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C. Lix, P. Zuddas, X. Guichet, J. Benavente, J.A. Luque-Espinar, et al.. Role of CO₂ in low to medium enthalpy geothermal systems in the Central Betic Cordillera (Spain). *Science of the Total Environment*, 2020, 705, pp.135652. 10.1016/j.scitotenv.2019.135652 . hal-02447029

HAL Id: hal-02447029

<https://hal-ifp.archives-ouvertes.fr/hal-02447029>

Submitted on 22 Apr 2020

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Role of CO₂ in low to medium enthalpy geothermal systems in the Central Betic Cordillera (Spain)

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Abstract

There is growing interest in geothermal energy, which is considered as an efficient energy solution to mitigate rising atmospheric CO₂. Besides known high enthalpy geothermal systems, increasing attention is paid to low temperature geothermal systems, as they are suitable for local use. Although geothermal production seems to be an environmentally advantageous renewable energy, it might result in significant CO₂ emissions. In this study, we investigate the relationship between temperature, fugacity of CO₂ ($f\text{CO}_2$), and mineral buffers in the reservoir conditions, taking the low- to medium- enthalpy thermal waters in the Central Betic Cordillera as case study. Using geochemical modeling, three main groups of waters have been identified depending on temperature, buffering mineral assemblage, and $f\text{CO}_2$ in their reservoir. A group of waters with a reservoir temperature ranging from 70 to 90°C and located in the intramountain sedimentary basins shows a $f\text{CO}_2$ in depth ranging from $\sim 6 \times 10^{-2}$ and 6×10^{-1} . The reservoir chemistry of this water group seems to be mainly controlled by carbonates and evaporites displaying a $f\text{CO}_2$ variation between depth and surface ($\Delta f\text{CO}_2$) of 10^{-1} . Another intermediate group of waters, located in an active extension zone, displays lower temperature (50-60°C) and $f\text{CO}_2$ in the reservoir (from 10^{-3} to 10^{-2}). Finally, the third group of waters, located on the metamorphic complexes contacts, show the highest estimated temperatures (130 - 140°C) and $f\text{CO}_2$ in the reservoir (1 to 10^2). The two latter groups suggest increasing buffering effect of alumino-silicates, in addition to carbonates and quartz. Therefore, we evidenced a strong relationship between temperature and $f\text{CO}_2$ in the reservoir as well as the potential mineral buffers. We discussed the potential of geothermal systems as clean energy source based on the estimation of the CO₂ emissions generated by the investigated thermal systems for a practical case of household heating.

1 Introduction

Geothermal energy has been widely developed across Europe and the World for the last 50 years, with main focus on the conventional high-temperature geothermal reservoirs. Nevertheless, low (30°C to 100°C) to medium (100 – 150°C) enthalpy geothermal systems have been recently subject to increasing interest (Blasco et al., 2017; Capecchiacci et al., 2015; Fusari et al., 2017) as they may be easily exploited for ground-source heat pump or greenhouses (Battistel et al., 2016). In the current context of global warming and energy transition, geothermal is generally considered to be an environmentally advantageous renewable source of energy. However, emissions of greenhouse gases, and especially CO₂, might be generated by geothermal exploitation. Although CO₂ release from geothermal electricity production has been shown to be significantly lower than from fossil fuel (Ármansson, 2003; Hunt, 2001), the efficiency of this energy to mitigate rising atmospheric CO₂ is a major concern for societal acceptance. Scientific research programs have been recently dedicated to the development of cost-effective non-carbon emitting geothermal energy (e.g., “Geothermal Emission Gas Control”, Horizon 2020, European program). The studies on the CO₂ emissions in geothermal systems are mainly dedicated to volcanic geothermal systems (e.g., Ármansson, 2018; Chiodini et al., 1998; Harvey et al., 2017; Seward and Kerrick, 1996). However, the expansion of the geothermal sector leads to consider a broader range of geothermal resources resulting in possible large CO₂ emissions, even in low- and medium- enthalpy geothermal systems.

