THERMODYNAMIC MODELLING

Abiogenic endmember compositions for Nisyros have been computed from equation (4) considering the following temperature dependencies for $f_{H_2O}$ of 2 m NaCl solutions and $K_3$, respectively:

$$\log f_{H_2O} = 5.462 - 2047/T \quad (S1)$$

$$\log K_3 = 10.5 - (5150 + 310*n)/T \quad (S2)$$

where $T$ is in K and $n$ the number of carbon atoms in ethane and propane, respectively (Chiodini et al., 2001; Taran and Giggenbach, 2003).

Carbon isotope data for CH$_4$ and CO$_2$ reflect hydrocarbon formation temperatures of 340 ± 10°C (Table 1). At these temperatures, the redox conditions of the bi-phase hydrothermal system can be constrained considering gas concentration data of the fumaroles. For the period from 1990-2002, molar ratios ($X$) of redox pairs CO/CO$_2$, H$_2$/H$_2$O and CH$_4$/CO$_2$ indicate that redox conditions at 340°C closely correspond to the FeO-FeO$_{1.5}$ buffer (Chiodini and Marini, 1998; Marini and Fiebig, 2005), for which $\log(X_{H_2}/X_{H_2O})$ is $-2.82$, roughly independent of temperature (Giggenbach, 1987). $X_{CO}/X_{CO_2}$ and $X_{CH_4}/X_{CO_2}$ ratios were also measured for the fumaroles sampled in this study and are indistinguishable from values observed for the period 1990-2002 (Table 1S). This agreement indicates that no significant change in redox conditions took place between 1990 and 2007. The $f_{CO_2}$ at the temperature of methane formation can be constrained from molar ratios of CO and H$_2$ using equation S3 (Chiodini & Marini, 1998), along with gas concentration data and methane formation temperatures reported by Fiebig et al. (2007):

$$\log f_{CO_2} = -2.485 + 2248/T - \log(X_{H_2}/X_{CO}) + \log f_{H_2O} \quad (S3)$$
At Nisyros, fCO$_2$ is ~1bar (Table 1S), such that logfCO$_2$ in equation (4) can be neglected.

**MIXING TRENDS DISPLAYED IN FIGURE 1**

Hydrocarbon distribution ratios of C1/C2 and C2/C3 are given through

\[ C_i/C_{i+1} = (n_{C_{i,ab}} + n_{C_{i,\alpha}})/(n_{C_{i+1,ab}} + n_{C_{i+1,\alpha}}) \]  
(S4)

with n$_{C_{i,ab}}$ and n$_{C_{i,\alpha}}$ denoting the moles of alkane hydrocarbons with carbon numbers i and i+1, predicted by thermodynamics according to equation (4) (ab) and by random breakage or linkage of C-bonds (\(\alpha\)), respectively. The Schulz-Flory distribution factor \(\alpha\) is defined by

\[ \alpha = n_{C_{i+1,\alpha}}/n_{C_{i,\alpha}} \]  
(S5)

The mole fraction of abiogenic equilibrium alkanes with C-numbers i and i+1 is represented by Y according to

\[ Y_{i+1/i} = n_{C_{i+1,ab}}/n_{C_{i,\alpha}} \]  
(S6)

Values for Y can be computed from equation (4). If reaction (5) applies for abiogenic hydrocarbon production, only methane is generated and Y becomes 0. For a given chain length, molar fractions of hydrocarbons generated through random breakage or linkage (X$_\alpha$) or through abiogenic processes (X$_a$) are interlinked through

\[ X_{ab} = 1 - X_\alpha = nC_{a}/nC = (1 - nC_\alpha/nC) \]  
(S7)

Considering equation (S4) to (S7), it can be derived for C1/C2 and C2/C3 ratios

\[ C1/C2 = 1/(1 - X_\alpha)*Y_{2/1} + \alpha* X_\alpha \]  
(S8)

\[ C2/C3 = ((1 - X_\alpha)*Y_{2/1} + \alpha* X_\alpha)/(1 - X_\alpha)*Y_{3/2} + \alpha*\alpha* X_\alpha \]  
(S9)

**TABLE**

Table DR1. Molar ratios, X, of gas components contained in dry gas samples and comparison of X$_{CH_4}$/X$_{CO_2}$ and X$_{CO}$/X$_{CO_2}$ ratios obtained in 2007 with those characteristic for the 12 year period (1990-2002; Marini & Fiebig, 2005). Also given are logfCO$_2$ values characteristic for
the Nisyros bi-phase hydrothermal system, which were calculated according to equation S3 and temperatures derived from carbon isotope partitioning between CO₂ and CH₄ (see Table 1).

REFERENCES CITED


Marini, L, and Fiebig, J., 2005, Fluid geochemistry of the magmatic-hydrothermal system of Nisyros (Aegean arc, Greece), in Hunziker, J.C., and Marini, L., eds., The geology, geochemistry and evolution of Nisyros volcano (Greece); implications for the volcanic hazards: Memoires de Geologie (Lausanne), v. 44, p. 121-163.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X(CO₂)</th>
<th>X(CH₄)</th>
<th>X(CO)</th>
<th>X(H₂)</th>
<th>log(CO/CO₂)</th>
<th>log(CO/CO₂)₁₂yr</th>
<th>log(CH₄/CO₂)</th>
<th>log(CH₄/CO₂)₁₂yr</th>
<th>logf(CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybotes Mikros (PP9S)</td>
<td>743300</td>
<td>1759</td>
<td>9.0</td>
<td>16000</td>
<td>-4.9</td>
<td>-4.8 to -5.5</td>
<td>-2.6</td>
<td>-2.5 to -3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Stefanos (S4)</td>
<td>791500</td>
<td>4400</td>
<td>2.2</td>
<td>6200</td>
<td>-5.6</td>
<td>-5.4 to -6.1</td>
<td>-2.3</td>
<td>-2.1 to -2.6</td>
<td>-0.1</td>
</tr>
<tr>
<td>Phlegeton (A)</td>
<td>809300</td>
<td>805</td>
<td>2.1</td>
<td>9230</td>
<td>-5.6</td>
<td>-5.3 to -6.0</td>
<td>-3.0</td>
<td>-2.4 to -3.2</td>
<td>-0.3</td>
</tr>
</tbody>
</table>