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GEOCHEMICAL TEMPERATURES OF THE THERMAL WATERS OF PHLEGRAEAN FIELDS (NAPLES, ITALY)

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ABSTRACT
Occurrence of mixing processes among geothermal liquids, groundwater and sea water is recognized in alkali-chloride thermal springs of Phlegraean Fields, Southern Italy. Geochemical temperatures estimated by means of binary and ternary mixing models range between 210 and 280°C and refer most likely to the first geothermal "reservoir" existing in Phlegraean Fields. Such indications are in agreement with data provided by deep drilling and are relevant not only for geothermal development but also for surveillance of this active volcanic area.

INTRODUCTION
Phlegraean Fields is an active volcanic area of Southern Italy which is presently being drilled for geothermal exploration by AGIP–ENEL joint-venture. Since early 70s many hydrogeochemical studies have been carried out, both for the surveillance of volcanic activity and in the framework of a multidisciplinary geothermal exploration programme: Dall’Aglio et al. (1972), Baldi et al. (1975), Cortecci et al. (1978), Corniello & Nicotera (1982), unpublished AGIP and IGGI reports.

Since summer 1982 the Phlegraean area is affected by a potentially pre-eruptive crisis, with severe uplift, seismicity and compositional changes in the fumaroles (Barberi et al., 1985). The interest in the knowledge of the hydrothermal system, particularly of its thermal regime, has therefore rapidly increased as it is obviously fundamental both for geothermal exploration and for volcanic surveillance.

Temperature distribution in the subsurface of Phlegraean Fields is controlled by the complicated structural and hydrogeological setting of the region. Direct information by geothermal drilling is available only for Mofete and San Vito areas (fig. 1).

In such a context the contribution of geochemistry can be very important. Gas geochemistry allowed, in fact, to estimate the minimum thermal condition (about 230-240°C) for the aquifer feeding Solfatara fumarole (Cioni et al., 1985). Although hydrogeochemical data are available in other areas of Phlegraean Fields, geothermometric temperatures are lacking or unsatisfactory in previous literature.

Hence aim of this work is to evaluate the geochemical temperatures of the deep geothermal component, considering the complex circulation patterns of the region. Binary and ternary mixtures among groundwater, sea water and geothermal water have been recognized and modelled.

REVIEW OF EXISTING INFORMATION
Two different interpretations were proposed for the origin of thermal springs of Phlegraean Fields. The first one considers that thermal springs are fed by shallow water heated up through condensation of uprising geothermal steam (Dall’Aglio et al., 1972). The second one, based upon isotopic and chemical data, outlines thermal water as the result of mixing process between local meteoric water and water of deep circulation and marine in origin. The geochemical temperature estimated for the only spring (Stufe di Nerone) considered unaffected by mixing process is about 170°C; this value was obtained by Baldi et al. (1975) considering the Na-K-Ca geothermometer (Fournier & True- sdall, 1973) and the quartz solubility (White, 1970). However considering the three Na/K, Ca/K and Na/Na temperature functions (Tonani, 1980; Dongarrà et al., 1983) discrepant geochemical temperatures of 97, 191 and 302°C are obtained. Therefore this water cannot be considered representative of the pure geothermal end member but it is most likely sea water heated up by geothermal steam input (AGIP reports).

The interpretation of isotopic data of water and dissolved sulfate for several thermal springs of Phlegraean Fields (Cortecci et al., 1978) is based entirely on the above mentioned geochemical model of Baldi et al. (1975). The $\Delta^{18}O(SO_4)^{2-}$ geothermometric estimates are therefore affected by this unreliable assumption. Unfortunately a re-interpretation of these data considering the mixing models provided by the present paper can not be implemented due to the lack of $\Delta^{18}O(H_2O)$ data for groundwaters of Phlegraean area.

Mixing processes, occurring at different degrees, among meteoric water, sea water and geothermal fluids are recognized also by Corniello & Nicotera (1982). Their work is a synthesis of geologic, hydrogeologic and hydrogeochemical information rather than a detailed hydrogeochemical study.
Antrodicchia, et al.

GEOCHEMICAL CLASSIFICATION OF THE THERMAL WATERS OF PHLEGRAEAN FIELDS

Only AGIP and IGGI data (table 1) have been processed, because of their similarity and complementarity as far as quality and analytical routine.

Attention has been focused on the geothermal liquids which uprise to feed hot springs and to contaminate groundwaters; therefore only alkaline-chloride waters have been examined (fig. 2).