The CO₂ concentration in geothermal waters is strongly related to the geological setting, and more specifically the lithology, of the reservoir. The role of carbonates might be predominant in generation of CO₂ as carbonate dissolution or thermal decomposition of carbonates might be major sources of CO₂ in fluid whereas carbonate precipitation in the reservoir or in the ascent of the water might be a sink of geothermal CO₂. The equilibrium relative to the carbonate minerals and the alumino-silicate minerals, often associated to the

chemical water-rock interactions, is an important parameter to consider as it “buffers” the fluid chemical composition and the CO₂ degassing. Therefore, understanding the relationship between the mineral buffer, the fugacity of CO₂ ($f\text{CO}_2$) (or its partial pressure of CO₂, $p\text{CO}_2$), and the temperature in the reservoir, is crucial to estimate the CO₂ release in geothermal systems. These links between $f\text{CO}_2$ and reservoir temperature have been subject to Chiodini and collaborators’ investigations since the early 1990’s, although they focused mainly on volcanic geothermal systems (e.g., Chiodini et al., 2007, 1998, 1995b)

The Central Betic Cordillera, in the South of Spain, has an interesting geothermal potential with abundant low to medium geothermal resources (Arrizabalaga et al., 2015; Sánchez Guzmán and García de la Noceda, 2010), major fault systems allowing a rapid ascent of the deep hot water (Cerón and López-Chicano, 2002), and moderate-intensity seismic activity. This region is characterized by several occurrences of thermal springs (water with temperature of more than 20°C, according to the average air temperature of this area), known as baños, which have been used, for some of them, as thermal bath since the Roman times. They are mainly exploited for balneotherapy or spa nowadays. The thermal waters in the Central Betic Cordillera are also characterized by large variability in $f\text{CO}_2$, and therefore in $p\text{CO}_2$. Low $f\text{CO}_2$ are observed in the sulfated waters (e.g., Baños Alhama de Granada) whereas large amount of CO₂ degassing are known in few springs (e.g., Capuchina de Lanjaron) (Pérez del Villar, 2009). The thermal springs of Baños Alicun de la Torres have been studied as natural analogs for CO₂ storage (Prado-Pérez and Pérez del Villar, 2011). Nevertheless, only old Spanish studies have considered globally the thermal waters in the Central Betic Cordillera (Benavente Herrera and Sanz de Galdeano, 1985; Cruz-Sanjulián et al., 1972; Cruz Sanjulián and Granda, 1979). Recent studies (Campos, 2006; López-Chicano et al., 2001a; Prado-Pérez and Pérez del Villar, 2011) characterized the geochemical and hydrogeological properties in specific individual thermal system.

The aim of this study is to evaluate the suitability of the thermal waters for the geothermal exploitation in the Central Betic Cordillera with regard to CO₂ emissions. Geochemical and isotopic indicators and thermodynamic calculations can be applied to get insights on the fluid geochemistry, temperature, and $f\text{CO}_2$ of the reservoir using the measured physical-chemical characteristics at the surface. The present study attempts to assess the potential mineral assemblages buffering the waters in the reservoir and the variations of $f\text{CO}_2$ at the regional scale.

2 Geological setting

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

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

2.1 Tectonic framework

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

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

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

2.2 Lithostratigraphy

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

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

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

2.3 Sample location

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

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

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

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

3 Material and methods

3.1 Water and dissolved gases sampling

Thirteen thermal water samples were collected in the Granada Basin and in the Betic Cordillera, from nine springs and four wells. Two wells were artesian whereas the other water samples were pumped. All water samples were filtered with 0.45 µm membrane filters and samples assigned to trace elements and Al analyses were filtered with 0.2 µm membrane filters. The water samples dedicated to cations, minor elements, and Al analyses were acidified using suprapure nitric acid (HNO₃).

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

3.2 Water analyses

3.2.1 Physical-chemical properties

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

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

3.2.2 Laboratory chemical analyses

The major cations and anions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , and Cl^-) were analyzed by ionic chromatography. The uncertainty on Mg^{2+} , K^+ , Na^+ , SO_4^{2-} determination is $\pm 5\%$ whereas that on Ca^{2+} and Cl^- is estimated to be $\pm 10\%$. Minor and trace elements (Ba, Sr, Al, Fe) were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES. The uncertainty on Ba and Sr determination is $\pm 10\%$ whereas that on Al is estimated to $\pm 20\%$. The silica concentrations were determined by a spectrophotometric method following the protocol from Centre d'Expertise en Analyse Environnementale du Québec, (2016), suitable for natural groundwater with Si concentration ranging from 0 to 20 mg/l. The total ionic balance does not exceed 8% for all water samples.

