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HYPOTHESES ON POSSIBLE EQUILIBRIA BETWEEN N_2 AND OTHER GASES AT LARDERELLO AND CERRO PRIETO[+]

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ABSTRACT

Considering various possible chemical reactions between N_2 and other gas species present in the geothermal fluid, the following reaction has been individuated:

$$C + 1/2\ N_2 + 7/2\ H_2 = NH_3 + CH_4$$

which is generally satisfied for plausible thermodynamic reservoir conditions (temperature and the relative contributions of steam and liquid to fluid production) at Larderello and Cerro Prieto.

INTRODUCTION

N_2, CH_4 and NH_3 are among the main components of uncondensable gas in the fluid of geothermal fields. A strong correlation was noted at Larderello between CH_4 and N_2 concentrations. Figure 1 shows the $\%CH_4$ in the uncondensable gas versus $\%N_2$ for three different zones of the field. The N_2/Ar ratio at Larderello is usually much higher than that of an air-saturated meteoric water (D'Amore and Nuti, 1977). Consequently N_2 may be assumed to be a reactive species connected in some way with methane.

An attempt was then made to individuate a chemical reaction capable of controlling the relative concentrations of N_2, CH_4 and NH_3 in the Larderello vapour-dominated system. Comparison was made with the water-dominated system of Cerro Prieto, which has much different reservoir thermodynamic conditions.

Chemical reactions considered

N_2 is generally considered at equilibrium with H_2 and NH_3 in the following reaction (D'Amore and Nuti, 1977; Ellis, 1979; Giggenbach, 1980; Nehring and D'Amore, 1984):

$$NH_3 = 1/2\ N_2 + 3/2\ H_2 \qquad (1)$$

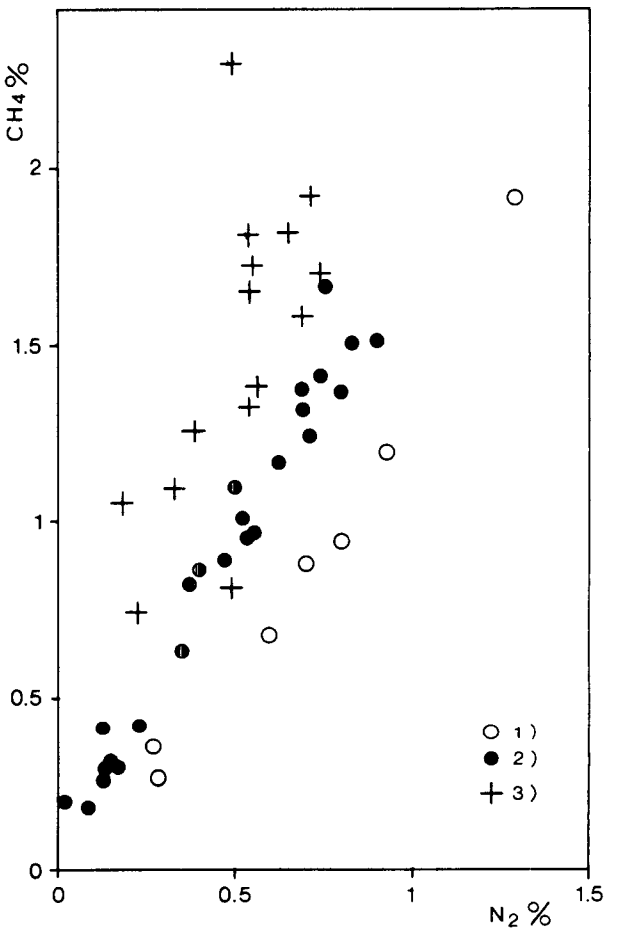

Figure 1. $\%CH_4$ in uncondensable gas versus $\%N_2$ for three different zones of the Larderello field. 1) Northeastern boundary zone; 2) central "classical" Larderello zone; 3) western and south-western zones of the field.

