PANTELLERIA ISLAND (SICILY, ITALY): A GAS GEOCHEMICAL SURVEY

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Abstract
A detailed geochemical survey was carried out in Pantelleria island during the years 1990-92. Geochemical methodologies were applied to the fluids sampled from springs, fumaroles and shallow wells. This led to the identification of an area of potential interest from a geothermal point of view, located in the southern part of the island. The estimated temperatures in the local reservoirs range from 225°C to 255°C. In 1992 an additional exploratory well was drilled in the identified area. The thermodynamic characteristics of the produced fluid partially confirmed the hypotheses about the reservoir that were based on the surface geochemical survey. Interesting physical parameters of the reservoir have also been computed. This paper is limited to the presentation of the results that are based only on gas compositions.

1. INTRODUCTION

The island of Pantelleria lies in the "Canale di Sicilia", about 80 km from the coast of Africa and about 100 km from that of Sicily, and is the summit of a large submarine volcano that emerges in the rift area of the channel. The most significant volcanic episodes, dating back to 10-50 ky, have produced two nested calderas that characterize the morphology of the island. Although only relatively few data are available on the surface water or gas chemistry (Barbier, 1969; Dongarra et al., 1983; Alaimo and D’Amore, 1993; Squarcia et al., 1993; Grassi et al., 1995), a lot of information can be found in the literature about volcanology, structural geology and petrology (e.g., Cometti et al., 1983; Mahood and Hiller, 1983 and 1986; Civetta et al., 1984; Mahood, 1984; Civetta et al., 1984; Orsi et al., 1981; De Vivo et al., 1992). With the aim of identifying the area of greatest geothermal interest and estimating the characteristics of the geothermal fluid, sampling surveys were carried out on almost all the known gas emanations of the island in February and June 1990 (Alaimo and D’Amore, 1994) (Figure 1). Four exploratory shallow wells were sited in different zones of the island (depths from 150 to 300 m) during 1992. Only one well, PT3, produced a thermal fluid, at a temperature of about 140°C. At the same time a new gas survey was performed on a limited number of gas manifestations. In December 1993 E.M.S. with CESEN S.p.A. as operator drilled two deep wells (max. depth 1200 m) (Chierici et al., 1995). Of these (Figure 1) well PPT2 was drilled in the "Airport" zone (north-west area). It was not a "producer" with 125°C at 950 m. Well PPT1 was drilled in "Favara" zone (south-east area, in the caldera) and produced a geothermal fluid after several weeks of air stimulation. Its maximum flow-rate was about 4 tons/h of steam with 0.15 tons/h of entrained water. The maximum value of well-head temperature was about 130°C. The reservoir measured temperature at 1000 m is close to 260°C.

The aim of this paper is to show:

a) that the application of geochemical methods to the gas composition will permit the location of the most interesting area for well siting during geothermal prospection;

b) that exploration drilling in the proposed area verified what was previously hypothesized about the physical conditions in the reservoir;

c) that gas geochemistry applied to the fluids sampled in the shallow and deep wells permits us to calculate some physical parameters of the producing reservoir.

2. DATA PRESENTATION

Table 1 reports the analytical gas compositions of the samples of the February and June 1990 surveys and the new data obtained during 1992 for shallow well PT3 and deep well PPT1 (1993). The gas composition is expressed in volume % for CO2, O2 and N2, and in ppm by volume for the other species.

Several gas samples, mostly of the February 1990 survey, show large contents of O2. Figure 2 shows that the N2/O2 ratio is close to that of air, while the gas bubbling in water and gas from the steaming ground of "Favara-Passo del Vento-Monte Gibele" area plot near the CO2 corner. The high concentrations of O2 therefore represent contamination by air during sampling, due mostly to weak flows. The concentrations of H2 and CH4 vary over a range of more than four orders of magnitude. CO content is always within about one order of magnitude. Very high contents of He are present in "Favara-Passo del Vento - Monte Gibele" area. H2S is present in large amounts only in wells PT3 and PPT1.

In order to explain, at least qualitatively, the almost complete absence of H2S in the natural manifestations and the great variability in the gas composition, we have to consider some conditions that may influence the original deep composition to various degrees. These are:

a) the very low gas flow;

b) the existence of a shallow aquifer with a maximum temperature close to 130°C (Dongarra et al., 1983). This aquifer was perched during drilling of the shallow and deep wells at different depths. Both the temperature and the thickness of this aquifer may vary (Grassi et al., 1995);
Table 1. Gas composition in the dry gas in volume % and mppm by volume for samples collected during the 1990 and 1992 surveys.

