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DEEP RESERVOIR TEMPERATURES OF LOW-ENTHALPY GEOTHERMAL SYSTEMS IN TUNISIA: NEW CONSTRAINTS FROM CHEMISTRY OF THERMAL WATERS

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ABSTRACT

Tunisia is characterized by hot and warm groundwaters (temperature up to 75 °C) which represent the surface manifestation of geothermal systems hosted in carbonate-evaporite rock sequences. The T-conditions of Tunisia deep thermal reservoirs are here evaluated for the first time at the regional scale. The results here shown clearly highlight the limitations inherent in the application of common geothermometric methods in the estimation of equilibrium temperatures in sedimentary environments. The modeling approach proposed by Chiodini *et alii* (1995), which makes use of the ratios between dissolved HCO₃, SO₄ and F, provides the most reliable results, and allows us to derive equilibrium temperatures up to 200 °C for the Tunisian thermal reservoirs. Very high equilibrium pCO₂ (100 bar) values are also estimated, likely indicative of the confined aquifer conditions.

KEYWORDS: Tunisia, Thermal groundwaters, Chemical geothermometers, Sedimentary environment

1. INTRODUCTION

TUNISIA, located in the Northern African margin, is known for the numerous thermo-mineral springs, widely dispersed throughout the entire country, and used as thermal baths since the Roman domination. Currently, hot and warm waters feed the thermal infrastructures called *Hammam* in which they are exploited for recreation purposes.

Thanks to the relatively important number of petroleum exploration wells, drilled in the whole Tunisian area, geothermal gradients ranging from 23° to 49 °C/km have been measured (Ben Dhia 1987), and even higher values, up to 90 °C/km, have been supposed to exist in Northern Tunisia (Ben Dhia and Bouri 1995). Structural and gravimetric data evidence a strict relation between the geothermal gradient trend and the main structural directions (Ben Dhia 1987), suggesting that anomalous heat flow in tectonically active Tunisian sectors is related to the presence of faults which allow ascent and surface discharge of deep fluids.

A number of studies (Edmunds *et alii* 2003, Yermani *et alii* 2003, Trabelsi *et alii* 2007) have put the focus on the chemical features of springs belonging to specific sectors of Tunisia. More recently, Fourré *et alii* (2011)

have presented a detailed geochemical analysis of thermal groundwaters at the scale of the entire country. The chemical features of thermal waters (springs and wells) were interpreted to result from water-rock interaction processes, taking place in different geologic environments (evaporitic deposits, limestone or sandstone formations), depending on the area in which the discharges are located. The same authors also reported on the first systematic characterization of dissolved helium and CO₂ (carbon) isotopic composition. They suggest that Tunisian geothermal aquifers are fed by deep-rising volatile phase characterized by a prevalently radiogenic helium (³He/⁴He in the range 0.02 Ra-0.4 Ra) associated with thermo-metamorphic CO₂ (δ¹³C_{CO₂} from 0 to + 4‰ vs V-PDB).

While the Tunisian aquifer systems were thoroughly investigated from a chemical and geological view points, information about the temperatures of deep geothermal reservoir/s, feeding the shallow manifestations, is still undetermined. Such deep temperatures estimations, if available, would contribute to implement/refine our current knowledge of the geothermal potentials of Tunisia. Indeed, apart from exploitation of geothermal resources for hammams, tourism (hotels and pools) and washing, the current

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orientation of Tunisian government policy (since 1980) is directed to the development of new oasis sectors in which thermal waters would be used for irrigation (Mohamed 2002).

In this context, we first attempt in this note the application of geothermometric techniques to the Tunisian groundwaters. We make use of our recently published (Fourrè *et alii* 2011) chemical dataset (concentrations of major and minor dissolved ions) of Tunisian groundwaters, with the aim to improve and deepen the present information about the T-conditions of Tunisian geothermal deep reservoirs.