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However, this reaction is not in equilibrium at Larderello for plausible temperatures and reservoir steam fractions (D'Amore et al., 1982). Three different chemical reactions involving carbon were considered, since significant amounts of graphite have been detected in the Paleozoic basement in this area (Gianelli and Puxeddu,1979; Bagnoli et al., 1979). These reactions are:

$$3C + 4NH_3 = 3CH_4 + 2N_2 \quad (2)$$

$$C + NH_3 + 1/2\ H_2 = 1/2\ N_2 + CH_4 \quad (3)$$

$$C + 1/2\ N_2 + 7/2\ H_2 = NH_3 + CH_4 \quad (4)$$

These reactions were tested to discover whether any were consistent with the data from 22 wells at Larderello with different reservoir temperatures and fluid characteristics. The reservoir temperature assumed for each well was based on production data and in-hole measurements. Steam fractions in the reservoir fluid, y, which satisfy equilibrium conditions for reactions (1), (2), (3) and (4), were computed. In Table 1 the y_{NN} and y_{CN} values of y obtained from eqs. (1) and (4) respectively are compared with the y_{FT}, y_H and y_S values obtained from eqs.(5), (6) and (7) respectively:

$$H_2O = H_2 + 1/2\ O_2 \quad (5)$$

$$H_2S = H_2 + 1/2\ S_2 \quad (6)$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \quad (7)$$

Computations were based on the hypotheses described by D'Amore and Celati (1983), D'Amore et al.(1982, 1983). The equations used to calculate y are shown in Table 3. Two different equations were used for reaction (6), for Larderello and Cerro Prieto, to express sulphur fugacity as a function of temperature.

Table 1 does not include the y values obtained from reactions (2) and (3), since those obtained with reaction (2) are all near zero, and reaction (3) generally provides negative values.

Cerro Prieto field was considered since coaly material has been found to be ubiquitous in shaly layers of the reservoir (Barker and Elders, 1979). Furthermore, a good correlation was noted in the 1977 data (Nehring and D'Amore, 1984) between CH_4 and N_2. However, data scattering increases considerably in 1982. The data considered for Cerro Prieto (see Table 2) are from 1982 analyses of the fluid of 26 wells (Nehring and D'Amore, 1984). The reservoir temperatures used were those indicated by the Ca-Na-K geothermometer (Nehring and D'Amore, 1984). Reactions (2) and (3) once again are not in equilibrium for values of y exceeding 10^{-3}.

For both fields the y_{NN} values obtained with eq.(1) are generally one order of magnitude lower than those obtained with eqs.(4),(5),(6) and (7), while y_{CN} , with only a few exceptions, is satisfactorily consistent with y_H, y_S and y_{FT} . y_S at Cerro Prieto is at times much different from y calculated with the other methods. As mentioned by D'Amore et al.(1983), y_{FT} at Larderello is sometimes higher than y_H and y_S , usually where the $\%CH_4$ in the uncondensable gas is low. The investigation of the origin of these discrepancies is beyond the scope of the present study. Nevertheless, of all the chemical reactions considered relating N_2 to NH_3, eq.(4) provides the results closest to those obtained from eqs.(5), (6) and (7).

Acknowledgement

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Table 1. Molar gas concentrations and steam fractions (y),calculated from eqs.(7),(5),(6),(4) and (1), for Larderello field

