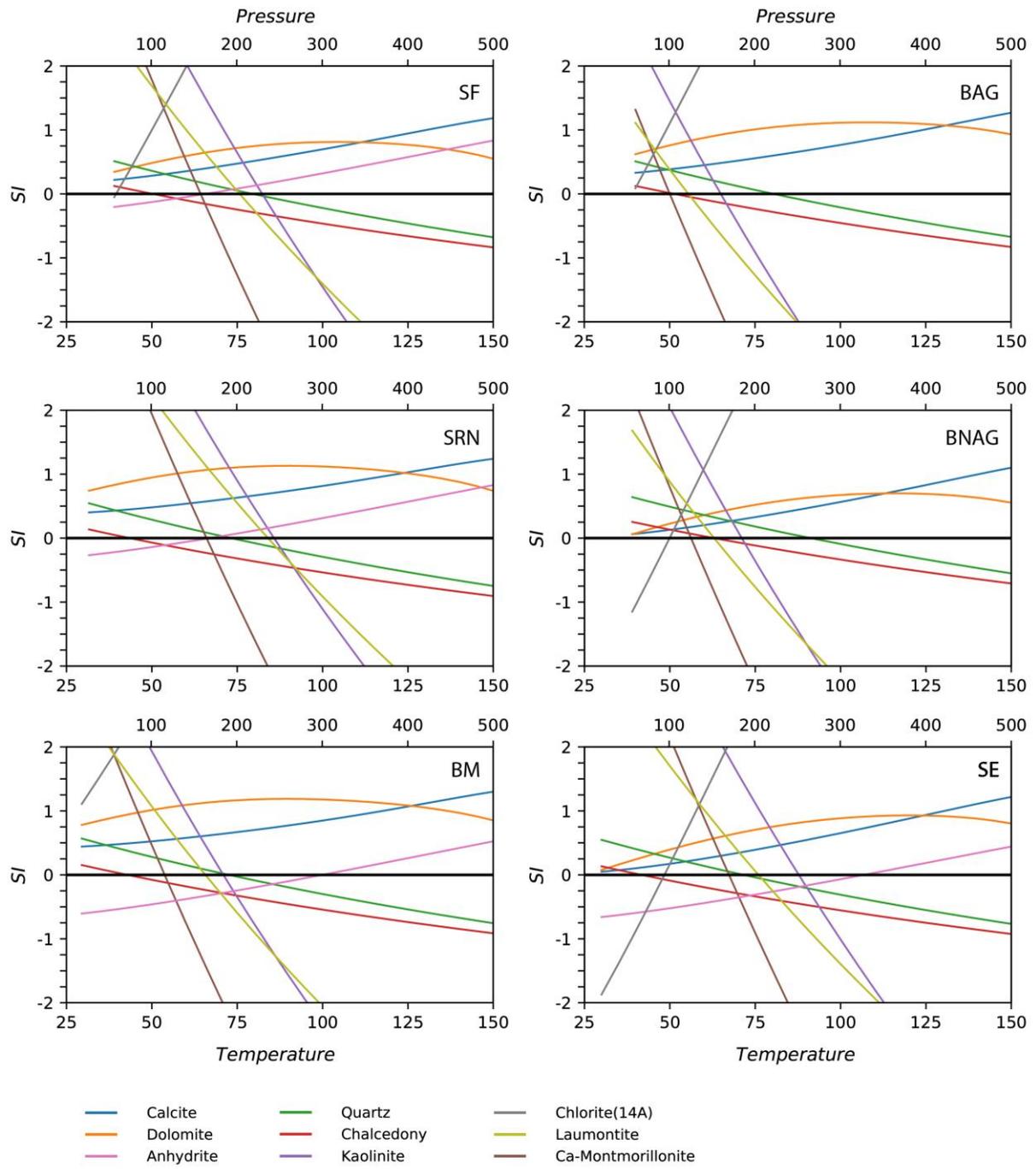
926 Figure 2



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