CONTENTS

Orlando Vaselli, Bruno Comacchio, foreword
8
Antonino Caproni, Davide M. Puglisi, Lucio Teddeucci, Perugia-Pergolese: Landscapes, Humanising the Dynamics of Strombolian eruptions through high-speed video analysis
11
Marcello Mella, Filippo Menichelli, Raffaele Cavai, Photographs of the shoshonitic-dome, newly added, Monti Sibillini (Lazio, Italy)
17
Chiara R. Cantani, Raffaella De Rosa, Bruce Horstwood, Pasqua Di Donato, Antonia Natale, H2O isotopic studies from Erminia Volcano and Vulcanello (Jonian Islands)
27
Riccardo Barzaghi, Caterina Scardia, Maurizio Sandri, Enrica Laccà, Philip Charles, Fabio de Francia, Studying volcanic activity in Central Europe through multidisciplinary approaches from a combined on/offshore network
37
Manuel Gutiérrez, Luis de la Cruz, Antonio Llobera, Environmenal condition at La Palma volcano, Spain (2009-2010)
39
Rosabella Di Napoli, Alessandro Artoni, Emanuele Ferrari, Stephen Boccia, Francesco Parise, Patrick Haeberli, Emanuele Cocito, Stefano Marchepini, Andrea Mongelli, Giovanni Pallero, Turin carbonatic exhalation and springs
45
Marco Ferrara, Barbara Nisi, Andrea Carbone, Federico Aresu, Matteo Scacchi, Matteo Lisi, Giorgio Martini, Simone De Paoli, Carlo Pini, Stefania Reali, Geothermal fields and geothermal systems in the volcanic region of the Monti Sibillini (Marche, Italy)
51
Orlando Vaselli, Barbara Nisi, Franco Tassi, Fabrizio Rustioni, Valeria Pancioli, Simona Cantarelli, Luciano Giannini, CO2 hazard vs tourist attraction at the Mt. Amiata Volcano (Italy)
53
Sebastian Vogel, GIS-based geomorphometric analysis of Somma-Vesuvius volcanic complex: estimating the altitude of Mt. Somma stratovolcano before its caldera-forming explosive activity
73
Conferences and Symposia
89
Chief-Editors

Bruno Capaccioni, Department of Earth and Environmental Geological Sciences, Piazza Porta San Donato 1, I 40126 Bologna (Italy)
Raffaello Cioni, Department of Earth Sciences, Via Trentino 51, I 09127 Cagliari (Italy)
Orlando Vaselli, Department of Earth Sciences, University of Florence, Via La Pira 4, I 50121 Florence (Italy)

Manuscripts may be submitted to one of the Editors.

* 

Publishing House Information

«Acta Vulcanologica» is published six-monthly (June and December) by Fabrizio Serra editore®, Pisa · Roma.

Subscriptions should be sent to Fabrizio Serra editore®, Casella postale no. 1, Succ. no. 8, I 56123 Pisa (Italy),
tel. +39 050 542332, fax +39 050 574888
fse@libraweb.net, www.libraweb.net

Pisa Office: Via Santa Bibbiana 28, I 56127 Pisa (Italy)
Rome Office: Carlo Emanuele I 48, I 00185 Rome (Italy)

I prezzi ufficiali di abbonamento cartaceo e/o Online sono consultabili presso il sito Internet della casa editrice www.libraweb.net.

Print and/or Online official subscription rates are available at Publisher’s web-site www.libraweb.net.

Payments can be made on our postal current account no. 17154550
or by credit card (American Express, Visa, Mastercard, Eurocard)

* 

Direttore responsabile: Alberto Pizzigati

Autorizzazione del Tribunale di Pisa n. 14 del 24 maggio 1991

* 

«Acta Vulcanologica» is a Peer-Reviewed Journal.
The eContent is Archived with Clockss and Portico.
DEEP RESERVOIR TEMPERATURES OF LOW-ENTHALPY GEOTHERMAL SYSTEMS IN TUNISIA: NEW CONSTRAINTS FROM CHEMISTRY OF THERMAL WATERS

Rossella Di Napoli*,1 · Alessandro Aiuppa1,2
Elise Fourré3 · Philippe Jean-Baptiste3 · Francesco Parello1
Patrick Allard4 · Sergio Calabrese1 · Elyes Gaubi5
Abdallah Ben Mamou5 · Mariano Valenza1

1. DiSTeM, Università di Palermo, Palermo, Italy
2. Istituto Nazionale di Geofisica e Vulcanologia - Seg. di Palermo, Palermo, Italy
3. LSCE, CEA - Saclay, Gif-sur-Yvette, France
4. IPGP, Paris, France
5. Laboratoire Ressources Minérales et Environnement, Université de Tunis El-Manar, Tunis, Tunisia

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...
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 theLate 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 2003, Yermani et alii 2003, Fehdi et alii 2009, 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 evaporate series) as only potential source of sulphate ions (Edmunds et alii 2003, Fourrè et alii 2011). Not surprisingly then, Ca and SO₄ 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 prevailingly 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 to investigate the hydrothermal properties of the Tunisian thermal manifestations (Fig. 1).