Alkaline-chloride waters are characterized by extremely variable TDS, from 20 meq/l to 1400 meq/l. Correlation diagrams such as Li vs Cl, B vs Cl, SiO₂ vs Cl (e.g. the SiO₂ vs Cl plot of fig. 3) show that alkaline-chloride waters fall within a rough triangular area the vertices of which are groundwater, sea water and reservoir brines of Mofete (from Carella & Guglielminetti, 1983; reservoir composition has been plot to simplify the reading of such diagram; the interpretation presented hereunder, however is not based on the reservoir data). Three groups of alkaline-chloride waters can be recognized:

1- Low salinity waters whose SiO₂ (B, Li) and Cl contents are close to those of groundwaters; their alkaline-chloride component cannot be surely related to sea water ingress or to geothermal water input.

2- Waters with variable Cl and low SiO₂ (B, Li) which can be considered binary mixtures between groundwater and sea water, although this is not evident from fig. 3 due to the scale adopted.

3- Waters whose SiO₂ (B, Li) content is too high to be explained only by means of sea water ingress; a geothermal component was therefore involved.

Moreover some samples of this last group are aligned between the groundwater component and the geothermal end member; hence they are very likely ternary mixtures, whilst samples with intermediate position within the triangle are very likely ternary mixtures. These three groups exhibit a non-random geographical distribution (see fig. 1): (1) group 1 is met far from the coastline; (2) group 2 is distributed along the western coast from Licola to Monte di Procida; (3) group 3 is found in the coastal region within the Phlegraean Fields caldera (Rosi et al., 1983).

The composition characteristics of group (3) could be explained also by exchange with rocks or rock leaching. The proposed mixing hypothesis is however strongly supported by the nice fitting with the geologic-hydrogeologic environment.

EVALUATION OF GEOCHEMICAL TEMPERATURES

Generalities

Considering the volcanic nature of the region it can be hypothesized that the deep geothermal fluids of the Phlegraean Fields are in equilibrium with a paragenesis comprehending quartz, albite, K-feldspar and a Ca-Al-silicate, such as epidote or other phases with similar values of Gibbs free energy of formation in the temperature range of interest. In such cases the Na/K, Ca/K, Ca/Na and the quartz geothermometers generally point out consistent geochemical temperatures. Actually deep drilling has locally demonstrated the existence of this hydrothermal paragenesis in productive intervals and Na/K, Ca/K, Ca/Na and quartz geochemical temperatures of reservoir fluids are coherent with the measured values (AGIP reports). In order to apply correctly geothermometric techniques to the alkali-chloride waters of group (3) (see previous paragraph) mixing processes among deep geothermal water, groundwater and sea water must be taken into consideration; the following hypotheses have therefore to be introduced:

1) Existence of overall equilibrium in reservoir; in other words we assume that the quartz geothermometer and two out of the three Na/K, Ca/K and Ca/Na temperature functions indicate the same temperature for the pure geothermal component; this hypothesis is confirmed by actual data from producing wells.

2) Mixing, cooling and other possible processes experienced by the uprising geothermal component do not cause gain nor loss of matter; phenomena such as precipitation of solid phases, exchange with rocks and leaching are not provided for.

3) The chemical composition of both groundwater component and sea water is known.

The following system of equations can be written (superscripts showing the electric charge of ionic species are omitted):

\[
\begin{align*}
(Na)_T &= \frac{Na^{+}(Na)}{g} \cdot 6 \cdot (Na)_{gr} \cdot 6 \\
(K)_T &= \frac{K^{+}(K)}{g} \cdot 6 \cdot (K)_{gr} \cdot 6 \\
(Ca)_T &= \frac{Ca^{2+}(Ca)}{g} \cdot 2 \cdot (Ca)_{gr} \cdot 2 \\
(SiO₂)_T &= \frac{(SiO₂)^{4+}(SiO₂)}{g} \cdot (SiO₂)_{gr} \cdot 4
\end{align*}
\]

\[
t + g + s = 1
\]

\[
T = \frac{833.3 \cdot \log (Na)_{T} - \log (Na)_{gr} - \log (Na)_{gr}}{0.55 \cdot \log (K)_{T} - \log (K)_{gr}}
\]

\[
T = \frac{1930 \cdot \log (Ca)_{T} - \log (Ca)_{gr}}{2.92 \cdot \log (K)_{T} - \log (K)_{gr}}
\]

\[
T = \frac{1164}{0.1213 - \log (SiO₂)_{T}}
\]

Indices M, T, G and S refer to the mixture and to geothermal water, groundwater and sea water, respectively. Concentrations are expressed as eq/l for ionic species and as mole/l for silica; densities are considered unity and are dropped from previous equations; T is temperature in Kelvin degrees. Lowercase letter g, s, t refer to the fraction of groundwater, sea water and geothermal component into the mass unit of the mixture (i.e. 1 kg). Having this system of equations and unknowns (T, (Na)ₜ, (K)ₜ, (Ca)ₜ, (SiO₂)ₜ, g, s, t)
it can be solved.