3.3 Gas analyses

3.3.1 Extraction and analyses of dissolved gases

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

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

Gas species (O_2 , N_2 , CH_4 , CO_2 and He) were analyzed by gas chromatography (Clarus 500, Perkin Elmer instrument with Carboxen 1000 columns with a hot wire detector and a flame ionization detector) using argon as carrier gas. The composition of dissolved gases, expressed in $cc.l^{-1}$ STP (Standard Temperature and Pressure), was calculated taking into account the volume of gas extracted, the volume of water sample, and the solubility of each gas species (Bunsen coefficient in cc gas/l water STP). The composition of bubbling gases was expressed in either %vol or ppm vol. The accuracy to analyze dissolved gases following the method described by Capasso and Inguaggiato (1998) is within 5.0%.

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

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

3.5 Geochemical calculations and modeling

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

3.5.1 Saturation index

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

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

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

3.5.2 Chemical geothermometers and geobarometers

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

medium temperatures (Blasco et al., 2018) and therefore they have been investigated in this study. SiO₂-quartz geothermometers from Fournier (1977), Fournier and Potter (1982), Michard (1979) and Verma (2000b) and SiO₂-chalcedony geothermometers from Arnórsson et al. (1983) and Michard (1990) were applied for the studied thermal waters. Although cationic (Na/K, Na/K/Ca, K-Mg) geothermometers have been proven efficient in high temperature systems (> 180°C), they are usually considered as unsuitable in low temperature systems due to the different mineral assemblage governing the water chemistry and equilibrium (Blasco et al., 2017; Chiodini et al., 1995a). Due to these limitations, the Na/K, Na/K/Ca and K-Mg geothermometers have not been applied in this study. The Ca-Mg geothermometer, developed in the first place by Marini et al. (1986) and revised by Chiodini et al. (1995a), is more appropriate for low temperature carbonate-evaporitic system and was therefore used here. This geothermometer assumes equilibrium of the waters with calcite, dolomite and anhydrite in the reservoir, which is a reasonable assumption in the investigated area where these minerals are extensively present.

In order to get an estimation of the fugacity of CO₂ (*f*CO₂) at depth, the geobarometrical relationship based on the (HCO₃⁻)²/SO₄²⁻ ratio, *f*CO₂, and temperature (Chiodini et al., 1995a) was applied using the following equation:

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

where Σ_{eq} is the sum of equivalents in the waters.

3.5.3 Geothermometrical modeling

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

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

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

An additional set of geothermometrical simulations has been performed at the end of the study including addition of CO_2 to the initial solution to test the hypothesis of CO_2 degassing in an open system.

3.5.4 Hydrogeochemical modeling between surface and depth conditions in closed system

In order to assess the geochemistry of the waters at reservoir conditions and the variation of the $f\text{CO}_2$ between the reservoir and the surface, we carried out hydrogeochemical simulations in closed systems. In sedimentary environments, the pH and $f\text{CO}_2$ of the waters are highly dependent on the interaction with carbonate minerals. Dolomite is particularly important in the Central Betic Cordillera where large amount are present. CO_2 generation might occurs during dolomite precipitation as shown by the following reaction:

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

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

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

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

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

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

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

The concentrations of chemical species, pH, CO_2 fugacity, and SI of minerals were computed during each step of modeling. By comparing the results of the geochemical modeling (Step 3) with the initial surface geochemical characteristics (Step 1), we evaluate the possible mineral assemblages in equilibrium at reservoir conditions.

These geochemical simulations rely on the assumption that the difference in the quartz saturation index ($\text{SI}_{\text{quartz}}$) during each step of the modeling does not lead to significant change in temperature. Even if $\text{SI}_{\text{quartz}}$ varies between -0.13 and 1.27, the H_4SiO_4 concentration remains

quite constant for all the thermal waters resulting in a change in apparent temperature (δT) lower than 5°C.