![Fig. 2. Relative N₂, CO₂ and O₂ contents in gas discharges on a molar basis.](image)

Although the variability of CO content in absolute concentrations in the gas is one order of magnitude, the ratio CO/CO₂ varies by more than four orders of magnitude. CO is generally considered not to re-equilibrate at low temperatures, which is probably why we observe a trend in the distribution of the values of log(CO/CO₂) as a function of the quantity (N₂ + O₂) (Figure 3). The very high values of the CO/CO₂ ratio in the strongly air-polluted samples are probably caused by some local selective accumulation of CO in the air-bearing soil due to the very low gas flow. In these samples CO is not maintaining chemical equilibrium with other reactive gaseous species (e.g. H₂). In figure 3 are reported also the values of the CO/CO₂ ratios in air and in air saturated water. Calculations are made considering the air a value of 200 ppm for CO and 360 ppm for CO₂ (E. Corazza pers. comm. 1994). The shape of the curve is due only to the constrain 0-100% for the (O₂ + N₂) axis.

![Fig. 3. (O₂ + N₂) in volume % reported vs log(CO/CO₂) with the best fitting line.](image)

Because of the large variability of the data relative to the natural manifestations, some criteria of selection have been adopted in order to apply thermodynamic calculations to the most reliable samples. The relations between H₂, CO and O₂ in the first criterion (Figure 4). Three groups of samples can be identified:

- Group A: with prevailing air, and variable contents of H₂ (low) and CO;
- Group B: with prevailing CO₂, almost no H₂, and very low values of CO/CO₂ (low absolute value of CO);
- Group C: with prevailing CO₂, rich in O₂ and relatively high value of CO (2-3 ppm).

![Fig. 4. Relative H₂, CO and O₂ contents in gas discharges on a molar basis.](image)
The relation between the relative contents of H₂, CH₄ and CO₂ has been used as a second criterion of selection (Figure 5). The samples plot along a general trend (with few exceptions) ranging from almost pure CO₂ towards a composition richer both in H₂ and CH₄, with relative ratios typical of geothermal gases. This group of samples corresponds to most of the samples of group C of Figure 4. The geographic distribution of the different groups of samples (shown in Figs. 4 and 5) indicates that group C is located in "Favara-Passo del Vento-Monte Gibele" area, group A around "Montagna Grande"; the most reliable samples of group B are the gases of the springs "Gadir", "Lago di Venere" and "Polla 1 and 2".

![Figure 5](image)

Fig. 5. Relative H₂, CH₄ and CO₂ contents in gas discharges on a molar basis. Inside the circle are the samples located in "Favara-Passo del Vento-Monte Gibele" area and wells PP3 and PPT1.

All the samples have been plotted in the N₂·Ar·He triangular diagram (Giggenbach, 1987 and Giggenbach and Matsuo, 1991) (Figure 6). The data have not been corrected for air. The trend, starting from air or air-saturated water suggests a deep crustal or a local basaltic origin for the group C and the gases from the wells. This is still a point to be clarified. Some indications will be produced by the determination of the 3He/4He ratio.

The physical conditions of a deep reservoir have therefore been determined by gas geochemistry using only the samples from the area "Favara-Passo del Vento-Monte Gibele".

![Figure 6](image)

Fig. 6. Relative N₂, He and Ar contents in gas discharges on a molar basis (gas analyses not corrected for air).

### 3. ASSESSMENT OF PHYSICAL CONDITIONS OF THE RESERVOIR

#### a) Calculation of the distribution of the deep temperatures in Pantelleria by means of H₂/CH₄ ratio.

In order to obtain a semi-quantitative evaluation of temperatures in the local aquifers of Pantelleria island, we assume that gas originates from these aquifers, equilibrates and, keeping some memory of its original temperature conditions (at least for the H₂/CH₄ ratio), rises to the surface in the form of local manifestations. Because the species H₂ and CH₄ have been detected in almost all the samples, we decided to use the ratio between these species to calculate the temperature of the local aquifer.