Well	Year	T°C	$\frac{n_{gas}}{n_{H_2O}} .10^3$	$\log\frac{n_{H_2}}{n_{H_2O}}$	$\log\frac{n_{H_2S}}{n_{H_2O}}$	$\log\frac{n_{CH_4}}{n_{H_2O}}$	$\log\frac{n_{N_2}}{n_{H_2O}}$	$\log\frac{n_{NH_3}}{n_{H_2O}}$	$\log\frac{n_{CO_2}}{n_{H_2O}}$	y_{FT}	y_H	y_S	y_{CN}	y_{NN}
a	1978	240	97.2	-3.19	-3.43	-3.46	-3.58	-3.58	-1.02	> 1	0.71	0.93	0.63	0.04
b	1978	250	35.4	-3.19	-3.33	-3.58	-4.09	-3.79	-1.47	0.87	0.60	0.54	0.62	0.04
c	1978	240	108.7	-3.21	-3.42	-2.99	-3.04	-3.55	-0.98	0.87	0.68	0.53	0.47	0.05
d	1978	260	13.0	-3.55	-3.46	-3.85	-4.37	-3.65	-1.92	0.31	0.22	0.32	0.17	0.02
e	1978	270	22.4	-3.18	-3.25	-3.36	-3.80	-3.58	-1.69	0.56	0.45	0.43	0.41	0.04
f	1978	280	14.1	-3.33	-3.35	-3.73	-4.12	-3.75	-1.89	0.40	0.27	0.26	0.36	0.02
g	1976	270	5.9	-3.67	-3.68	-3.87	-4.54	-4.30	-2.28	0.17	0.14	0.14	0.19	0.02
h	1978	270	12.2	-3.35	-3.41	-3.70	-4.18	-4.05	-1.96	0.40	0.30	0.29	0.42	0.04
i	1978	270	12.6	-3.33	-3.39	-3.67	-4.03	-3.98	-1.95	0.41	0.32	0.30	0.43	0.04
j	1978	270	15.7	-3.25	-3.24	-3.54	-3.99	-3.98	-1.85	0.49	0.38	0.43	0.51	0.05
k	1978	260	5.6	-3.62	-3.64	-4.11	-4.49	-4.19	-2.30	0.24	0.19	0.20	0.26	0.02
l	1978	230	59.5	-3.47	-3.62	-3.92	-3.73	-3.69	-1.23	0.79	0.44	0.41	0.43	0.03
m	1978	240	13.2	-3.40	-3.50	-3.78	-4.30	-3.70	-1.92	0.51	0.44	0.44	0.34	0.02
n	1978	240	4.9	-3.79	-3.83	-4.40	-4.63	-4.40	-2.35	0.23	0.18	0.19	0.27	0.02
o	1977-78	220	48.4	-3.67	-3.71	-3.88	-3.87	-3.56	-1.32	0.52	0.32	0.40	0.21	0.015
p	1971-78	220	7.1	-3.80	-3.92	-4.20	-4.27	-4.23	-2.17	0.28	0.24	0.24	0.27	0.02
q	1971-78	220	20.6	-3.37	-3.56	-3.49	-3.85	-3.81	-1.71	0.66	0.65	0.57	0.48	0.04
r	1973-78	210	10.7	-3.62	-3.68	-3.73	-4.23	-3.96	-2.00	0.41	0.43	0.52	0.27	0.02
s	1971-78	220	12.1	-3.61	-3.65	-3.89	-4.47	-3.42	-1.94	0.41	0.37	0.46	0.17	0.01
t	1971-78	210	3.5	-3.96	-3.93	-4.20	-4.73	-4.26	-2.50	0.18	0.19	0.29	0.15	0.01
u	1976-78	220	16.7	-3.53	-3.79	-4.48	-5.48	-3.07	-1.79	0.76	0.45	0.33	0.17	0.00
v	1971-78	210	6.5	-3.62	-3.73	-3.55	-4.09	-4.32	-2.24	0.31	0.43	0.46	0.35	0.04

Table 2. Molar gas concentrations and steam fractions (y), calculated from eqs.(7),(5),(6),(4),(1), for Cerro Prieto field (1982 data)