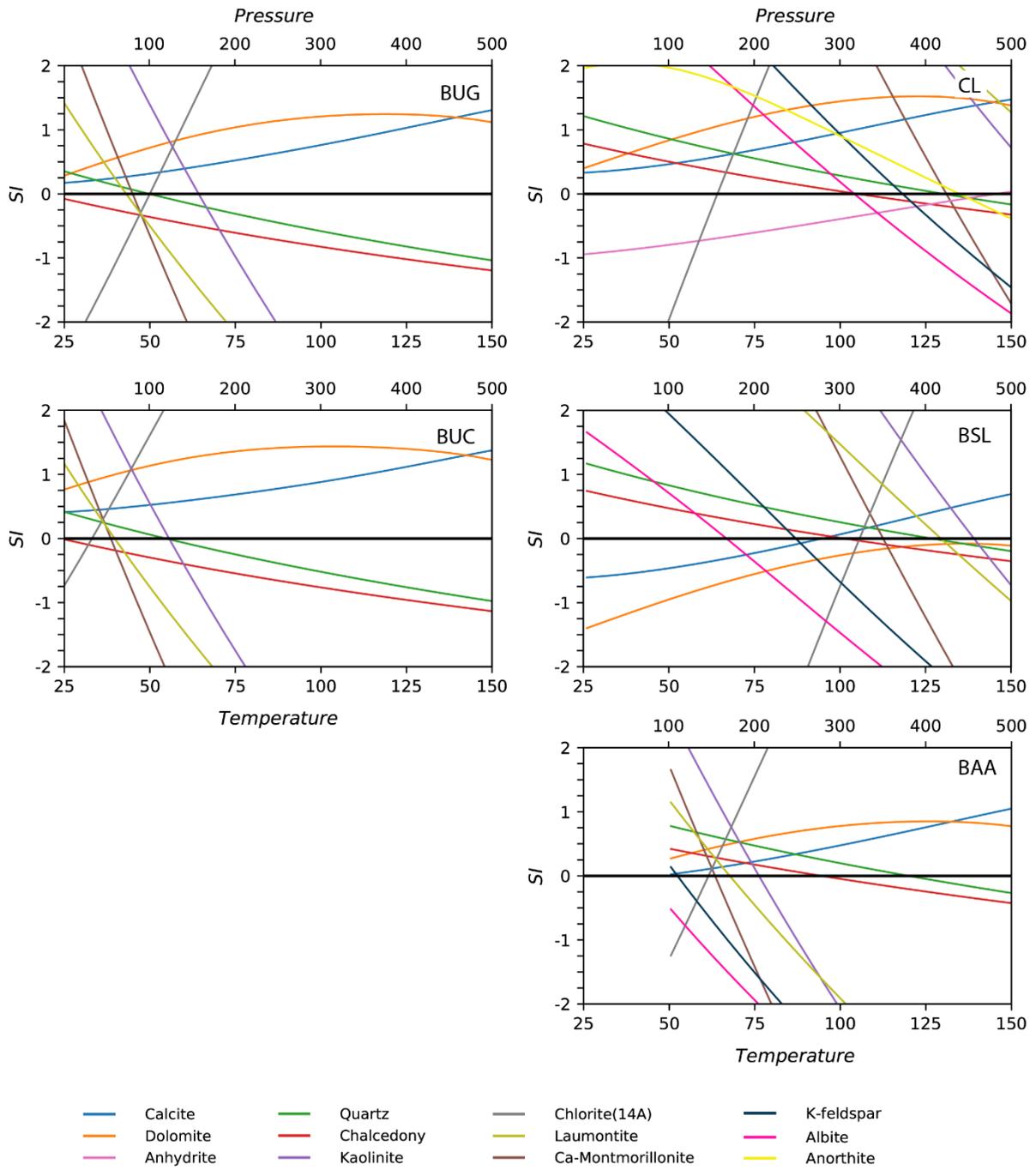
929 Figure 3