4 Results

4.1 Chemical characteristics of the waters

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

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

The waters located in the graben formed in the Alpujárride Complex and close to the SE-NW faults have a chemical composition of Ca²⁺-Mg²⁺-SO₄²⁻-HCO₃⁻ type, displaying interaction with both carbonates and sulfates.

The waters in the evaporitic basins are mainly Ca²⁺-Mg²⁺-SO₄²⁻ water-type resulting from clear interaction with evaporitic material and especially calcium sulfate. The samples BAG and BNAG have a higher HCO₃⁻ content, with a composition close to the samples from the graben in the Alpujárride Complex. The composition of the BZ water also differs from the others with a Ca²⁺-Na⁺-K⁺-SO₄²⁻-Cl⁻ water-type, showing significant interaction with evaporitic and detrital material.

The thermal waters located at contacts between metamorphic complexes display larger dispersion in their chemical composition. The samples BSL and CL are Na⁺-Cl⁻ type whereas BAA is Na⁺-Cl⁻-HCO₃⁻ type.

4.2 Saturation indices

The results of the saturation indices calculations at the outlet temperature are shown in Table 2. The waters are mainly close to equilibrium or slightly oversaturated with respect to calcite and dolomite whereas they are undersaturated with respect to gypsum, anhydrite, and halite. However, the thermal waters of AT and BSL display slight undersaturation to undersaturation with respect to the carbonate minerals (calcite and dolomite). Waters are oversaturated with respect to quartz and close to equilibrium with respect to chalcedony. Concerning the saturation indices with respect to alumino-silicates, the waters are oversaturated with respect to kaolinite and Ca-montmorillonite whereas they display large range of saturation with respect to K-feldspar and albite, spanning from undersaturated to highly oversaturated, independently of the relationship with the tectonic structures. The saturation indices of the waters with respect to the considered minerals are pH-dependent and therefore dependent of possible CO₂ degassing of the thermal waters.

4.3 CO₂

Dissolved CO₂ concentrations range from 9.51 to 597.5 cc/L, corresponding to $f\text{CO}_2$ spanning from 0.02 to 0.78, i.e pCO₂ from 0.02 to 0.78 atm (Table 3). The water samples characterized by higher amounts of dissolved CO₂ display lower pH values, suggesting that CO₂ is the main species responsible of water acidity. The high-CO₂ springs of CL, BAA and BUG are also characterized by bubbling gases with similar composition as the dissolved gases (Lix et al., 2018).

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

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

degradation of organic matter in the soil (of the recharge area), (2) carbonate dissolution, (3) degassing of mantle-derived CO₂. Biological degradation processes in soils usually results in $\delta^{13}\text{C}$ values ranging from -23‰ and -9‰ (Clark and Fritz, 1997), which is not well representative of the studied samples. Therefore, the $\delta^{13}\text{C}_{\text{TDIC}}$ values indicate mainly inorganic origin of CO₂ although possible mixing with organic carbon sources cannot be ruled out. Discriminating the carbon source between carbonate dissolution and mantle-derived CO₂ might be more complex as their $\delta^{13}\text{C}$ values overlap. The isotopic composition of dissolved and bubbling gases in these thermal waters show however a dominant crustal component (Lix et al., 2018). Purely inorganic origin of CO₂ has been considered in these thermodynamical calculations, given the results of $\delta^{13}\text{C}$ of the TDIC.

4.4 Reservoir temperature and pressure

4.4.1 Chemical geothermometers and geobarometers

The temperatures provided by the silica and Ca-Mg geothermometers are compiled in Table 4. The reservoir temperatures estimated with the different SiO₂-quartz geothermometers range from 42 to 146°C corresponding to a mean spanning between 51 and 143°C with a relative standard deviation lower than 6°C. The SiO₂-chalcedony geothermometers yields lower temperatures ranging from 20 to 115°C. The SiO₂-quartz are more reliable than the SiO₂-chalcedony geothermometers since quartz might be the phase controlling the dissolved silica in the thermal waters in the Betic Cordillera. Indeed, quartz occurrences and mineralizations have been described in the Internal Zones of the Betic Cordillera as well as in the Neogene basins whereas chalcedony have not been described in mineral assemblages. Although the kinetics of quartz reaction is very slow below 100°C (Rimstidt and Barnes, 1980), the mineral equilibrium approach developed in this study might support the temperatures obtained from quartz geothermometers.