2. THE STUDY AREA

Tunisia is the northernmost country in Africa, located in the Maghreb area between Algeria, to the west, and Libya, to the Southeast. Mediterranean Sea laps the northern and eastern Tunisia's shores, while the South of the country hosts the Sahara desert.

The structural evolution of Tunisia was related to the tectonic movements involving, since the Late Permian, African and European plates.

Three main structural domains (FIG. 1) are distinguished from the North to the South of Tunisia (Martinez and Truillet 1987): Atlasic, Eastern/Sahel and Saharan domains. The Atlasic domain includes the northern and the central-western sectors of the Tunisian region. Triassic basal series (shallow marine sandstones, shales, dolomites and thick evaporite and salt deposits - Bedir *et alii* 2000) are generally overlain by a thick Cretaceous cover; in the «diapir zone» (FIG. 1), however, the Triassic evaporites (Perthuisot 1978, Mlayah *et alii* 2009) outcrop as ~1000m thick extrusions (NE-SW trending) of gypsum, anhydrite, dolomite and abundant halite. The nappes of Numidian Flysch (Tellian domain; Ben Ferjani *et alii* 1990) extend along the northern coast of Tunisia. They formed during the Late Miocene major orogeny and are composed of thick (3,000-4,000 m) Oligo-Miocene series of sandstones and shales (Rouvier 1977).

The N-S Axis, a regionally significant thrust fault system (Coiffait 1974), separates the Atlasic and the Eastern/Sahel domains (FIG. 1). In the latter, Mesozoic deep marine carbonate are overlain by Quaternary Pleistocene and Holocene sandstones (Bedir *et alii* 1996, 1998, 2000).

The «Grand Accident sud atlasique» (Russo and Russo 1934) (or North Saharan Flexure - Gabtni *et alii* 2005) represents the tectonic boundary between the folded Atlasic domain and the un-deformed Saharan domain. The stable Saharan platform, which characterizes the latter domain, is located in the southernmost part of Tunisia, and is made up of a strongly deformed Precambrian basement (Laaridhi-Ouazaa 1994), covered by a thin and relatively un-deformed sequence of Paleozoic sandstones and carbonates, and Mesozoic evaporites (Ben Ferjani *et alii* 1990).

3. RESULTS AND DISCUSSION

In this study, we use a subset of the original data set of Fourrè *et alii* (2011) (45 water samples; wells and springs)

to investigate the hydrothermal properties of the Tunisian thermal manifestations (FIG. 1).

3.1. Main hydrogeochemical Features of Tunisian Groundwaters

Figure 1 shows that hot and warm groundwaters ($T > 25\text{ }^{\circ}\text{C}$) emerge through the entire Tunisian region; the highest temperatures, from 55 to 75 $^{\circ}\text{C}$, are observed in the Atlasic and Saharan domains.

From a geochemical viewpoint, the Tunisian groundwaters belong to all water-types identified by Langelier-Ludwig diagram (see Fourrè *et alii* 2011): chloride-sulphate waters (both Na- or Ca-dominated) are the most abundant, while bicarbonate-dominated compositions are observed in a group of thermal groundwaters emerging in a zone stretching along the northern Tunisian coast (Fourrè *et alii* 2011). According to Fourrè *et alii* (2011), the extensive occurrence of evaporitic deposits, (mainly dated Triassic), both outcropping (diapiric zone) and in the subsurface (cfr. section 2), is a major control factor on the chemical compositions of Tunisia thermal waters. As displayed by Figure 2a, hot and warm discharges, belonging to all of three Tunisian domains, while being systematically under-saturated relative to halite, generally have Na/Cl molar ratio ~ 1 ; since seawater contribution to the aquifer systems can be ruled out based on $\delta\text{D}-\delta^{18}\text{O}$ water systematics (Fourrè *et alii* 2011), these Na-Cl compositions can be taken as evidence that leaching of halite is buffering thermal water composition to a large extent. A few of samples, displaying Na/Cl molar ratio > 1 , could reflect the occurrence of cation exchange processes, during which preferential Na-release to weathering solutions, at the expense of other cation species, is expected (Edmunds *et alii* 2003, Yermani *et alii* 2003, Fehdi *et alii* 2009, Fourrè *et alii* 2011).