Two chemical reactions have been used at equilibrium conditions:

\[
\begin{align*}
\text{CH}_4 + 2 \text{H}_2\text{O} &= \text{CO}_2 + 4 \text{H}_2 \\
\text{H}_2\text{O} &= \text{H}_2 + 1/2 \text{O}_2
\end{align*}
\]

A linear combination of equations (1) and (2) generates a new equation in which the H₂/CH₄ ratio is a function of the temperature \(T\) (K), CO₂ partial pressure and O₂ fugacity, considering that the solubilities of H₂ and CH₄ have very similar values. As regards the O₂ fugacity, a simple equation correlating the log of its value with the temperature \(T\) (K) can be used from D’Amore and Gianelli (1984). The final geothermometer is:

\[
\log_{10}\left(\frac{\text{H}_2\text{O}}{\text{CH}_4}\right) = -1.103 + 0.976 \times 10^2 \frac{1}{T} - 3.1232 \times 10^{-4} T
\]

The value of \(P(\text{CO}_2)\) for each gas manifestation is unknown. In first approximation, and to give some homogeneity to the results, we decided arbitrarily to use the computed value of \(P(\text{CO}_2)\) for shallow well PT3 (0.8 bar, as shown in the section relative to this well) for all samples. The distribution of the computed temperatures as contours is reported in Figure 7. This is in good agreement with the temperatures extrapolated at sea level from physical measurements in shallow wells (Squarcì et al., 1993). The distribution of computed temperatures suggests a maximum geothermal anomaly in the "Favara-Passo del Vento-Monte Gibele" area, with values close to 250-260°C in "Favara-Passo del Vento" and about 200°C in "Monte Gibele" (Table 2). For the other localities all computed temperatures are relatively low, as for example in "Gadir", with 130-140°C, and in "Lago di Venere" (or "Polla") with 95°C.

![Figure 7](image)

Fig. 7. Contours reporting the distribution of temperatures in the local reservoir using the H₂/CH₄ ratio (eq. 3) for gas discharges showing a high CO₂.

1) shallow exploratory wells, 2) deep exploratory wells, 3) isotherm (°C), 4) old caldera rim, 5) young caldera rim.
b) Application of some geothermometers in "Favare-Passo del Vento-Monte Gibele" area.

Assuming that the area "Favare-Passo del Vento-Monte Gibele" is the most promising for geothermal uses, we focused our attention on this area, using other geothermometers to confirm the previous results. Using the data of Table 1 for the three zones, the values of the logarithms of the mean ratios of CO/CO₂, H₂/CO₂ and CH₄/CO₂ to be used in the next geothermometric calculations are reported in Table 2.

<table>
<thead>
<tr>
<th>Zone</th>
<th>log(TH/CO₂)</th>
<th>log(TH₂/CO₂)</th>
<th>log(CH₄/CO₂)</th>
<th>log(H₂S/CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Favare</td>
<td>-5.32±0.30</td>
<td>-1.24±0.10</td>
<td>-1.49±0.08</td>
<td>-1.24±0.10</td>
</tr>
<tr>
<td>P. Vento</td>
<td>-5.70±0.17</td>
<td>-1.13±0.07</td>
<td>-1.66±0.23</td>
<td>-1.13±0.07</td>
</tr>
<tr>
<td>M. Gibele</td>
<td>-5.79±0.66</td>
<td>-2.23±0.16</td>
<td>-1.83±0.34</td>
<td>-2.23±0.16</td>
</tr>
<tr>
<td>Well PT3</td>
<td>-6.64</td>
<td>-1.39</td>
<td>-1.56</td>
<td>-1.39</td>
</tr>
<tr>
<td>Well PPT1</td>
<td>-4.70</td>
<td>-2.18</td>
<td>-2.28</td>
<td>-2.18</td>
</tr>
</tbody>
</table>

Table 2. Average values of three gas ratios and temperatures (°C) computed by different methods for the "Favare-Passo del Vento-Monte Gibele" area and the two wells PT3 and PPT1.