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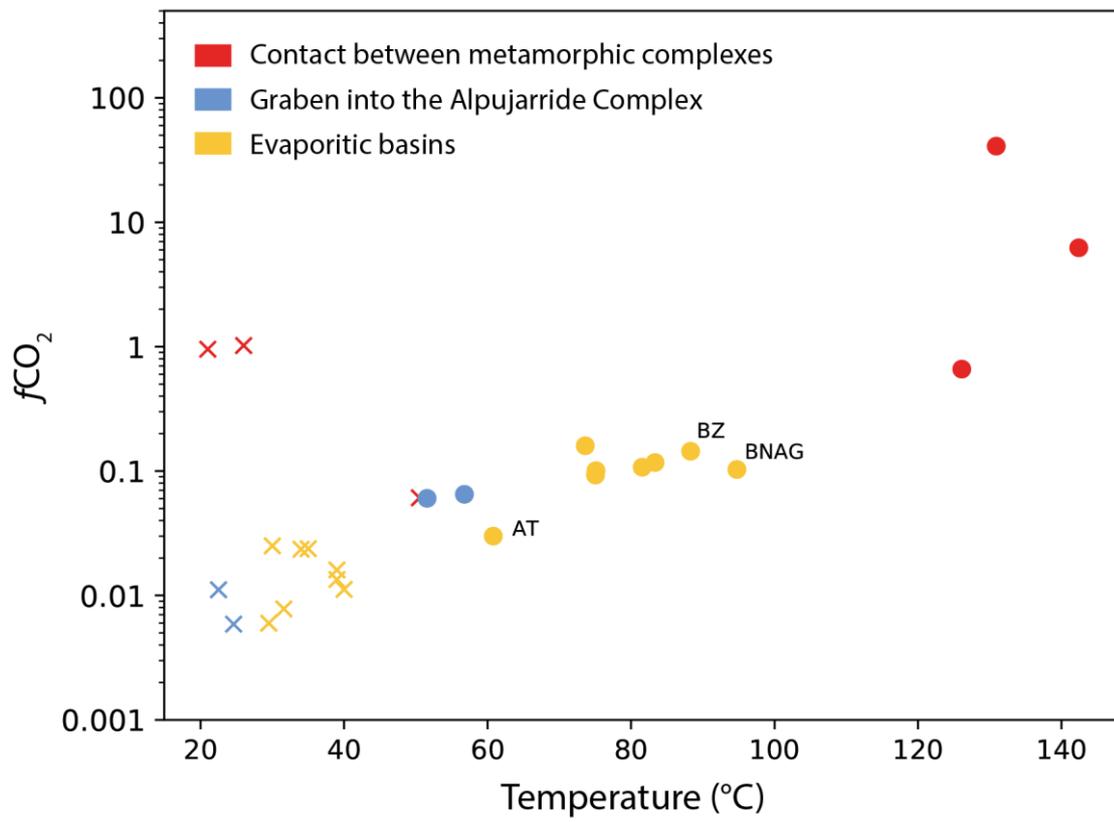
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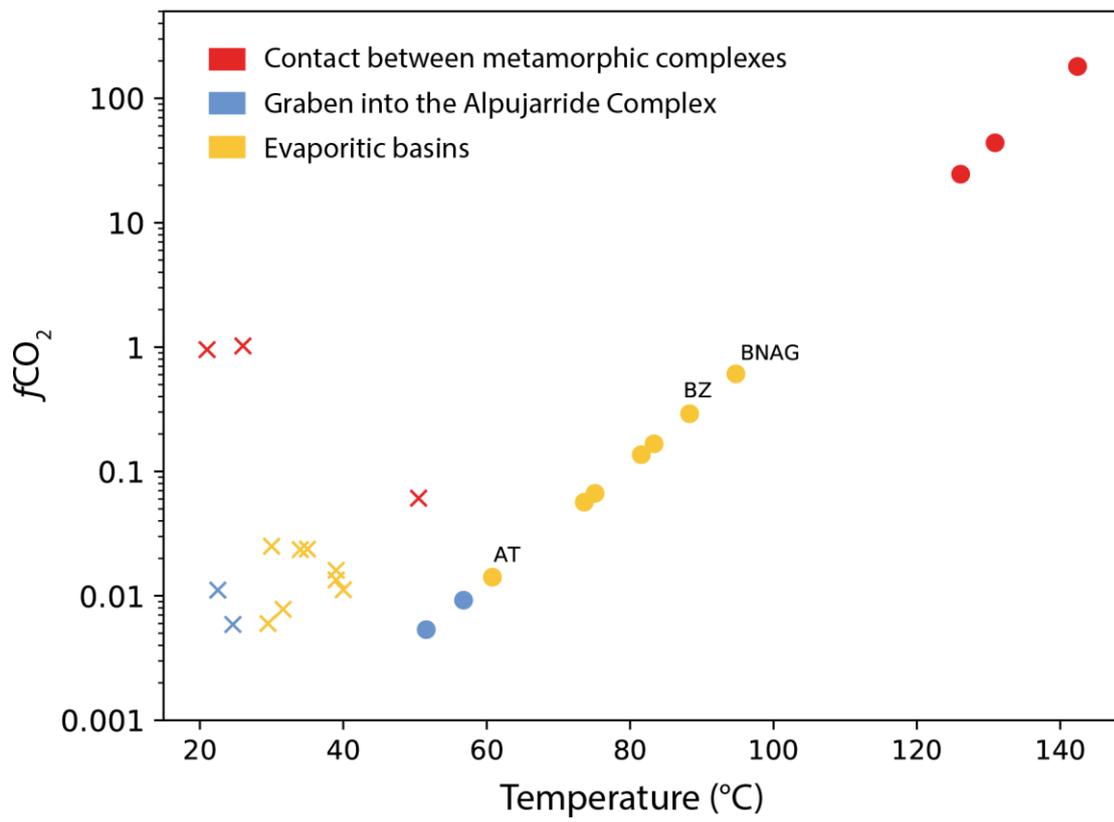
935 Figure 5



