DATA REPOSITORY ITEM 2009118

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:

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

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

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_2O and CH_4/CO_2 indicate that redox conditions at 340 °C closely correspond to the $FeO\text{-}FeO_{1.5}$ 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):

$$\log f_{CO_2} = -2.485 + 2248/T - \log(X_{H_2}/X_{CO}) + \log f_{H_2O} \quad \text{(S3)}$$

At Nisyros, f_{CO_2} is ~1bar (Table 1S), such that $\log f_{CO_2}$ in equation (4) can be neglected.

MIXING TRENDS DISPLAYED IN FIGURE 1

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

$$C_i/C_{i+1} = (nC_{i,ab} + nC_{i,\alpha})/(nC_{i+1,ab} + nC_{i+1,\alpha}) \quad \text{(S4)}$$

with nC_{ab} and nC_α 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 (α), respectively. The Schulz-Flory distribution factor α is defined by

$$\alpha = nC_{i+1,\alpha}/ nC_{i,\alpha} \quad \text{(S5)}$$

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

$$Y_{i+1/i} = nC_{i+1,ab}/ nC_{i,\sim} \quad \text{(S6)}$$

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_α) or through abiogenic processes ($X_{a\sim}$) are interlinked through

$$X_{\sim b} = 1 - X_\alpha = nC_{a\sim}/nC = (1 - nC_\alpha/nC) \quad \text{(S7)}$$

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

$$C1/C2 = 1/((1 - X_\alpha)*Y_{2/1} + \alpha* X_\alpha) \quad \text{(S8)}$$

$$C2/C3 = ((1 - X_\alpha)*Y_{2/1} + \alpha* X_\alpha)/((1 - X_\alpha)*Y_{2/1}*Y_{3/2} + \alpha*\alpha*X_\alpha) \quad \text{(S9)}$$

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 $\log f_{CO_2}$ values characteristic for

the Nisyros bi-phase hydrothermal system, which were calculated according to equation S3 and temperatures derived from carbon isotope partitioning between CO_2 and CH_4 (see Table 1).

REFERENCES CITED

Chiodini, G., and Marini, L., 1998, Hydrothermal gas equilibria: The H_2O-H_2-CO_2-CO-CH_4 system: Geochimica et Cosmochimica Acta, v. 62, p. 2673-2687.

Chiodini, G., Marini, L., and Russo, M., 2001, Geochemical evidence for the existence of high-temperature hydrothermal brines at Vesuvius volcano, Italy: Geochimica et Cosmochimica Acta, v. 65, p. 2129-2147.

Fiebig, J., Woodland, A.B., Spangenberg, J., and Oschmann, W, 2007, Natural evidence for rapid abiogenic hydrothermal generation of CH_4: Geochimica et Cosmochimica Acta, v. 71, p. 3028-3039.

Giggenbach, W.F., 1987, Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand: Applied Geochemistry, v. 2, p. 143-161.

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.

Taran, Y.A., and Giggenbach, W.F., 2003, Geochemistry of light hydrocarbons in subduction-related volcanic and hydrothermal fluids: Society of Economic Geologists, special Publication, v. 10, p. 61-74.

Sample	$X(CO_2)$	$X(CH_4)$	X(CO)	$X(H_2)$	$\log(CO/CO_2)$	$\log(CO/CO_2)_{12yr}$	$\log(CH_4/CO_2)$	$\log(CH_4/CO_2)_{12yr}$	$\log f(CO_2)$
Polybotes Mikros (PP9S)	743300	1759	9.0	16000	-4.9	-4.8 to -5.5	-2.6	-2.5 to -3.0	0.0
Stefanos (S4)	791500	4400	2.2	6200	-5.6	-5.4 to -6.1	-2.3	-2.1 to -2.6	-0.1
Phlegeton (A)	809300	805	2.1	9230	-5.6	-5.3 to -6.0	-3.0	-2.4 to -3.2	-0.3