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)
samples are bicarbonate-type waters: these have Ca/HCO₃ molar ratios of ~ 0.5 (the typical calcite molar ratio). All water samples are somewhat affected by calcite dissolution, however, as demonstrated by Satu-
Filtration Indexes for calcite being recurrently \( \approx 0 \) (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):

\[
\begin{align*}
\text{K-feldspar} + \text{Na}^+ &= \text{Na-feldspar} + \text{K}^+ \\
2.8 \text{ K-feldspar} + 1.6 \text{ water} + \text{Mg}^{2+} &= 0.8 \text{ K-mica} + 0.2 \text{ chlorite} + 5.4 \text{ silica} + 2\text{K}^+ \end{align*}
\]

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...
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 geoindicator 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 illustration 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 (unlike) 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 prevailingly 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 (Σeq). In their study, Chiodini et alii (1995) proposed that con-
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 (HCO\(_3\))\(^2\)/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\(_3\)/SO\(_4\) content were identified as geo-indicators for both pCO\(_2\) and T (Chiodini \textit{et alii} 1995).

In Figure 5, we show the application of Chiodini’s \textit{et alii} (1995) «sedimentary» geothermometers to the Tunisian thermal manifestations. In the ternary HCO\(_3\)-F-SO\(_4\) diagram of Figure 5, we report a selection of the Fourrè’s \textit{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 \textit{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 \textit{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 Atlasic 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 \textit{et alii}, 1995, Frondini 2008) and CO\(_2\) production is fueled by thermo-metamorphic reactions in the crust (Fourrè \textit{et alii} 2011). No samples from the Saharan domain are available here; however two water samples (samples 41 and 42 in Fourrè \textit{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 \textit{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 geological 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 \textit{et alii} 2011), the geothermometric methodology proposed by Chiodini \textit{et alii} (1995) seems to provide the most reliable assessment of deep reservoir temperatures. From this, we conclude that the tectonically active Atlasic 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.

References


# CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orlando Vaselli, Bruno Capaccioni, Foreword</td>
<td>9</td>
</tr>
<tr>
<td>Antonio Capponi, Danilo M. Palladino, Jacopo Taddeucci, Piergiorgio Scarlato, Parameterizing the dynamics of Strombolian eruptions through high-speed video analysis</td>
<td>11</td>
</tr>
<tr>
<td>Maurizio Mulas, Filippo Mundula, Raffaello Cioni, Stratigraphy of the rheomorphic, densely welded, Monte Ulmus Ignimbrite (sw Sardinia, Italy)</td>
<td>17</td>
</tr>
<tr>
<td>Chiara B. Cannata, Rosanna De Rosa, Bruce Houghton, Paola Donato, Andrea Nudo, Pele's hair: case studies from Kilauea Volcano and Vulcanello (Aeolian Islands)</td>
<td>27</td>
</tr>
<tr>
<td>Rosario Raffaele, Luciano Scarfi, Martine Sapin, Mireille Laigle, Philippe Charvis, Jordi Diaz, Sebastiano Imposa, Seismic activity in Central Lesser Antilles subduction zone from a combined on-/offshore network</td>
<td>35</td>
</tr>
<tr>
<td>Mariantonietta Longobardi, Luca D'Auria, Antonietta Maria Esposito, Relative location of hybrid events At Stromboli Volcano, Italy</td>
<td>39</td>
</tr>
<tr>
<td>Rossella Di Napoli, Alessandro Aiuppa, Elise Fourné, Philippe Jean-Baptiste, Francesco Parello, Patrick Allard, Sergio Calabrese, Elyes Gaubi, Abdallah Ben Mamou, Mariantonietta Longobardi, Luca D'Auria, Antonietta Maria Esposito, Relative location of hybrid events At Stromboli Volcano, Italy</td>
<td>43</td>
</tr>
<tr>
<td>Marco Doveri, Barbara Nisi, Andrea Cerrina Feroni, Alessandro Ellero, Matia Menichini, Matteo Lelli, Giulio Masetti, Simone Da Prato, Claudia Principe, Brunella Raco, Geological, hydrodynamic and geochemical features of the volcanic aquifer of Mt. Amiata (Tuscany, Central Italy): an overview</td>
<td>51</td>
</tr>
<tr>
<td>Orlando Vaselli, Barbara Nisi, Franco Tassi, Daniele Rappuoli, Valeria Pancioli, Simone Ucciero, Luciano Giannini, CO2 hazard vs touristic attraction at the Mt. Amiata Volcano (Italy)</td>
<td>73</td>
</tr>
<tr>
<td>Sebastian Vogel, gis-based geomorphometric analysis of Somma-Vesuvius volcanic complex: estimating the altitude of Mt. Somma stratovolcano before its caldera-forming explosive activity</td>
<td>81</td>
</tr>
</tbody>
</table>

Conferences and Symposia                                               | 89   |