Well	T°C	$\frac{n_{gas}}{n_{H_2O}} .10^3$	$\log\frac{n_{H_2}}{n_{H_2O}}$	$\log\frac{n_{H_2S}}{n_{H_2O}}$	$\log\frac{n_{CH_4}}{n_{H_2O}}$	$\log\frac{n_{N_2}}{n_{H_2O}}$	$\log\frac{n_{NH_3}}{n_{H_2O}}$	$\log\frac{n_{CO_2}}{n_{H_2O}}$	y_{FT}	y_H	y_S	y_{CN}	y_{NN}
M5	280	1.74	-4.26	-4.07	-4.13	-5.03	-4.56	-2.83	0.027	0.027	0.029	0.035	0.0045
M11	288	1.27	-4.58	-4.11	-4.32	-4.69	-4.64	-2.97	0.010	0.013	0.008	0.017	0.0010
M14	263	3.79	-3.61	-3.86	-3.82	-4.75	-4.63	-2.49	0.18	0.19	0.12	0.27	0.035
M19A	284	1.58	-4.30	-4.07	-4.19	-5.04	-4.60	-2.87	0.023	0.027	0.023	0.033	0.0037
M25	284	1.83	-4.24	-3.98	-4.12	-5.00	-4.55	-2.81	0.027	0.025	0.042	0.036	0.0042
M26	269	1.63	-4.36	-3.96	-4.19	-5.00	-4.60	-2.86	0.024	0.026	0.077	0.032	0.0047
M29	260	1.49	-4.37	-4.17	-4.25	-5.07	-4.63	-2.89	0.029	0.031	0.044	0.037	0.0053
M30	275	1.27	-4.31	-4.15	-4.33	-5.07	-4.61	-2.97	0.027	0.026	0.025	0.039	0.0047
M31	280	2.30	-3.98	-3.87	-3.93	-4.78	-4.46	-2.72	0.056	0.055	0.078	0.072	0.011
M35	275	1.04	-4.37	-4.26	-4.23	-5.00	-4.75	-3.07	0.020	0.022	0.009	0.033	0.0056
M43	281	1.13	-4.62	-4.18	-4.36	-5.12	-4.72	-3.02	0.009	0.008	0.011	0.015	0.0008
M48	308	1.09	-4.23	-4.22	-4.47	-5.07	-4.57	-3.04	0.020	0.009	< 0	0.039	< 0
M50	294	1.57	-4.22	-4.06	-4.17	-4.93	-4.57	-2.88	0.023	0.020	0.003	0.038	0.0032
M51	301	1.99	-4.06	-3.97	-4.13	-4.89	-4.53	-2.77	0.038	0.026	0.002	0.056	0.0046
M53	319	2.17	-3.99	-3.95	-4.12	-5.10	-4.51	-2.74	0.036	0.014	< 0	0.050	< 0
M84	317	4.51	-3.33	-3.60	-3.95	-4.77	-4.26	-2.44	0.25	0.13	0.059	0.36	0.024
M90	284	1.25	-4.37	-4.20	-4.18	-4.88	-4.69	-2.40	0.016	0.017	0.003	0.030	0.0043
M91	306	1.18	-4.34	-4.06	-4.38	-4.94	-4.56	-3.01	0.013	0.005	< 0	0.026	< 0
M101	301	1.46	-4.40	-3.92	-4.12	-4.95	-4.45	-2.93	0.010	0.006	0.013	0.014	< 0
M102	318	8.88	-3.34	-3.43	-3.54	-4.82	-3.76	-2.10	0.23	0.13	0.14	0.16	0.0045
M104	313	7.56	-3.27	-3.51	-3.50	-4.74	-4.10	-2.20	0.26	0.17	0.12	0.25	0.020
M105	304	2.04	-3.97	-3.92	-4.12	-4.79	-4.42	-2.77	0.046	0.031	0.005	0.056	0.0035
M114	271	0.94	-4.82	-4.23	-4.30	-5.11	-4.78	-3.10	0.005	0.006	0.020	0.009	0.0006
M130	290	2.00	-4.13	-3.97	-4.10	-4.04	-4.31	-2.77	0.035	0.030	0.031	0.056	0.0085
E2	318	1.61	-4.21	-3.95	-4.39	-5.09	-4.46	-2.87	0.002	0.002	< 0	0.028	< 0
E4	316	2.46	-3.65	-3.79	-4.19	-4.56	-4.55	-2.70	0.11	0.057	< 0	0.22	0.021

Table 3. Chemical reactions and related equations used in the text.