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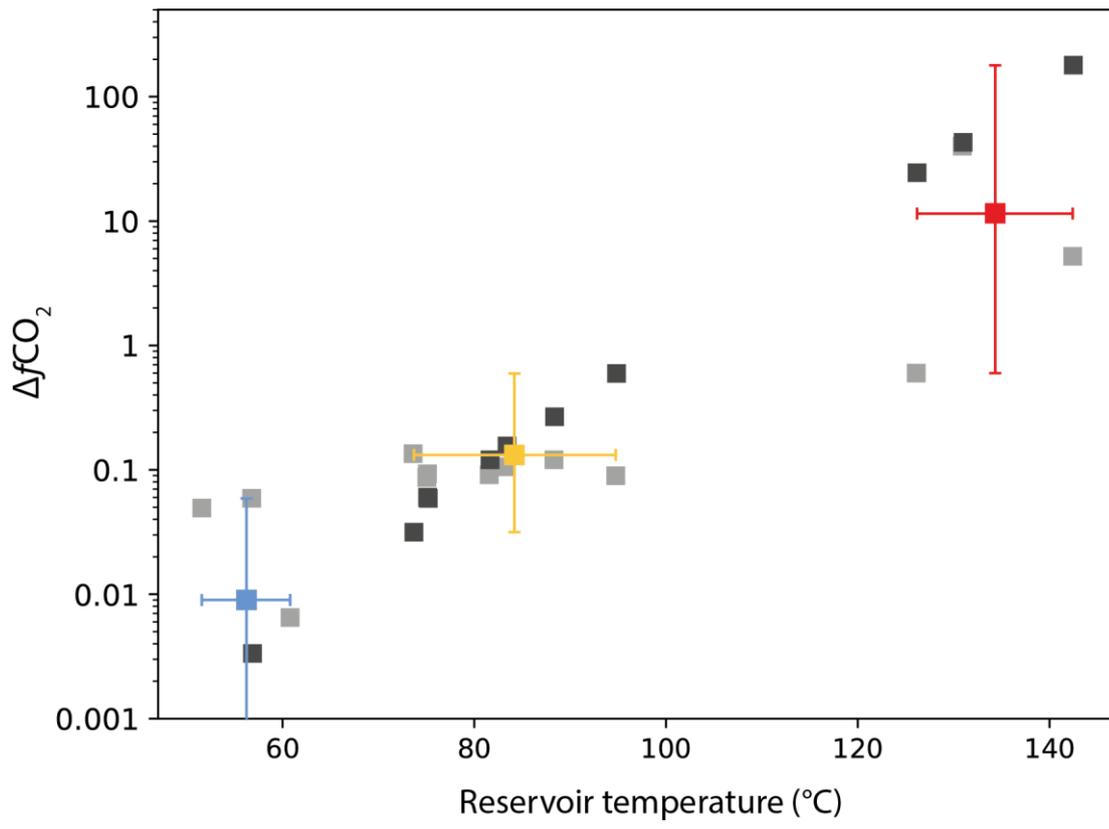
938 Figure 6



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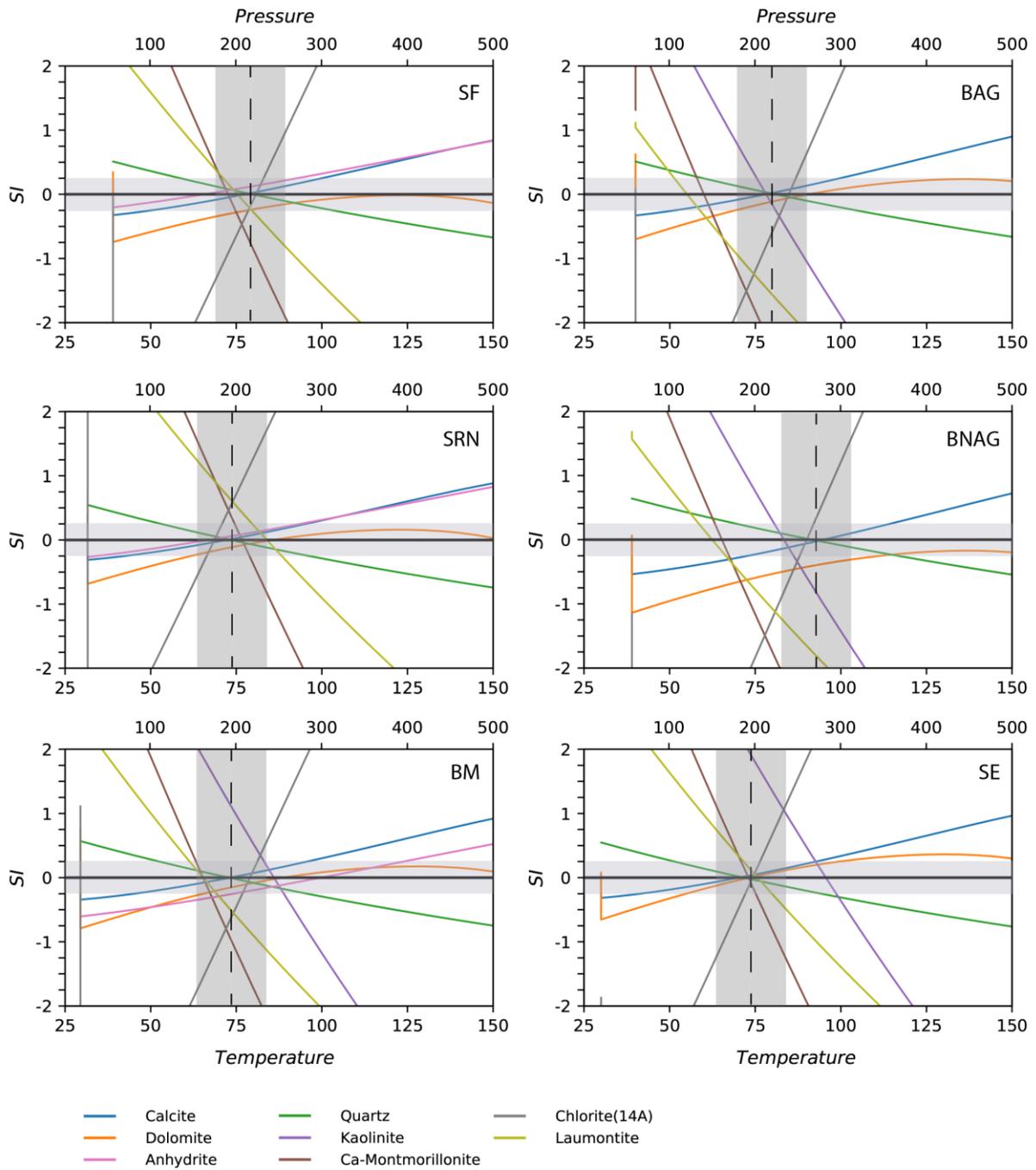
941 Figure 7