In addition to chloride (which concentrations range from 0.6 to 800 mmol/l; Fourrè *et alii* 2011), sulphate (from 1 to 158 mmol/l; Fourrè *et alii* 2011) is the second most abundant anion species in Tunisia thermal groundwaters. There is no supporting evidence for any sulfur contribution from oxidation of S-bearing magmatic gases (a process which would hardly fit the non-volcanic character of Tunisia); this leaves leaching of anhydrite/gypsum (from Triassic evaporite series) as only potential source of sulphate ions (Edmunds *et alii* 2003, Fourrè *et alii* 2011). Not surprisingly then, Ca and SO_4 are in 1:1 molar proportion in groundwaters, and Saturation Indexes approach unity (attainment of chemical equilibrium) for both gypsum (FIG. 2b) and anhydrite (not displayed) in most cases.

The prevalingly lower bicarbonate contents (from 0.1 to 26 mmol/l - Fourrè *et alii* 2011) in Tunisia groundwaters (relative to chlorine and sulphate) reflect the minor leaching aptitude of calcite, relative to more soluble evaporitic minerals (halite, anhydrite and gypsum). Indeed, in spite carbonate formations are widespread all over Tunisia (Triassic evaporitic sequences and Cretaceous to Cenozoic limestones), only a few Tunisian