The thermal waters located in the evaporitic basins (Granada and Guadix-Baza Basins) show estimated reservoir temperature from SiO₂-quartz ranging from 74 to 95°C. Assuming a thermal gradient of 30°C/km, which can be expected in the studied area (Fernández et al., 1998), these temperatures would correspond to depths and hydrostatic pressures varying from 2.5 to 3.2 km and from 250 to 320 atm respectively. The thermal waters BUC and BUG, located close to the SE-NW faults, show the lowest estimated reservoir temperature, ranging from 51 to 58°C and corresponding to hydrostatic pressure spanning between 170 and 200 atm respectively. The thermal waters located at the contacts between metamorphic complexes (BAA, CL, and BSL) show the highest estimated reservoir temperatures ranging from 126 and 142°C, corresponding to depths of 4 - 4.5 km and a hydrostatic pressures of 400 to 450 atm.

The Ca-Mg geothermometer provides temperatures ranging mainly between 71 and 91°C with little variation between the different thermal waters (Table 4). The obtained temperatures are in good agreement with those of SiO₂-quartz geothermometers for the waters located in the evaporitic Granada Basin. However, the Ca-Mg geothermometer give similar reservoir temperatures regardless of the geological context of the studied thermal waters, due to low variations in their Ca/Mg ratios, ranging mainly from 1.5 to 2.4. Therefore, it seems that this geothermometer might not be suitable for all investigated thermal waters in the central Betic Cordillera.

The results of the geobarometrical method based on the (HCO₃⁻)²/SO₄²⁻ ratio (Chiodini et al., 1995a) give values of fugacity of CO₂ (*f*CO₂) in depth ranging from 0.04 to approximately 23. The high values (> 5) are obtained for the thermal waters located on the contact of metamorphic complexes (CL, BSL, and BAA).

4.4.2 Geothermometrical modeling

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

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

Although we can expect the carbonates as part of the buffering mineral assemblage in depth due to their ubiquity in the sedimentary basin and in the Central Betic Cordillera, they cannot reach equilibrium in the reservoir conditions. As shown in Figures 3 and 4, the waters are close to equilibrium or oversaturated with respect to calcite and dolomite in the outlet conditions and these minerals have retrograde solubility. The apparent oversaturation in the outlet conditions might result from CO₂ outgassing process and a corresponding increase in pH during the ascent of the waters to the surface.

4.4.3 Hydrogeochemical modeling

The results of the simulations show that, globally, $f\text{CO}_2$ in the outlet conditions varies between 6×10^{-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 step of the simulation after equilibration with dolomite show values ranging from $\sim 2 \times 10^{-2}$ and 40 (Figure 5), whereas the values of $f\text{CO}_2$ after equilibration with alumino-silicates and carbonates vary between 5.4×10^{-3} and 1.8×10^2 (Figure 6). The logarithmic relationship between $f\text{CO}_2$ and temperature for the waters equilibrated with the both carbonates and alumino-silicates might reflect strong control by the equilibrium mineral assemblage on the chemical water composition and CO₂ content.

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

- Group of waters located in the evaporitic basins

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

atm) ranging from 6.5 to 6.8 and an estimated $f\text{CO}_2$ spanning between 9×10^{-2} and 1.6×10^{-1} (Figure 5). The simulations taking into consideration carbonates and alumino-silicates give similar ranges of pH (from 6.5 to 6.7) and $f\text{CO}_2$ (from 6×10^{-2} to 2×10^{-1}) to those obtained with dolomite equilibrium for the water points located in the Granada basin (Figure 6). However, the two samples BNAG and BZ show slightly higher $f\text{CO}_2$ ranging from 3×10^{-1} and 6×10^{-1} . The thermal water of Alicun de las Torres (AT), showing a lower reservoir temperature similar to BUC and BUG samples, have an estimated low $f\text{CO}_2$ at depth for both simulations ranging from 1×10^{-2} to 3×10^{-2} (Figure 5 and 6). The variation in $f\text{CO}_2$ between the steps 1 and 3 of the simulation, $\Delta f\text{CO}_2$, estimated for this group of thermal waters ranges from 3×10^{-2} to 6×10^{-1} (Figure 7). This corresponds to a difference in calculated CO_2 concentration between the steps 1 and 3 of the simulations ranging from ~ 1 to 5 mmol/L.