When binary mixture between geothermal water and groundwater is considered, only two geothermometric functions are required, e.g. the Na/K one and the quartz geothermometer. These two functions together with three mass balances and the equation $g + t = 1$ constitute a system of 6 equations and 6 unknowns ($T$, (Na)$_T$, (K)$_T$, (SiO$_2$)$_T$, $g$, $t$) that can be solved.

These systems are solved by an interactive procedure that performs checks on data and call function HYBRD of MINPACK package (Garbow et al., 1980).

Application of the mixing models to the thermal waters of Phlegraean Fields

The following constraints have been introduced for this specific application:

(1) Sea water is represented by the average composition reported by Drever (1982), being not available any complete analysis of the local sea water. An average value of 80 micromole/l has been taken for silica, although values much lower than this, such as those measured for Pozzuoli Gulf water (Macchi, 1972) do not change significantly the geochemical temperature nor the re-calculated composition of the pure geothermal component, being the silica content of sea water much smaller than that of the mixtures.

(2) Groundwater component has been carefully selected for each water point, considering both the numerous groundwater samples collected in the near area and the temporal changes observed at each water point. For 4 springs (Mercurio I, Speradella, Polloio and Grotta) the ground water component is compatible with the composition of the alkaline bicarbonate family, which has been therefore considered in calculations. This chemical type originates by the interaction between meteoric water and volcanic rocks, mainly pyroclastics, and is in fact widespread in the region.

Compositional variations versus time for other water points (Regina well, Damiani well, Edoardo well, Terme Puteolane spring and Stufe di Nerone spring) point out that the groundwater component has a peculiar composition which has been estimated and used in calculations.

Where only one or few samples are available the average composition of the low salinity alkaline-bicarbonate family has been assumed representative of the groundwater component (see table 2).

Spring II of Tempio di Mercurio constitutes a very peculiar case: in fact the occurrence of strong dilution process suggests that one of the collected samples can be considered representative of the groundwater component (see fig. 4).

Mixing models have been applied to a total of 93 samples from 24 different water points; for 10 water points the model does not find any solution. 8 of them have relatively low salinity (Cl < 30 mg/l), hence the fraction of geothermal water is so low that the model cannot "see" it. One of them (Stufe di Nerone spring) exhibits peculiar characters (it is likely sea water receiving steam inputs, as already said). The other one (Terme Puteolane spring) possibly undergoes processes which are not provided for by these mixing models.

Results are in table 3 and fig. 1.

Comparing the geochemical temperatures obtained by means of mixing models with those calculated through direct application of geothermometers formulas, remarkable differences are observed except for the Na/K temperatures of binary mixtures groundwater-geothermal water: in fact in these cases the mixing straightline almost overlaps the Na/K isotherm (in the Na/K correlation plots) passing through the pure geothermal component and its mixtures with groundwater. When sea water is involved in the mixing process mixing lines cut the Na/K isotherms and the geochemical temperature of the pure geothermal component is different from the apparent ones of its mixtures. Mixing lines are straight lines in all correlation plots; hence they always cut Ca/K and Ca/Na isotherms which have parabolic shape: this is the reason for Ca/K and Ca/Na temperatures of pure geothermal component are different from the apparent geochemical temperatures calculated for its mixtures.

CONCLUSIVE REMARKS

All geochemical temperatures but one are in the range 210-280°C, which is typical of phylilitic-propylitic and propylitic hydrothermal paragenesis. These parageneses are characterized by the presence of quartz, albite, microcline and epidote, that is just the mineral phases that control Na/K, Ca/K, Ca/Na and silica geothermometers. This consistency among fluid composition and mineral paragenesis corroborates the temperature evaluation and allows us to hypothesize that examined springs and wells are fed by geothermal fluids circulating within fractured zones which are characterized by phylilitic-propylitic and/or propylitic paragenesis. These zones very likely represent the first reservoirs existing in Phlegraean Fields and are limited upward by impervious rocks. In fact no geochemical temperatures lower than 210°C (but a value of 187°C) and linked to different hydrothermal paragenesis, have been observed. These conclusions are in good agreement with data provided by deep drilling (AGIP report) and are relevant not only for geo-thermal development but also for surveillance of this active volcanic area. In fact these water points indicate that circulation of hydrothermal fluids is widespread in Phlegraean Fields; in turn they represent a sort of natural tapping points of hydrothermal aquifers and should be studied to monitor the state of volcanic activity.

The use of geochemical changes in surface thermal waters as potential precursors of an impending volcanic eruption can be attempted only if processes occurring at shallow depth such as mixing of hot uprising fluids with groundwater and sea water are carefully studied.

ACKNOWLEDGMENTS

The authors would like to express sincere thanks to Prof. Franco Barberi for the critical reading of the manuscript and to Dr. Guido Verdiani of AGIP S.p.A. for the helpful co-operation.
### Table 1. Chemical data list.