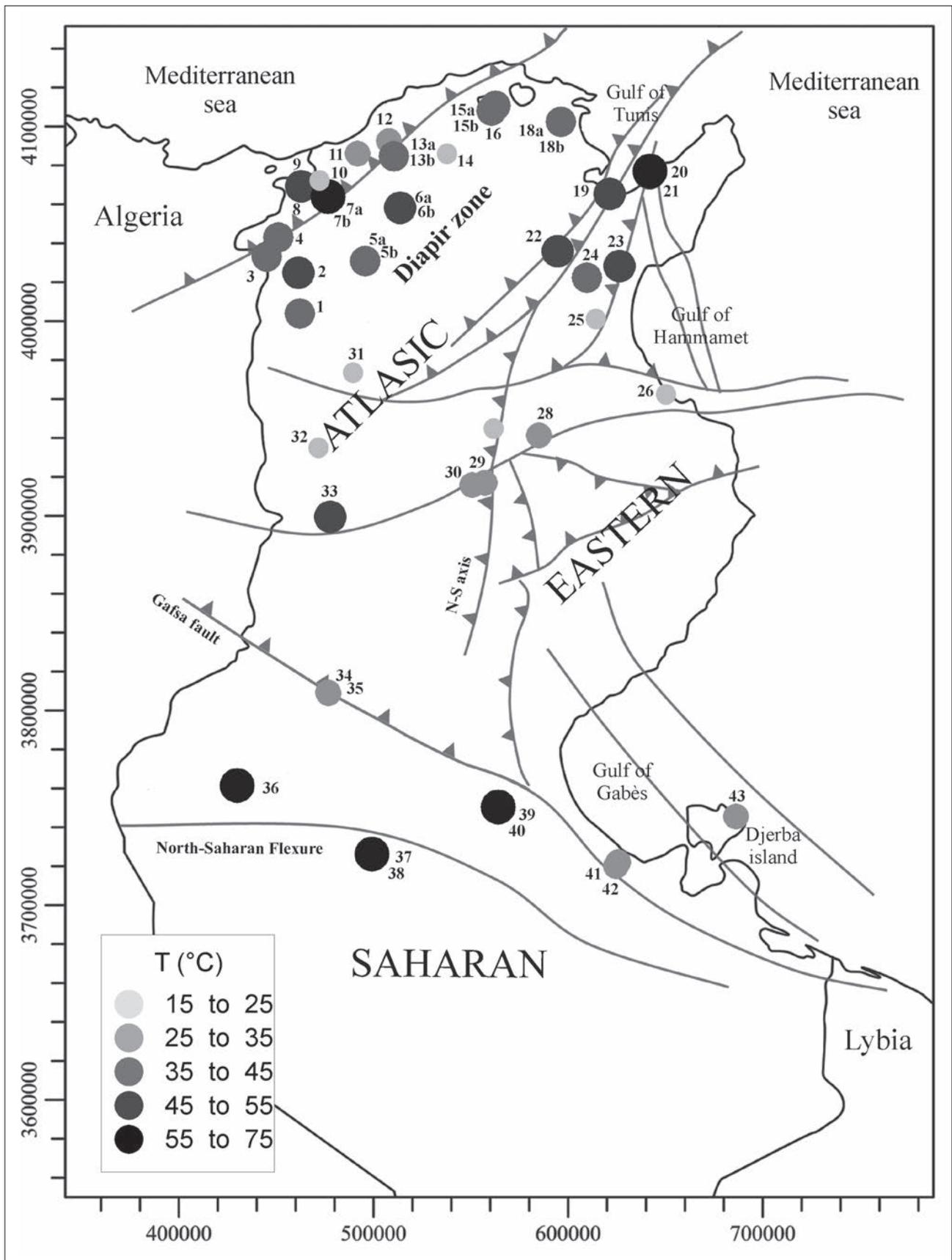


FIG. 1. Classed post map showing the spatial distribution of discharge temperatures in Tunisia thermal waters. The numbers indicative of thermal waters samples are taken from Fourrè *et alii* (2011). The structural setting is modified from Fourrè *et alii* 2011.

samples are bicarbonate-type waters: these have Ca/HCO₃ molar ratios of ~ 0.5 (the typical calcite mo-

lar ratio). All water samples are somewhat affected by calcite dissolution, however, as demonstrated by Satu-