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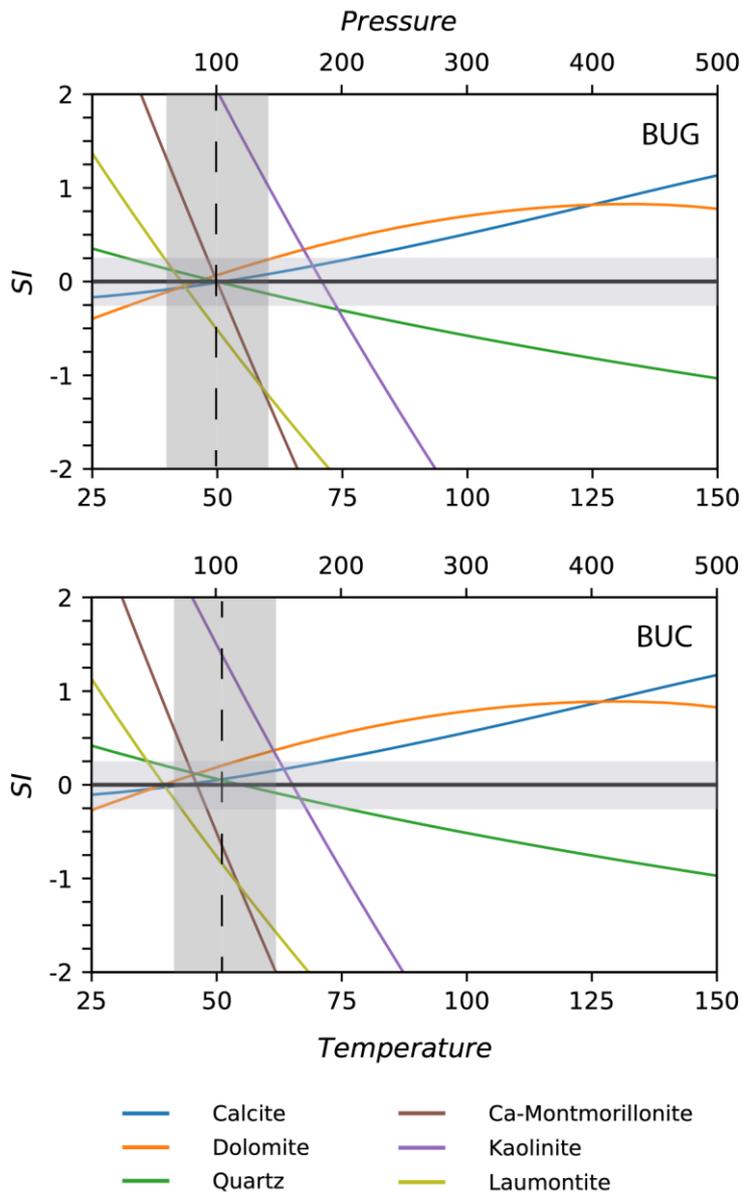
944 Figure 8



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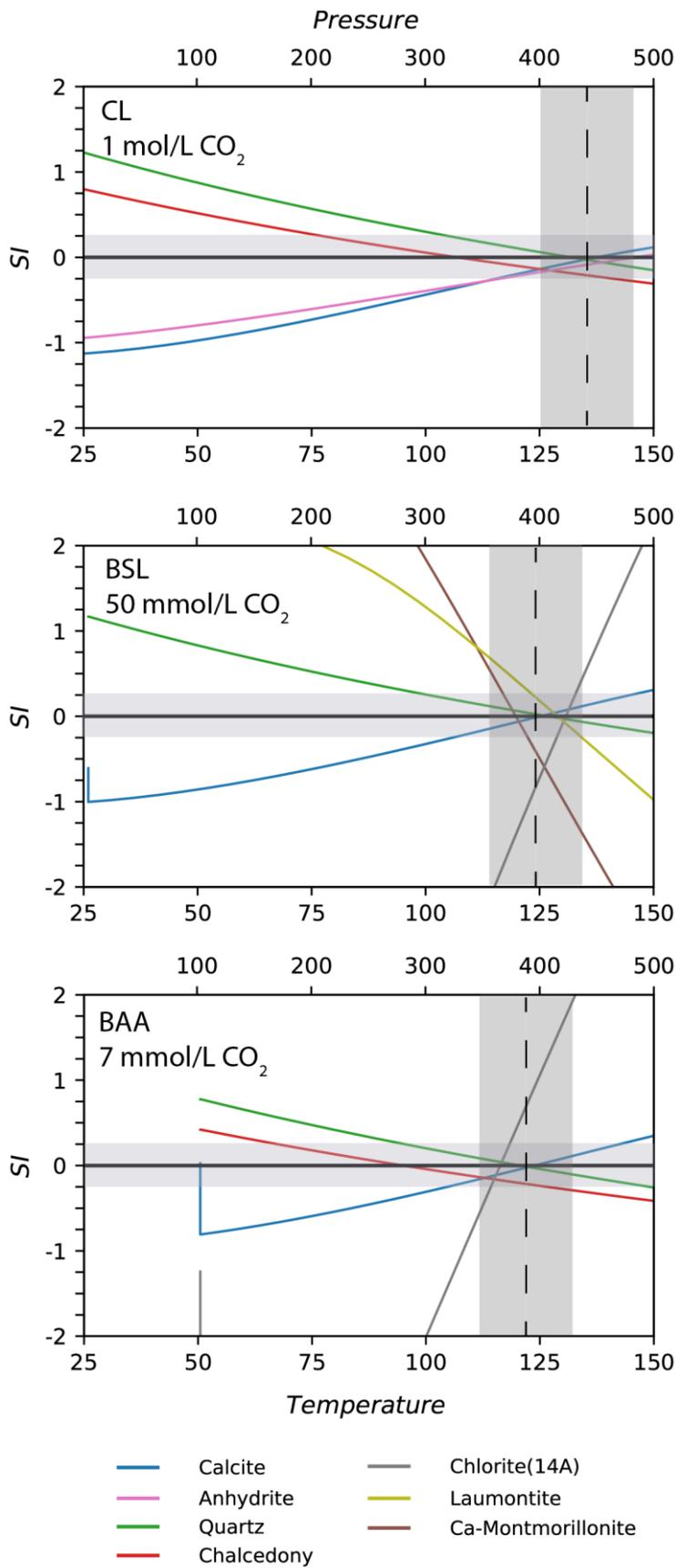
947 Figure 9