<table>
<thead>
<tr>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Cl</th>
<th>SiO₂</th>
<th>pH</th>
<th>B</th>
<th>Li</th>
<th>n.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>1.8</td>
<td>3.4</td>
<td>0.9</td>
<td>5.4</td>
<td>0.8</td>
<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>1.1</td>
<td>1.3</td>
<td>0.4</td>
<td>0.9</td>
<td>5.4</td>
<td>0.8</td>
<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
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<td>0.9</td>
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<td>5.4</td>
<td>0.8</td>
<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Table 2. Average composition of low salinity alkali-bicarbonate waters (data are expressed as in Table 1).

<table>
<thead>
<tr>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Cl</th>
<th>SiO₂</th>
<th>pH</th>
<th>B</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
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<td>0.6</td>
<td>0.9</td>
<td>5.4</td>
<td>0.8</td>
<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
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<td>1.3</td>
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<td>0.9</td>
<td>7.2</td>
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<td>0.4</td>
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<td>3.4</td>
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<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
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<td>1.3</td>
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<td>0.9</td>
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<td>7.2</td>
<td>0.3</td>
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<td>0.9</td>
<td>5.4</td>
<td>0.8</td>
<td>4.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

All concentration data are expressed by three figures: the first and the second refer to tens and units, the third one is the exponent of basis 10 with changed sign.

Ca, Mg, Na, K, HCO₃⁻ (+ CO₃⁻), SO₄²⁻ and Cl are in equivalent/l.

pH is reported omitting the point after first figure.

Temperature is in degree centigrade.
REFERENCES


Table 3. Average geochemical temperature (in °C) of the pure geothermal end member feeding the considered water points. Numbers in parenthesis indicate the number of examined samples for each water point.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ternary mixtures</th>
<th>Binary mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average st. dev.</td>
<td>Average st. dev.</td>
</tr>
<tr>
<td>a. Water points periodically sampled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grotta (8)</td>
<td>216</td>
<td>20</td>
</tr>
<tr>
<td>Mercurio I (6)</td>
<td>215</td>
<td>10</td>
</tr>
<tr>
<td>Mercurio II (7)</td>
<td>211</td>
<td>7</td>
</tr>
<tr>
<td>Pollio (7)</td>
<td>239</td>
<td>9</td>
</tr>
<tr>
<td>Sprudel (15)</td>
<td></td>
<td>238</td>
</tr>
<tr>
<td>Viola (3)</td>
<td></td>
<td>187</td>
</tr>
<tr>
<td>Procolo (3)</td>
<td></td>
<td>235</td>
</tr>
<tr>
<td>Fangia (3)</td>
<td></td>
<td>253</td>
</tr>
<tr>
<td>Damiani (2)</td>
<td></td>
<td>221</td>
</tr>
<tr>
<td>b. Water points sampled only in 1977 survey</td>
<td></td>
<td></td>
</tr>
<tr>
<td>832</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>725/725a</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>857</td>
<td>205</td>
<td></td>
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<tr>
<td>738</td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>


Antrodichias, et al.

Figure 1. Geographic distribution of alkali-chloride waters. Triangles indicate low salinity waters whose alkali-chloride component cannot be safely related neither to sea water intrusion nor to geothermal water uprising. Squares are binary mixtures sea water-groundwater. Circles refer to waters whose features point out the presence of a geothermal component; solid circles are ternary mixtures geothermal water-sea water-groundwater; half solid circles are binary mixtures geothermal water-groundwater; open circles indicate mixtures which cannot be quantitatively defined. Numbers are geochemical temperatures in degree C. Lowercase letters refer to the name (or sample number, if the name is unknown) of the water point: (a)=Tempio di Mercurio, spring II; (b)=Tempio di Mercurio, spring I; (c)=sample 832; (d)=sample 731; (e)=Grotta dell’Acqua Santa spring; (f)=Tilio spring; (g)=samples 735 and 745; (h)=Precolo well; (i)=sample 871; (j)=sample 781; (k)=Amanzino well; (l)=Terme di Agnano, Sprudel spring; (m)=Terme di Agnano, Fangata spring; (n)=Vesuvius well; (o)=sample 752; (p)=Stufe di Nerone well; (q)=Pompeii well; (r)=sample 114; (s)=sample 730; (t)=Tempio di Giove Serapide spring; (u)=Terme di Giove Serapide spring.

Figure 2. Langelier diagram; see fig. 1 for the explanation of the symbols of alkali-chloride waters whose analyses are reported in table 1. Asterisks = Mofete wells. Crosses = waters with composition different from alkali-chloride. Represents the average composition of the low salinity alkaline-bicarbonate family.

Figure 3. SiO₂ versus Cl⁻ correlation plot; see figure 1 for the explanation of the symbols.

Figure 4. Temporal changes of chemical parameters at Tempio di Mercurio spring II.