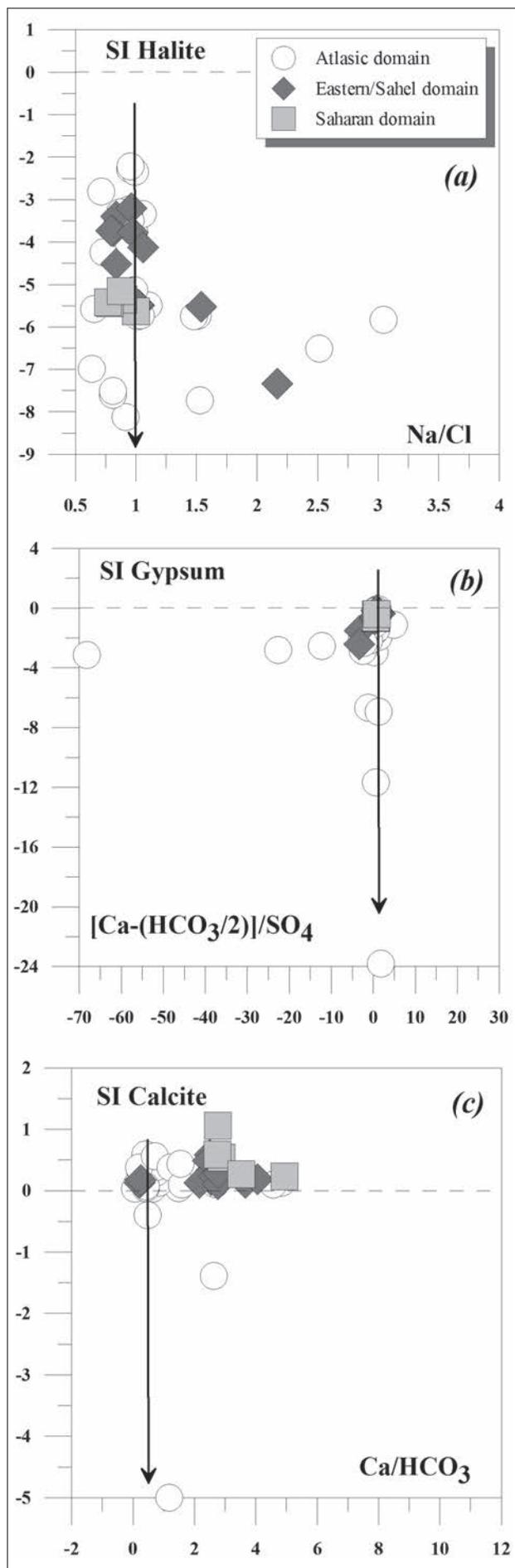


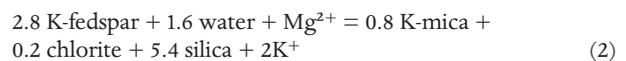
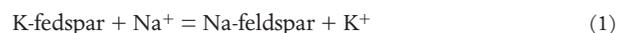
FIG. 2. Binary plots of (a) SI halite vs Na/Cl, (b) SI gypsum vs $[Ca-(HCO_3/2)]/SO_4$ and (c) SI calcite vs Ca/HCO₃. These binary plots suggest that leaching of soluble mineralogical phases (halite, gypsum and/or anhydrite, and calcite) making up the reservoir rocks, is the main process determining the chemical composition of Tunisia thermal waters. Samples from Atlasic domain are represented by white circles, dark-grey diamonds indicate thermal waters in Eastern/Sahel domain, and grey squares are for samples from the Saharan domain. Data are taken from the Fourrè *et alii* 2011 database.

ration Indexes for calcite being recurrently ~ 0 (FIG. 2c). It follows then that carbonate mineral leaching by groundwaters, while widespread in Tunisia, is in most conditions masked by dissolution of more soluble species (as evaporitic minerals); only where these minerals are absent, bicarbonate waters are left free to form.

3.2. Geothermometric Evaluation of Tunisian deep Reservoir Temperatures

Geothermometric techniques based on the compositional features of hydrothermal fluids represent the most viable way to obtain information on deep reservoir temperatures (at least where no direct deep well measurements are available), and so they represent one a most important geochemical tool in geothermal exploration, and for exploitation of resources (D'Amore and Arnorsson 2000). The use of geochemical geothermometers stands on the assumption that fluids discharged at the surface carry with them imprints of their deeper histories (Giggenbach 1991). A fundamental assumption is made that the hydrothermal reactions achieve equilibrium at T-P reservoir conditions, and that no re-equilibration (e.g., lower-T water-rock reactions with wall-rocks) affects thermal fluids upon their migration from the deep reservoir to the surface.

Among the ion solute geothermometers, the Na-K-Mg geothermal indicator is based on combination of the two following temperature-dependent exchange reactions (Giggenbach 1988):



Giggenbach (1988) presented a simple graphical procedure to verify the extent to which water samples attain the above-described equilibrium conditions at reservoir T. The application of such a technique to Tunisian groundwater samples is shown in the ternary plot of Figure 3. The diagram shows that the majority of thermal discharges, belonging to three Tunisian domains (Atlasic, Eastern and Saharan), fall in the field of «immature waters» (Giggenbach 1988). In light of their Mg-rich compositions, these waters are thought either not to have attained high-T equilibrium with deep reservoir rocks (because of their fast and shallow hydrothermal flow), or to have suffered extensive re-equilibration at near-surface conditions (after a deep equilibration period). Whatever the case, these water samples are un-