- Group of waters in the graben in the Alpujárride complex

The results of the equilibrium simulations with dolomite in the reservoir conditions ($51 < T < 58^\circ\text{C}$ and $170 < P_{\text{hydro}} < 200$ atm) for the waters located in the graben into the Alpujárride Complex give a pH of the waters of approximately 6.8 and an estimated $f\text{CO}_2$ of 6×10^{-2} (Figure 5). The simulation of these waters in equilibrium with both carbonates and alumino-silicates (calcite, dolomite, quartz, kaolinite, and Mg-chlorite) give higher values of pH ranging from 7.3 to 7.4 and lower values of $f\text{CO}_2$ spanning between 5×10^{-3} and 9×10^{-3} (Figure 6). The estimated variation in $f\text{CO}_2$ between the depth and the surface, $\Delta f\text{CO}_2$, ranges from ~ 0 to 6×10^{-2} (Figure 7), corresponding to maximum 1 mmol/L of CO_2 .

- Group of waters located at contact with metamorphic complexes

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

depth is lower considering the equilibrium with dolomite only (ranging from 6×10^{-1} to 6) than considering the equilibrium with the carbonate and alumino-silicate assemblage (ranging from 25 to 180) (Figures 5 and 6). The estimated Δf_{CO_2} for this group of thermal waters spans from 6×10^{-1} to 1.8×10^2 (Figure 7), corresponding to 20 mmol/L to 0.85 mol/L of CO_2 .

4.4.4 Geothermometrical modeling with CO_2 degassing (open system)

- Group of waters located in the evaporitic basins

The geothermometrical simulations with the lowest estimation of CO_2 addition deduced from the hydrogeochemical modeling, 1 mmol/L, result in a common reservoir temperature of 75 to 90°C for the waters of the evaporitic basins (Figure 8). Waters are at potential equilibrium with the following mineral buffer: carbonates (calcite and dolomite), anhydrite, quartz, and possibly Mg-chlorite or Ca alumino-silicate (laumontite or a Ca-montmorillonite). These results show that low amounts of CO_2 degassing (~ 1 mmol/L) are necessary in an open system to reach the equilibrium with dolomite and alumino-silicates. Evaporites are also part of the buffer mineral assemblage in this sedimentary environment.

- Group of waters in the graben in the Alpujárride Complex

The geothermometrical simulations in an open system with addition of 0.5 mmol/L CO_2 show estimated reservoir temperatures ranging from 50 to 60°C for the waters located in the graben in the Alpujárride Complex (Figure 9) with the following mineral buffer: carbonates (calcite and dolomite), quartz, and Ca alumino-silicate (Ca-montmorillonite). Higher amounts of added CO_2 do not lead to a common equilibrium of mineral phases at a specific temperature.

- Group of waters located at contact with metamorphic complexes

Modeling of CO_2 degassing in an open system with geothermometrical simulations shows that 7 mmol/L to 1 mol/L of added CO_2 are necessary for the waters to be at equilibrium at

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

5 Discussion

5.1 Role of the mineral buffers in CO₂ estimation

The thermal waters in the Central Betic Cordillera are characterized by large heterogeneity in their geochemistry in the outlet conditions and in their geothermal characteristics. The three groups of waters, which were defined based on water composition and geology at the thermal water locations, can be also distinguished by the temperature and $f\text{CO}_2$ in the reservoir. The groups of thermal waters have distinct reservoir temperatures, estimated with the SiO₂-quartz geothermometer, ranging from low-enthalpy (~55°C) to medium-enthalpy (~140°C) geothermal systems. Using the results of the geochemical and geothermometrical modeling we discuss in this section the mineralogical buffers and chemical properties of the reservoirs and the variations in $f\text{CO}_2$ between depth and the surface ($\Delta f\text{CO}_2$) in both closed and open system for the three groups of waters. For all groups the assessed $\Delta f\text{CO}_2$ indicates CO₂ degassing during the ascent of the water to the surface. The equilibrium with respect to mineral phases in the reservoir conditions seems to have a strong control on CO₂ release (Figure 7).