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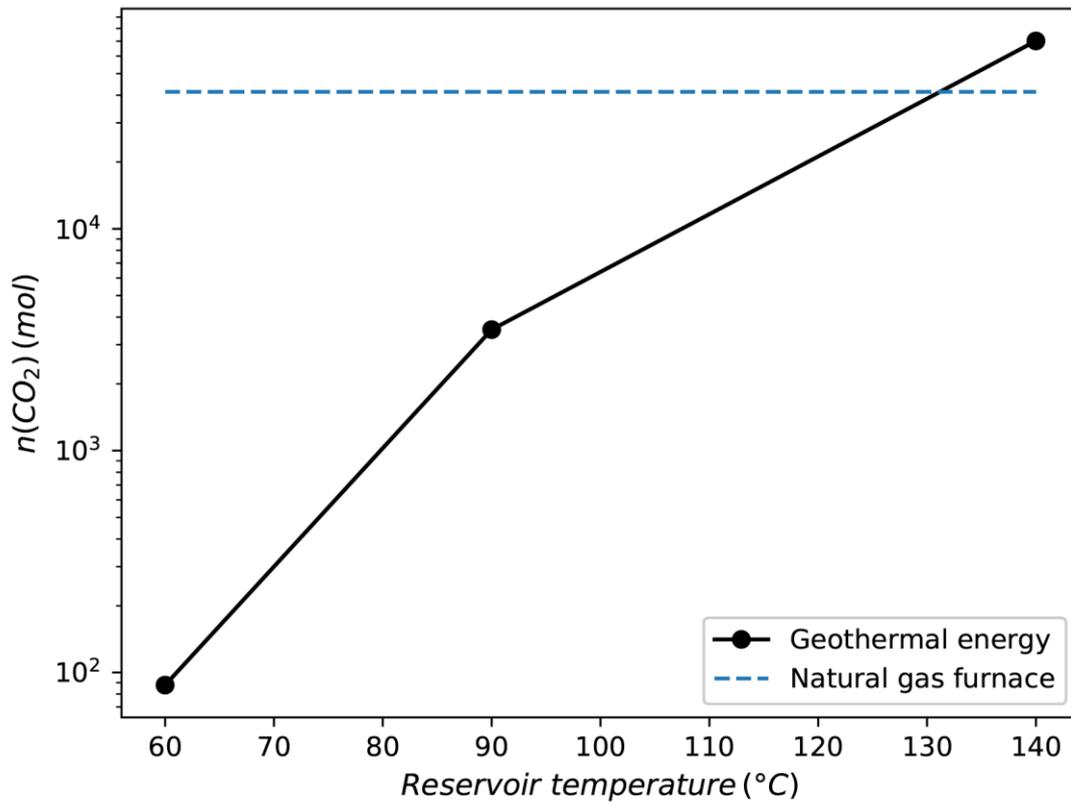
950 Figure 10