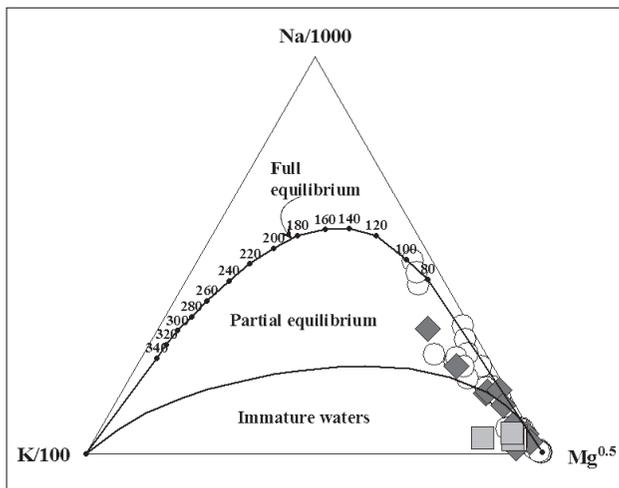


FIG. 3. Na/1000-K/100-Mg^{0.5} triangular diagram, modified from Giggenbach (1988). Curves describe the compositions of thermal waters at full (upper curve) or partial (bottom curve) equilibrium with reservoir rocks in a range of temperatures (Giggenbach 1988). Labeled T values on the full-equilibrium line represent equilibrium temperatures calculated by Na-K-Mg geothermometer. Samples are as in Figure 2.

suitable to derive the deep temperature estimations. Only a few Tunisian thermal waters (from the Atlasic domain), plot over, or just below, the full equilibrium curve of Figure 3, where «mature», fully equilibrated, reservoir fluids typically cluster (Giggenbach 1988). Only for these water samples, the application of the Na-K-Mg ionic geothermometer can be thought to provide meaningful results: they indicate geothermal reservoir equilibration temperatures ranging from ~ 70 to ~ 90 °C. Somewhat more variable temperature estimates (T from ~ 70 to ~ 160 °C) are obtained, instead, for partially mature waters (FIG. 3). It should be noted, however, that even for the «mature» fluids the above estimated temperatures might be somewhat untrustworthy: in a sedimentary environment such as Tunisia, while feldspars are probably commonly available for reactions 1-2 to take place (e.g., in the Numidian Flysch of the Tellian nappes, or in the recurrent volcanic formations interbedded with sedimentary rocks; Ben Ferjani *et alii* 1990), the significant Na contribution deriving from leaching of halite (FIG. 2a) may exercise a more decisive control factor on Na/K ratios than cation exchange processes.

An alternative estimation of subsurface reservoir temperatures can be obtained by taking advantage of silica content in thermal water discharges, and the temperature-dependent solubilities of individual silica minerals (Fournier 1973). As shown by Figure 4, however, approximately all of Tunisia thermal waters plot along the chalcedony equilibrium curve, at the sampling temperature conditions. This most probably suggests that the SiO₂-contents in Tunisia thermal waters are buffered by chalcedony solubility at near-discharge conditions, and that no deep water SiO₂ geothermometric estimation can therefore be derived from these shallow manifestations. In spite of this, for the sake of illustra-