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

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

The presence of evaporites needs to be considered for the geothermal systems in sedimentary environment as it might enhance CO_2 release through a dedolomitization process. Prado-Pérez and Pérez del Villar (2011) showed that the thermal water AT may result from dedolomitization at depth followed by CO_2 degassing. Dedolomitization, which is a process described in other natural systems (Auqué et al., 2009; López-Chicano et al., 2001b), corresponds to dolomite dissolution and calcite precipitation caused by the dissolution of gypsum and/or anhydrite. CO_2 loss, before or after outlet of the thermal waters, might occur as evidenced by the presence of fossil and present-day massive thermogenic travertine deposits (Prado-Pérez and Pérez del Villar, 2011) in the Alicun de las Torres site. This process of dedolomitization is most probably occurring in other geothermal systems in the evaporitic Granada and Guadix-Baza basins.

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

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

complexes, which displays the highest estimated reservoir temperature (130 – 140°C), the mineral buffer assemblage at depth is more difficult to assess due to the large CO₂ degassing. Indeed, these waters show the highest measured dissolved CO₂ concentrations (> 39 cm³/L) distinguishing them from the other thermal springs in the Central Betic Cordillera. They are at equilibrium with quartz and dolomite, and close to equilibrium with Mg-chlorite and laumontite in the reservoir conditions. The $\Delta f\text{CO}_2$ is lower with the dolomite buffer than with the carbonate and alumino-silicate buffer (Figure 7).

The results of the simulations show that CO₂ degassing is lower in open system than in closed system, highlighting the importance to evaluate the efficiency of the system to rapidly ascend water from depth to the surface. Calcite precipitation might result from the CO₂ degassing process due to pH increase and kinetic constrains compared to dolomite precipitation. The amount of precipitated calcite can be evaluated during a given time range using the amount of CO₂ loss during the ascent of the water and the estimated flow rate of the springs found in literature and checked in the field (ranging from 0.2 to 100 L/s). Assuming a time range comprised between 1,000 and 100,000 yr, the amount of calcite precipitated is estimated to range from $\sim 10^2$ to 10^6 m³ for the waters in the basins or their borders. This estimation is in good agreement with the volume of travertines that can be deduced from the study of Martín-Algarra et al. (2003) in the northeastern part of the Granada Basin (from 10^4 to 10^5 m³ for the last 200,000 yr).

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

Using thermodynamic calculations (hydrogeochemical and geothermometrical simulations), we show the key role of the reservoir temperature and the buffer mineral assemblage on the estimation of $f\text{CO}_2$ and therefore $p\text{CO}_2$. A recent study on the geochemical characterization of geothermal systems pointed out that the CO₂ trapping mechanism is mainly

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

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

In order to estimate the environmental impact associated with the CO_2 degassing of the investigated thermal waters, the CO_2 emissions generated by these thermal systems were estimated for potential household heating purpose and were compared to those produced by a natural gas heating system. The average household energetic consumption (Q) for heating system of a 100 m² house in Western Europe is 11,600 kWh/yr, equivalent to 4.18×10^{10} J/yr (Lapillonne et al., 2014).

Using this average household energetic consumption, we can estimate the amount of CO_2

597 (nCO₂) that would be emitted from a natural gas furnace used to heat a 100 m² 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 x 10⁴ mol of CH₄ and would hence produce the equal amount of CO₂.

601 This value can be then compared to the amount of CO₂ 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°C), the amount of water that has to be
605 pumped to heat a 100 m² 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 ΔT is the temperature range of the internal heating cycle (20°C with T_{max}
609 = 60°C and T_{min} = 40°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 m² house would therefore be 2.77 x10⁷ 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 x10⁷ and 6.15 x10⁶ mol
616 respectively. Using the average CO₂ concentration estimated for each thermal water groups (2
617 x10⁻⁴, 5 x10⁻³, 8 x10⁻¹ mol/L), we can estimate the amount of natural CO₂ degassed during

household heating ranging between 1.0×10^2 and 8.9×10^4 mol. The estimated amount of CO_2 released from geothermal waters used in heating is lower by 1 to 2 orders of magnitude than the amount of CO_2 generated by a natural gas furnace for the two first groups of thermal waters ($T_{\text{depth}} < 130^\circ\text{C}$) (Figure 11). However, similar quantity of CO_2 could be released from the thermal waters with the higher T_{depth} as those produced by a natural gas furnace.