The following geothermometric methods have been used on these data (all results are summarized in Table 2):

1) Carbon monoxide is considered to be in chemical equilibrium with CO₂, CH₄ and H₂O (Bertram et al., 1985; D’Amore et al., 1987; Giggenbach, 1987; Chioldini and Cioni, 1989) according to the following reaction:

\[ \text{CH}_4 + 3\text{CO}_2 \rightleftharpoons 4\text{CO} + 2\text{H}_2\text{O} \]  

(4)

The best way to calculate the temperature, and at the same time to verify the equilibrium conditions, is to use the logarithmic diagram from Giggenbach (1987 and 1991), reporting on the axes \( \log(\text{CO}_2/\text{TH}) \) vs \( \log(\text{CO}_2/\text{TH}) \) (Figure 8). The points of the surface manifestations and the shallow well in this area cluster between 220 and 240°C for a liquid water-dominated system (eq. 4a in Table 2). Equation 4 can be used, as in D’Amore (1991), where the quantity 4log(TH/CO₂) - log(CH₄/CO₂) is reported vs temperature. As in Figure 9, the computed temperatures shown in Table 2 (eq. 4b) refer to equilibrium in a pure liquid phase. The only exception is well PPT1, where a vapour phase has been considered, for the reason described in the next section, i.e. a high fraction of steam.

![Fig. 8. Evaluation of CH₄ - CO - CO₂ equilibration conditions (Giggenbach, 1987) for selected temperatures in pure vapour, two phase and pure liquid conditions.](image)

Fig. 8.

![Fig. 9. CO - CO₂ - CH₄ chemical equilibrium reported vs. temperature in the vapour phase (y = 1) or in the liquid phase (y = 0) as in eq 35 and figure 3 of D’Amore, 1991.](image)

In the study area temperatures vary between 220 and 270°C (when this method is applied to the gas of well PPT1 we don’t obtain a suitable result : 224°C).

2) Equation 1 can be used in combination with the following chemical reaction to calculate both temperature and CO₂ partial pressure:

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \]  

(5)

This reaction is very slightly temperature dependent (e.g. D’Amore, 1991) and can be used as a geobarometer to calculate the CO₂ partial pressure (Chioldini and Cioni, 1989). Between 150 and 300°C, using eq. 6 in a pure liquid phase, we obtain:

\[ \log(\text{P}(\text{CO}_2)) = 3.77 \pm 0.05 + \log(\text{CO}_2) \]  

(7)

In a pure vapour phase the coefficient is 3.52.

For a pure liquid phase eq. 1 can be arranged as:

\[ 4\log(\text{H}_2/\text{CO}_2) - 3\log(\text{H}_2\text{O}/\text{CO}_2) = 6.69 + 21144.08/T + 4.635 \log T + 4\log(\text{B}(\text{H}_2)) - 3\log(\text{B}(\text{CO}_2)) - 3\log(\text{B}(\text{CH}_4)) - 4\log(\text{P}(\text{CO}_2)) \]  

(8)

where B(i) is the vapour-liquid distribution coefficient for each gas "i", and a known function of temperature for each gaseous species (D’Amore and Truedell, 1988). The results of the computed temperatures are reported in Table 2 (for well PPT1 the calculations have again been performed for a fluid with a high value of steam fraction). The temperature values seem to be fairly comparable.

c) Use of the H₂S content in calculating some physical parameters of the reservoir for wells PT3 and PPT1.

From Table 1 it is evident that only the two wells produce relatively large contents of H₂S in the dry gas. For well PPT1 the gas/H₂O ratio has also been measured. For both wells it is then possible to use the method described in D’Amore et al. (1987) and in Saracco and D’Amore (1989) to compute the following parameters of the geothermal reservoir: temperature, in-place steam fraction “y” with respect to total water, P(CO₂), and, from these parameters, the gas/total water ratio and redox conditions (such as log(P(O₂)) and log(P(S²))).

Three chemical reactions are involved: the Fisher-Tropsch (eq. 1), the CO-CH₄-CO₂-H₂O equilibrium (eq. 4) and a reaction involving H₂S (e.g. D’Amore et al. 1982):

\[ \text{H}_2 + 3/2\text{FeS}_2 + 2\text{H}_2\text{O} = 3\text{H}_2\text{S} + 1/2\text{Fe}_2\text{O}_3 \]  

(9)

The original equations, showing all the terms, are very long and complex (Saracco and D’Amore, 1989), so we decided to convert them to the following simplified expressions:
\[ 4\log(H_2CO_3) - 4\log(CH_4CO_2) = f_1(T) + f_2(y, Bi) - 4\log(P(CO_2)) \]  
(10)

\[ 3\log(H_2S\cdot CO_3) - 4\log(H_2CO_3) = f_2(T) + f_2(y, Bi) - 2\log(P(CO_2)) \]  
(11)

\[ 4\log(CO_2/CO_2) - 4\log(CH_4/CO_2) = f_3(T) + f_3(y, Bi) \]  
(12)

where Bi indicates the vapour-liquid distribution coefficients for all gaseous species considered in each reaction. The set of equations is solved by a numerical approach. When temperature, P(CO_2) and y values have been obtained it is possible to calculate the gas/H_2O ratio from the value of the CO_2/H_2O ratio:

\[ CO_2/H_2O = [P(CO_2)/P(H_2O)] \times [1 + (1-y)/Bi(CO_2)] \]  
(13)