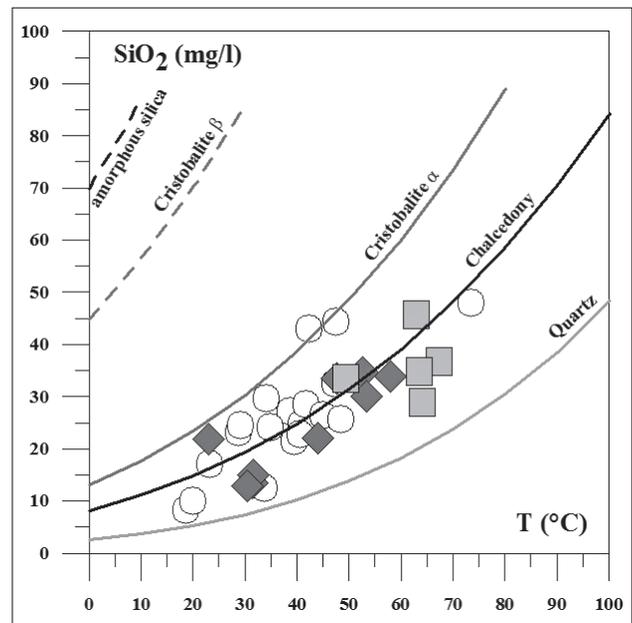


FIG. 4. Dissolved silica contents vs measured temperature at discharge conditions for Tunisian thermal waters. Curves correspond to theoretical solubility curves for different silica minerals: amorphous silica, cristobalite β , cristobalite α , chalcedony and quartz (Fournier 1973, 1991). Samples as in Figure 2.

tion only, the equilibrium temperatures which would be obtained using the quartz geothermometer (Fournier 1973): range from ~ 40 to ~ 100 °C. These values would be realistic only in the (unlikely) case that quartz is controlling silica contents at depth, and that no precipitation occurs upon migration of waters from deep reservoir to surface.

As previously shown, the challenges in applying the most commonly used geothermometric techniques (Na-K-Mg and the SiO₂ contents) to the Tunisian thermal waters is to be ascribed to the mineralogy of the host rocks (dominated by carbonatic, terrigenous and evaporitic successions, rather than silicates) and to the prevailing low subsurface temperatures, which lead to slow kinetics of water-rock reactions (and ultimately preventing equilibrium conditions to be achieved). In this context, a typical mineralogical assemblage, composed by calcite, dolomite, anhydrite, fluorite and (more marginally) SiO₂-bearing minerals, is thought (Marini *et alii* 1986) to fix, at equilibrium conditions, activities of dissolved species in thermal springs in sedimentary environments. More recently, Chiodini *et alii* (1995) implemented the model previously introduced by Marini *et alii* (1986), and proposed a set of geo-indicators suitable for application to thermal waters issuing from medium- to low-temperature hydrothermal systems, hosted in carbonate-evaporite reservoirs. These indicators are based on theoretically derived (Chiodini *et alii* 1995) relations, fixing the dependences of total concentrations of some dissolved chemical species in thermal fluids on independent variables such temperature (1/T), log pCO₂, and total ionic salinity (Σ_{eq}). In their study, Chiodini *et alii* (1995) proposed that con-

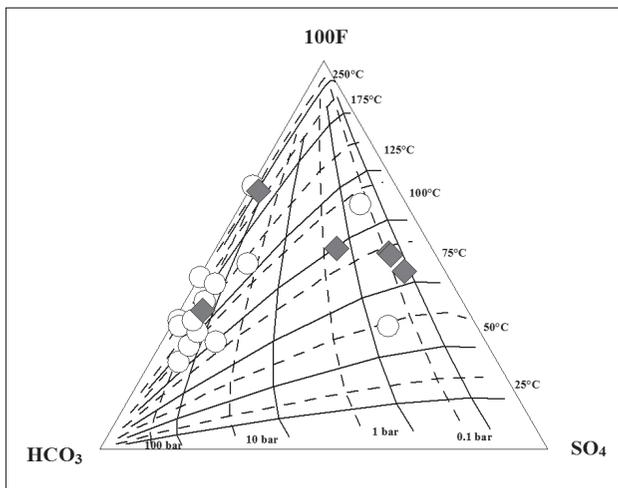


FIG. 5. $\text{HCO}_3\text{-SO}_4\text{-100F}$ ternary diagram (modified from Chiodini *et alii* 1995). T- pCO_2 grids are represented. The isotherms and isobars are calculated for Σeq of 0.01 and 0.1 eq/l, which represent the minimum and maximum values of total ionic salinity of Tunisia thermal waters (Cl contents from 0.6 to 200 mmol/l). Water samples as in Figure 2.

centrations of dissolved Ca, Mg, SO_4 and F are those most sensible to temperature, making them (along with SO_4/F^2 and Ca/Mg ratios) potentially valuable geothermometers. On the contrary, the $(\text{HCO}_3)^2/\text{SO}_4$ ratio was shown to be a most suitable geo-barometer (being controlled by pCO_2), while the HCO_3/F ratio and the HCO_3 content were identified as geo-indicators for both pCO_2 and T (Chiodini *et alii* 1995).

