

Supplementary Materials

Section 1: Geothermometry

The equilibrium conditions have been tentatively evaluated by using bubbling gases. Only subsystems having comparable kinetics have been examined. The equilibrium temperatures of the gaseous species H₂O, CO₂, CH₄ and CO have been calculated using the following reactions after Italiano and Nuccio [1]:



and



For which the corresponding expressions for equilibrium constants, K, are (in logarithmic form):

$$\text{Log}K_1 = 2\text{Log}[(\chi\text{CO}_2)(\gamma\text{CO}_2)\text{Pt}(\chi\text{CO})^{-1}(\gamma\text{CO})^{-1}\text{Pt}] - \text{log}f_{\text{O}_2} \quad (3)$$

$$\text{Log}K_2 = 1/2[(\chi\text{CO}_2)(\gamma\text{CO}_2)\text{Pt}(\chi\text{CH}_4)^{-1}(\gamma\text{CH}_4)^{-1}\text{Pt}] - \text{log}f_{\text{O}_2} + \text{log}f_{\text{H}_2\text{O}} \quad (4)$$

where χ is the molar fraction, γ is the activity coefficient, Pt is the total pressure, and f is the fugacity. Using numerical equilibrium constants for K₁ and K₂, the O₂ dependence for Equations (3) and (4) can be expressed as:

$$\text{Log}f_{\text{O}_2} = 2\text{Log}[\text{CO}_2]/[\text{CO}] - 29600/T + 9,6 \quad (5)$$

$$\text{Log}f_{\text{O}_2} = 1/2\text{Log}[\text{CO}_2]/[\text{CH}_4] - 23248/T + 6,51 \quad (6)$$

Combining functions (5) and (6), the temperature dependence can be expressed by the general form:

$$T = B[1/2\text{Log}(\chi\text{CO}_2)(\chi\text{CH}_4)^{-1} - 2\text{Log}(\chi\text{CO}_2)(\chi\text{CO})^{-1} - A]^{-1} \quad (7)$$

where A and B are constants derived from K₁ and K₂. The thermodynamic equilibrium constants are listed in Giggenbach [2]. The equilibrium temperatures are estimated by Eq. (7) and the oxygen fugacity is calculated using either Eq. (5) or Eq. (6) by introducing the temperature value estimated by Eq. (7).

- [1] F. Italiano and P. M. Nuccio, "Geochemical investigations of submarine volcanic exhalations to the east of Panarea, Aeolian Islands, Italy," *Journal of Volcanology and Geothermal Research*, vol. 46, no. 1-2, pp. 125–141, 1991.
- [2] W. E. Giggenbach, "Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand," *Applied Geochemistry*, vol. 2, no. 2, pp. 143-161, 1987.

Section 2: Solubility coefficients

The gas solubility in water is mainly expressed by the Bunsen's coefficient (β) which is the concentration of dissolved gas in water measured at STP when the gas pressure is 1 atmosphere. The Bunsen's coefficient depends on temperature and salinity, and it can be calculated by the following equation after Whitfield [1]:

$$\beta = \chi_i \cdot 55.555 \cdot 25400 \quad (1)$$

where χ_i is the molar fraction of the gas "i". χ_i is computed using the expression:

$$R \ln \chi_i = A + B/T + C \ln T + DT \quad (2)$$

where R is the gas constant expressed in cal. $K^{-1} \cdot mol^{-1}$ ($R = 1.9872$), T is the temperature in $^{\circ}K$ and A, B, C, D are constants. The latter constants are listed in Whitfield [1].

The Bunsen's coefficients of the gaseous species composing the geothermal fluids at different temperatures are listed in Table 1. The solubility of CO and CH₄ in water is roughly similar (especially if compared to that of CO₂), and for this reason GWI processes do not alter the CO/CH₄ ratio in the hydrothermal gases. After this assumption we can assert that the GWI extent does not affect the calculated equilibrium temperatures.

Table 1: Bunsen's solubility coefficients (β) of gaseous species at temperatures of 10, 20, 30, 40, 50 $^{\circ}C$

| T [$^{\circ}C$] | T [$^{\circ}K$] | He | H ₂ | O ₂ | N ₂ | CO | CH ₄ | CO ₂ |
|-------------------|-------------------|-------|----------------|----------------|----------------|--------|-----------------|-----------------|
| 10 | 283.3 | 8.983 | 19.601 | 38.093 | 18.854 | 28.000 | 43.183 | 1188.259 |
| 20 | 293.3 | 8.751 | 18.106 | 31.092 | 15.706 | 23.179 | 34.329 | 870.332 |
| 30 | 303.3 | 8.662 | 17.147 | 26.421 | 13.643 | 19.946 | 28.495 | 666.255 |
| 40 | 313.3 | 8.695 | 16.592 | 23.270 | 12.299 | 17.759 | 24.572 | 530.401 |
| 50 | 323.3 | 8.833 | 16.359 | 21.158 | 11.457 | 16.298 | 21.918 | 437.210 |

- [1] M. Whitfield, "Activity coefficients in Natural Waters," in R. M. Pytkowicz (Eds.), *Activity Coefficients in Electrolyte Solutions* (vol.2, pp. 153-300), CRC Press Inc. Boca Raton USA, 1978