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953 Figure 11



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Sample and location	Code	Type	Depth	Temp.	pH	EC	Ca	Mg	Na	K	Alk.	Cl	SO <sub>4</sub>	Si	Al	Ba	Fe	Sr	TDS	CBE
			(m)	(°C)																
<i>Contacts metamorphic complexes</i>																				
Banos Salado de Lanjaron 36°55.4189'N; 3°29.5869'W	BSL	S		26	5.8	8.18	6.59	3.06	29.5	2.60	12.9	44.0	1.31	1.56	8.85E-03	1.04E-03	3.13E-01	0.19	3.72	7.29
Capuchina de Lanjaron 36°55.1523'N; 3°29.4182'W	CL	S		21	6.1	34.15	32.6	12.3	167	14.0	28.7	275	5.24	1.53	7.13E-02	7.34E-04	4.98E-01	0.62	18.17	7.40
Banos de Alhamilla 36°57.6531'N; 2°23.7875'W	BAA	S		51	7.1	1.92	0.88	0.78	9.65	0.23	7.93	3.99	1.64	1.38	4.92E-04	4.62E-04	9.66E-04	0.02	1.15	7.04
<i>Grabens into Alp. Complex</i>																				
Banos Urquizar Chico 36°58.3477'N; 3°34.5347'W	BUC	S		25	7.6	0.99	2.62	1.75	0.42	0.05	3.99	0.41	2.49	0.27	6.99E-04	2.28E-04	b.d.l	0.05	0.68	0.87
Banos Urquizar Grande 36°58.2261'N; 3°34.5854'W	BUG	S		23	7.3	1.50	2.92	1.92	3.22	0.22	4.21	4.66	2.33	0.24	1.23E-03	2.33E-04	b.d.l	0.04	0.91	1.49
<i>Evaporitic basin</i>																				
Banos de la Malaha 37°06.2946'N; 3°43.6034'W	BM	W	200	30	7.4	3.08	8.05	4.59	5.25	0.22	2.89	5.10	12.1	0.45	1.60E-03	1.18E-04	2.98E-02	0.16	2.13	2.35
Santa Fe 37°09.3813'N; 3°45.2023'W	SF	W	510	39	7.0	4.69	13.7	7.30	6.82	0.34	2.58	7.15	21.1	0.53	2.09E-03	5.10E-05	6.50E-03	0.16	3.38	2.73
Sondeo Romilla la Nueva 37°10.0216'N; 3°48.8567'W	SRN	W	740	32	7.3	6.13	14.3	8.80	15.5	0.41	2.72	18.9	23.2	0.45	5.13E-03	8.92E-05	4.25E-02	0.17	4.26	4.48
Sierra Elvira 37°13.7033'N; 3°43.3372'W	SE	S		30	6.9	3.82	7.80	5.28	10.8	0.27	3.77	12.4	11.6	0.43	3.74E-03	1.35E-04	b.d.l	0.11	2.52	2.93
Banos Alhama de Granada 37°01.1221'N; 3°58.9970'W	BAG	S		40	7.4	1.13	2.44	1.30	1.45	0.15	3.59	1.39	2.05	0.55	6.85E-04	3.49E-04	b.d.l	0.04	0.67	0.02
Banos Nuevo Alhama de Granada 37°01.3410'N; 3°58.7548'W	BNAG	S		39	7.2	1.24	2.63	1.36	1.87	0.17	2.89	1.89	2.60	0.72	6.95E-04	2.71E-04	4.42E-04	0.06	0.73	0.08
Alicun de las Torres 37°30.5418'N; 3°06.4172'W	AT	S		34	6.7	2.24	8.25	4.35	2.32	0.12	2.06	2.32	11.4	0.31	8.89E-04	1.38E-04	b.d.l	0.11	1.83	0.87
Banos de Zujar 37°34.556'N; 2°49.463'W	BZ	W	-	35	6.8	12.8	15.8	8.01	56.1	0.62	2.91	61.4	23.3	0.62	1.71E-02	1.98E-04	5.74E-03	0.23	6.80	3.03

Table 1: Sample details including sample location and water chemistry. Location of sampling points refer to WGS84 system. Type of water points: S = spring; W = well. EC is electrical conductivity in mS/cm. Concentrations of dissolved elements and TDS are expressed in mmol/kg of solution and in mg/L respectively. CBE (Charge Balance Error) is expressed in %. b.d.l = below detection limit.