In Figure 5, we show the application of Chiodini's *et alii* (1995) «sedimentary» geothermometers to the Tunisian thermal manifestations. In the ternary $\text{HCO}_3\text{-F-SO}_4$ diagram of Figure 5, we report a selection of the Fourrè's *et alii* (2011) samples, which range (as for their composition) from Na-Cl, to Ca- SO_4 and Na,Ca- HCO_3 thermal waters. These samples are characterized by Cl contents ranging from 0.6 to 200 mmol/l (Fourrè *et alii* 2011) and F from 0.008 to 0.241 mmol/l; the most saline water samples (Cl > 23 mmol/l, and up to 800 mmol/l) from the original Fourrè's *et alii* (2011) database are not considered here, since they show unusually F-depleted compositions (F < 0.002 mmol/l), and are therefore unsuitable for our estimations. These very low fluorine concentrations may partially reflect the large analytical uncertainties associated with F detection by ion chromatography in high-Cl waters.

Figure 5 shows that water samples collected in the Atlas and Eastern domains display a spread of equilibrium temperatures, from 50 to 250 °C, and equilibrium CO_2 partial pressure of ~ 100 bar. This latter features is suggestive for that our sampled thermal manifestations are the surface expression of fluids rising from deep confined aquifers, where pCO_2 is controlled by the hydrostatic conditions (Chiodini *et alii*, 1995, Frondini 2008) and CO_2 production is fueled by thermo-metamorphic reactions in the crust (Fourrè *et alii* 2011). No samples from the Saharan domain are available here;

however two water samples (samples 41 and 42 in Fourrè *et alii* 2011) collected in the southernmost part of the Eastern domain, near the boundary between Eastern and Saharan domains, could be used to deduce information about T conditions in Southern of Tunisia. They allow estimating lower temperatures (~ 75) and pCO_2 values (~ 0.1 bar), at least relative to North-Central Tunisia waters, suggesting a lower geothermal gradient and a minor CO_2 production by thermo-metamorphic reactions in this tectonically stable sector of the Tunisian crustal sector (Fourrè *et alii* 2011).

4. CONCLUSIONS

Thermal waters with discharge temperatures from 35 to 75 °C are widespread throughout Tunisia. These thermal manifestations represent the surface expression of hydrothermal reservoirs, which reflect the anomalously high heat flow and the significant network of active geologic faults in the country (Ben Dhia 1987).

In this short note, we have attempted at a first regional-scale assessment of deep-reservoir T conditions in Tunisia geothermal systems, making use of different geothermometric techniques. We conclude that, due to the prevalent sedimentary nature of host rocks in the country (with mineralogical assemblage dominated by calcite, dolomite, anhydrite, and fluorite), the conventional geothermometric techniques provide unreliable (Na-K-Mg) or poorly significant (SiO_2) information on deep subsurface hydrothermal temperatures. In contrast, we confirm that, in geothermal systems characterized by medium-low temperatures and hosted in carbonate-evaporite rocks, such as those prevailing in Tunisia, (Fourrè *et alii* 2011), the geothermometric methodology proposed by Chiodini *et alii* (1995) seems to provide the most reliable assessment of deep reservoir temperatures. From this, we conclude that the tectonically active Atlas and Eastern domains host thermal aquifers characterized by relatively medium to high temperatures (up to 250 °C), and very high equilibrium pCO_2 (~ 100 bar). The latter are probably indicative of deep confined conditions of the thermal aquifers. Lower temperatures, and less significant CO_2 -producing thermo-metamorphic reactions, are associated with the tectonically stable Saharan domain.

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