These estimations of CO_2 emissions in this simple practical application of heating a 100 m^2 house show that the geothermal energy is globally a cleaner energy than natural gas but might release as much CO_2 as a natural gas furnace in certain conditions (high reservoir temperature and $f\text{CO}_2$). These estimations are based on possible gas venting during the heat production, which are usually neglected in life cycle assessment of carbon intensity of geothermal system (McCay et al., 2019).

These estimations, giving us the order of magnitude of CO_2 emissions that could be generated by the investigated geothermal systems, lead to explore possible exploitations of the geothermal resource. Direct electricity production (e.g. enhanced geothermal systems) might be considered for the thermal waters with the highest reservoir temperature ($T_{\text{depth}} = 140^\circ\text{C}$) emitting large quantity of CO_2 . This use would have to be coupled to CO_2 capture and storage to make it a renewable and clean energy.

6 Conclusions

Our study provides the first characterization of the reservoir conditions (T, P, and geochemistry) for the thermal waters in the central part of the Betic Cordillera. The $f\text{CO}_2$ at depth were tentatively assessed with both a chemical geobarometer and direct geochemical simulations. The variation of $f\text{CO}_2$ ranges from approximately 6×10^{-3} to 10^2 at the scale of the area. Based on the geology of the thermal water locations and the results of the 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 approximatively 70 to 90°C and $f\text{CO}_2$ varying between 6×10^{-2} and
646 6×10^{-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 5×10^{-3} to 7×10^{-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 approximatively
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 CO_2 generation and release at depth. In the case study of
663 the Central Betic Cordillera, 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 CO_2 , water, and rocks for the
667 geothermal systems in sedimentary basins.

The estimations of CO₂ emissions generated by the thermal systems for potential household heating purpose indicate that the geothermal energy is globally a clean energy but might release as much CO₂ as a natural gas furnace for the thermal waters with the highest reservoir temperature. This study points out the importance to estimate properly the amount of CO₂ degassing in geothermal waters depending of the reservoir conditions. Our results highlight the importance of considering geochemical estimates for heat exchanger design. In the case of thermal waters with the highest temperatures and high CO₂ contents, heat exchangers allowing to maintain fluids under pressure might be preferred to avoid CO₂ release in the atmosphere.

678 **Acknowledgments:**

679 The Authors thank N. Labourdette and E. Aubry for their help in water analyses and Claudio
680 Inguaggiato for helping collecting gas samples during the sampling survey. The Authors are
681 also grateful to M. Rouelle, M. Azaroual, and P. Sarda for the fruitful discussions during various
682 stages of this study. The Authors thank the two Reviewers for their fruitful comments that
683 helped to improve the quality and the clarity of the manuscript. This work was supported by
684 IFPEN and Sorbonne Université. We also thank the Istituto Nazionale di Geofisica e
685 Vulcanologia – Palermo (INGV) for gas analyses.

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Sample and location	Code	Type	Depth (m)	Temp. (°C)	pH	EC	Ca	Mg	Na	K	Alk.	Cl	SO ₄	Si	Al	Ba	Fe	Sr	TDS	CBE
<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>Graben 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 ₂ (g)	fCO ₂ (g)
<i>Contacts metam. complexes</i>														
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
<i>Graben into Alp. Complex</i>														
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
<i>Evaporitic basin</i>														
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. CO₂(g) corresponds to the log10 of CO₂ fugacity (fCO₂). SI were calculated with the PHREEQC code at the outlet temperature (measured in the field).

Sample	O ₂ cc/L	N ₂ cc/L	CO ₂ cc/L	pCO ₂ atm	H ₂ ppm	CO ppm	CH ₄ ppm	TDIC mmol/L	δ ¹³ C _(TDIC) ‰	δ ¹³ C _(CO2) ‰
<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 ₂ -Quartz				SiO ₂ -chalcedony		Ca/Mg	<i>f</i> CO ₂
		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 CO₂ (*f*CO₂) obtained with Chiodini et al. (1995a)'s geobarometer.