Redox conditions can be computed from a chemical reaction involving O_2 (eq. 2) and a reaction involving S2, such as

\[ H_2S = H_2 + 1/2 \, S_2 \]  
(14)

The equations to calculate redox conditions are reported in Saracco and D’Amore (1989) and in D’Amore (1991). The application of this method produces the following results

<table>
<thead>
<tr>
<th>well</th>
<th>PT3</th>
<th>PPTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature (°C)</td>
<td>245</td>
<td>287</td>
</tr>
<tr>
<td>steam fraction y</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>P(CO_2) (bar)</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>gas/H_2O (molar ratio)</td>
<td>1 x 10^{-3}</td>
<td>0.025</td>
</tr>
<tr>
<td>log P(O_2)</td>
<td>-37.6</td>
<td>-34.2</td>
</tr>
<tr>
<td>log P(S_2)</td>
<td>-13.4</td>
<td>-12.0</td>
</tr>
</tbody>
</table>

Applying the log(CH_4/CO_2) vs log(CO_2/CO_2) diagram (Figure 8) produces similar results for the evaluation of temperature and steam fraction. Well PT3 shows a temperature of 233°C in an almost pure liquid phase, while well PPTI shows a temperature of 288°C with a relatively large amount of steam in the reservoir.

The computed gas/H_2O is four times higher than the measured value at well-head. This could be due to mixing with large amounts of shallow water with respect to the deep fluid. We can then use both values of gas/H_2O. Using the measured gas/H_2O value we obtain 26±4°C and y = 0.045 (point 1 in Figure 10). If the computed gas/H_2O value is used we obtain 290°C and y = 0.15 (point 2 in Figure 10).

4. CONCLUSIONS

A geochemical method based on the H_2/CH_4 ratio applied to all gas emanations on the island, provided a first evaluation of the areal distribution of temperature in the aquifers where H_2 and CH_4 equilibrate. An area with computed temperatures exceeding 200°C was identified in the south-east part of the island in the zone "Favare, Passo del Vento and Monte Gibele". Other geothermometers were applied to the gas compositions of area "Favare" and "Passo del Vento" show an average computed temperature of 255±14 and 248±19°C respectively, while "Monte Gibele has the lowest temperature in the area, with 223±15°C. The shallow well PT3 (150 m) is located very close to "Favare" zone. Application of the same geothermometers produces an average temperature of 247±14°C. As we know the H_2/S content in the dry gas, it is possible to use a more sophisticated approach to calculate some physical parameters of the local reservoir. The obtained temperature is 245°C very close to the value computed with the other methods. The computed gas content in the reservoir is very low (about one liter of gas per kg of water) with a value of P(CO_2) = 0.8 bar. The computed amount of the in-place steam fraction in phase equilibrium with the liquid water is very small (y < 0.01). The reservoir parameters computed from the gas of deep well PPTI (260°C measured at about 1000 m), applying the same method, are very different. First, the computed temperature is close to 285°C with a relatively high gas content (about 30 liters per kg of water) and a value of P(CO_2) = 1.1 bar. The measured well-head gas/H_2O ratio is about four times less. The computed steam fraction is relatively high (y = 0.14) and typical of a two-phase system. Indeed, the well is producing wet steam at about 100°C and a flow rate of 3 tons/h. A possible explanation of the observed discrepancy between the measured and computed gas/H_2O ratio and the low temperature at well-head, could be due to fast inflow of cold shallow water.

We could hypothesize the existence of two separate water layers (gas geochemistry is unable to tell us whether they are connected) that form the overall reservoir. The gas sample from well PT3 seems to come from the upper, liquid, lower-temperature reservoir. The gas sample from well PPTI seems to come from a very hot deep vapour-dominated reservoir. More deep exploratory wells are needed to assess the potential of the local geothermal system and the hot deep vapor-dominated reservoir. Well PPTI should also be reopened for new tests and fluid sampling at different well-head conditions.

REFERENCES