Sample	Calcite	Dolomite	Gypsum	Anhydrite	Halite	Quartz	Chalcedony	K-feldspar	Kaolinite	Albite	Anorthite	Ca-Mont.	CO <sub>2</sub> (g)	fCO <sub>2</sub> (g)
<b><i>Contacts metam. complexes</i></b>														
BSL	-0.61	-1.39	-1.40	-1.61	-4.66	1.14	0.74	3.15	8.02	1.65	-1.03	7.96	0.01	1.03
CL	0.32	0.34	-0.63	-0.86	-3.21	1.25	0.83	5.42	10.44	3.90	1.93	11.01	-0.02	0.96
BAA	0.02	0.27	-1.83	-1.89	-6.17	0.74	0.42	0.14	2.52	-0.52	-2.79	1.65	-1.21	0.061
<b><i>Graben into Alp. Complex</i></b>														
BUC	0.41	0.75	-1.19	-1.42	-8.46	0.40	-0.01	-0.67	3.23	-2.31	-2.68	1.90	-2.23	0.006
BUG	0.16	0.23	-1.21	-1.44	-6.52	0.37	-0.05	0.18	4.36	-1.25	-2.25	3.05	-1.95	0.011
<b><i>Evaporitic basin</i></b>														
BM	0.43	0.78	-0.37	-0.57	-6.33	0.54	0.15	0.56	4.06	-0.57	-1.42	3.14	-2.22	0.006
SF	0.21	0.34	-0.07	-0.22	-6.13	0.48	0.12	0.37	4.18	-0.73	-1.20	3.23	-1.79	0.016
SRN	0.39	0.74	-0.06	-0.25	-5.35	0.52	0.14	1.15	5.12	0.25	-0.35	4.34	-2.10	0.008
SE	0.04	0.07	-0.43	-0.63	-5.65	0.52	0.13	0.91	5.65	0.00	-0.81	4.81	-1.60	0.025
BAG	0.32	0.62	-1.30	-1.44	-7.41	0.48	0.12	-0.39	2.49	-1.80	-2.54	1.31	-1.95	0.011
BNAG	0.06	0.06	-1.18	-1.33	-7.17	0.61	0.25	0.07	3.20	-1.29	-2.26	2.24	-1.87	0.013
AT	-0.32	-0.73	-0.37	-0.55	-7.03	0.31	-0.06	-0.83	4.02	-1.99	-2.45	2.63	-1.63	0.024
BZ	0.01	-0.07	-0.10	-0.27	-4.32	0.62	0.25	2.00	6.90	1.52	0.84	6.46	-1.62	0.024

Table 2: Saturation indices (SI) of the main mineral phases of interest in the investigated area. CO<sub>2</sub>(g) corresponds to the log<sub>10</sub> of CO<sub>2</sub> fugacity (fCO<sub>2</sub>). SI were calculated with the PHREEQC code at the outlet temperature (measured in the field).

Sample	O <sub>2</sub> cc/L	N <sub>2</sub> cc/L	CO <sub>2</sub> cc/L	pCO <sub>2</sub> atm	H <sub>2</sub> ppm	CO ppm	CH <sub>4</sub> ppm	TDIC mmol/L	δ <sup>13</sup> C <sub>(TDIC)</sub> ‰	δ <sup>13</sup> C <sub>(CO<sub>2</sub>)</sub> ‰
<i>Contacts metam. complexes</i>										
BSL	0.07	1.74	576	0.78	6.82E-04	2.88E-04	5.29E-03	46.6	-5.2	-6.6
CL	0.08	1.94	597	0.71	b.d.l	1.41E-04	8.66E-05	63.0	-4.7	-7.5
BAA	1.49	12.1	39.4	0.088	9.72E-04	3.16E-04	1.53E-02	9.1	-9.0	-13.6
<i>Graben into Alp. Complex</i>										
BUG	1.57	18.6	16.2	0.020	b.d.l	2.69E-05	6.36E-04	4.6	-9.0	-16.2
<i>Evaporitic basin</i>										
SF	1.81	17.0	9.51	0.017	b.d.l	3.51E-05	1.38E-02	2.9	-1.5	-6.6
SE	0.13	18.3	22.2	0.033	b.d.l	b.d.l	2.39E-04	4.5	-8.8	-14.5
BAG	0.67	17.6	10.7	0.020	b.d.l	b.d.l	7.43E-04	3.8	-7.6	-13.3
AT	0.44	16.7	27.0	0.044	1.10E-03	7.03E-05	2.48E-05	2.7	-5.0	-9.8
BZ	0.62	13.8	16.3	0.027	1.51E-03	2.02E-04	3.37E-02	3.5	-3.4	-8.4

Table 3: Dissolved gases and carbon isotopic composition of the selected investigated thermal waters. TDIC was calculated using PHREEQC. b.d.l = below detection limit.

Sample	Outlet temp.	SiO <sub>2</sub> -Quartz				SiO <sub>2</sub> -chalcedony		Ca/Mg	<i>f</i> CO <sub>2</sub>
		Michard (1979)	Verma (2000b)	Fournier and Potter (1982)	Fournier (1977)	Arnorsson (1983)	Michard (1990)	Chiodini (1995a)	Chiodini (1995a)
<i>Contacts metam. complexes</i>									
BSL	26	145	143	146	139	115	102	86	16.34
CL	21	133	130	134	129	103	92	88	23.82
BAA	51	128	124	128	127	97	87	60	5.63
<i>Graben into Alp. Complex</i>									
BUC	25	57	47	57	62	26	24	75	0.54
BUG	23	52	42	51	58	21	20	74	0.66
<i>Evaporitic basin</i>									
BM	30	76	67	76	79	45	41	81	0.08
SF	39	83	74	83	85	52	47	87	0.05
SRN	32	76	67	76	79	45	41	75	0.04
SE	30	74	66	75	78	43	40	71	0.16
BAG	40	84	76	85	86	53	48	89	0.74
BNAG	39	96	89	97	97	65	59	91	0.38
AT	34	61	52	61	66	30	28	88	0.05
BZ	35	90	82	90	91	58	53	84	0.06

Table 4: Temperature (°C) obtained with selected geothermometers and fugacity of CO<sub>2</sub> (*f*CO<sub>2</sub>) obtained with Chiodini et al. (1995a)'s geobarometer.