Reaction 1 $NH_3 = 1/2\ N_2 + 3/2\ H_2$ $(y = y_{NN})$

$$3/2 \log(n_{H_2}/n_{H_2O})_{WH} + 1/2 \log(n_{N_2}/n_{H_2O})_{WH} - \log(n_{NH_3}/n_{H_2O})_{WH}$$
$$= -4.63 - 255.2/T + 1.55 \log T + 3/2 \log A_{H_2} + 1/2 \log A_{N_2} - \log A_{NH_3}$$

Reaction 2 $3C + 4NH_3 = 3CH_4 + 2N_2$

$$3 \log(n_{CH_4}/n_{H_2O})_{WH} + 2 \log(n_{N_2}/n_{H_2O})_{WH} - 4 \log(n_{NH_3}/n_{H_2O})_{WH}$$
$$= -18.42 + 6038.6/T + 6.20 \log T + 3 \log A_{CH_4} + 2 \log A_{N_2} - 4 \log A_{NH_3}$$

Reaction 3 $C + NH_3 + 1/2\ H_2 = 1/2\ N_2 + CH_4$

$$\log(n_{CH_4}/n_{H_2O})_{WH} + 1/2 \log(n_{N_2}/n_{H_2O})_{WH} - 1/2 \log(n_{H_2}/n_{H_2O})_{WH} - \log(n_{NH_3}/n_{H_2O})_{WH}$$
$$= 0.569 + 1597.5/T + \log A_{CH_4} + 1/2 \log A_{N_2} - 1/2 \log A_{H_2} - \log A_{NH_3}$$

Reaction 4 $C + 1/2\ N_2 + 7/2\ H_2 = NH_3 + CH_4$ $(y = y_{CN})$

$$\log(n_{NH_3}/n_{H_2O})_{WH} + \log(n_{CH_4}/n_{H_2O})_{WH} - 7/2 \log(n_{H_2}/n_{H_2O})_{WH} - 1/2 \log(n_{N_2}/n_{H_2O})_{WH}$$
$$= 0.14 + 2737.5/T + \log A_{NH_3} + \log A_{CH_4} - 7/2 \log A_{H_2} - 1/2 \log A_{N_2}$$

Reaction 5 $H_2O = H_2 + 1/2\ O_2$ $(y = y_H)$

$$\log f_{O_2} = -3.808 - 13708.3/T - 2.075 \cdot 10^6/T^2 \quad \text{(D'Amore and Gianelli,1984)}$$

$$\log(n_{H_2}/n_{H_2O})_{WH} = 4.556 - 5922/T + 1.038 \cdot 10^6/T^2 + \log A_{H_2}$$

Reaction 6 $H_2S = H_2 + 1/2\ S_2$ $(y = y_S)$

Larderello : $\log f_{S_2} = 5.706 - 9767/T$ (temperature validity range = 210° - 280°C)

$$\log(n_{H_2S}/n_{H_2O})_{WH} = 7.539 - 6410.75/T - 0.79 \log T + 1.038 \cdot 10^6/T^2 + \log A_{H_2S}$$

Cerro Prieto : $\log f_{S_2} = 0.761 - 7186.4/T$ (temperature validity range = 260° - 320°C)

$$\log(n_{H_2S}/n_{H_2O})_{WH} = 5.067 - 5120.5/T + 1.038 \cdot 10^6/T^2 - 0.79 \log T + \log A_{H_2S}$$

Reaction 7 $CH_4 + 2H_2O = CO_2 + 4H_2$ $(y = y_{FT})$

$$4 \log(n_{H_2}/n_{H_2O})_{WH} + \log(n_{CO_2}/n_{CH_4})_{WH}$$
$$= -0.26 - 5227/T + 4 \log A_{H_2} + \log A_{CO_2} - \log A_{CH_4}$$

T = temperature, °K; $A_i = (y + \frac{1-y}{B_i})$; n = number of moles; WH = wellhead; f_{O_2} = oxygen fugacity; f_{S_2} = sulphur fugacity; y = molar steam fraction in the reservoir.