

# Geochemistry of H<sub>2</sub>- and CH<sub>4</sub>-enriched hydrothermal fluids of Socorro Island, Revillagigedo Archipelago, Mexico. Evidence for serpentinization and abiogenic methane

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## ABSTRACT

Socorro Island is the exposed part of an approx. 4000-m-high volcanic edifice rising from the oceanic floor to approx. 1000 m asl at the northern part of the Mathematician Ridge, Western Pacific. The volcano is active, with the most recent basaltic eruption in 1993. Moderate fumarolic activity and diffuse degassing with a total CO<sub>2</sub> flux of approx. 20 total day<sup>-1</sup> are concentrated in the summit region of the volcano composed of a group of rhyolite domes. Low-temperature, boiling point, fumaroles discharge gas with high H<sub>2</sub> (up to 20 mol% in dry gas) and CH<sub>4</sub> (up to 4 mol%). Both carbon and He isotopic ratios and abundances correspond to those in MORB fluids ( $\delta^{13}\text{C}_{\text{CO}_2} \approx -5\text{‰}$ ;  $^3\text{He}/^4\text{He} = 7.6 R_a$ ,  $\text{CO}_2/^3\text{He} = (2-3) \times 10^9$ , where  $R_a$  is the atmospheric ratio  $^3\text{He}/^4\text{He}$  of  $1.4 \times 10^{-6}$ ). Light hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>) are characterized by a high C<sub>1</sub>/C<sub>2+</sub> ratio of approx. 1000. Methane is enriched in <sup>13</sup>C ( $\delta^{13}\text{C}_{\text{CH}_4}$  from  $-15$  to  $-20\text{‰}$ ) and <sup>2</sup>H ( $\delta^2\text{H}$  from  $-80$  to  $-120\text{‰}$ ), and hydrocarbons show an inverse isotopic trend in both  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  (ethane is isotopically lighter than methane). These isotopic and concentration features of light hydrocarbons are similar to those recently discovered in fluids from ultramafic-hosted spreading ridge vents and may be related to the serpentinization processes: H<sub>2</sub> generation and reduction of CO<sub>2</sub> to CH<sub>4</sub> within high-temperature zone of volcano-seawater hydrothermal system hosted in basaltic and ultramafic rocks beneath a volcano edifice. The thermodynamic analysis of this unusual composition of the Socorro fluids and the assessment of endmember compositions are complicated by the near-surface cooling, condensation and mixing with meteoric water.

Key words: abiogenic hydrocarbons, isotope geochemistry, spreading centers, steam-dominated hydrothermal systems, volcanic gas

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## INTRODUCTION

Methane-rich fluids discharging in environments where sedimentary matter is limited or almost absent may have methane and light hydrocarbons of abiogenic origin, synthesized under reduced conditions in the Earth's crust from the oxidized carbon (CO<sub>2</sub>, carbonates) and hydrogen. Such fluids have been found as cold seeps in ophiolites (Abrajano *et al.* 1990; Lyon & Giggenbach 1990; Sano *et al.* 1993), in moderate- and high-temperature ultramafic-hosted spreading ridge vents (Charlou *et al.* 2002; Proskurowski *et al.* 2008; Konn *et al.*, 2008), in gases

associated with deep-seated waters of Precambrian shields (Sherwood Lollar *et al.* 2002, 2006, 2008), and in occluded gases from igneous alkaline rocks of Kola Peninsula (Galimov & Petersilie 1967; Potter *et al.* 2004). These gases are characterized by high H<sub>2</sub> and CH<sub>4</sub> contents and sometimes by a rare 'inverse' trend in the carbon isotope composition of the light hydrocarbons, with ethane isotopically lighter than methane, in contrast to 'thermogenic' trend with the enrichment in <sup>13</sup>C of longer chains, common for most natural hydrocarbons. Boiling-point fumaroles of Socorro Island, a giant shield basaltic volcano built at the former spreading center on the ocean floor in the

Eastern Pacific, produce gases with very high concentrations of  $H_2$  and  $CH_4$ , which have been rarely observed in other hydrothermal or volcanic gases (Taran *et al.* 2002).

In this study, new data are presented on the Socorro gases with an emphasis on the hydrocarbon isotopic geochemistry. The carbon and hydrogen isotopic composition of  $C_1$ – $C_4$  hydrocarbons in Socorro gases are characterized by the inverse isotopic trend in both C and H isotopes. These trends are discussed in terms of the mixing of gas produced from the high-temperature hydrothermal serpentinization of mafic and/or ultramafic rocks and a typical hydrothermal fluid composed of magmatic gases and air-saturated meteoric water located above a magma chamber inside the volcano edifice.

## GEOLOGICAL SETTING

Socorro Island ( $18^{\circ}47'N/110^{\circ}57'W$ ) is the largest island of the Revillagigedo Archipelago and is located 700 km west of Manzanillo on the Pacific coast of Mexico (Fig. 1A). Its area is approx.  $120\text{ km}^2$  and it lies at the northern end of the Mathematician Ridge near the intersection with the Clarion Fracture Zone. The northern Mathematician Ridge marks the location of a mid-ocean ridge spreading center that was abandoned at approx. 3.5 Ma when activity shifted to the East Pacific Rise (Mammerickx *et al.* 1988). Volcanic activity in this region has continued to the present as demonstrated by the 1952–1953 eruption of San Benedicto Island, 50 km north of Socorro, and a submarine basaltic eruption approx. 3 km west of Socorro Island in 1993 (Siebe *et al.* 1995). Socorro Island represents the emergent peak of a large basaltic volcano that rises from a sea floor depth of approximately 3000–1050 m above sea level. The highest point of the island is the summit of a pantelleritic dome, Cerro Everman, where significant fumarolic activity occurs. The surface landscape is dominated by lava flows, domes, scoria, and cinder

cones. According to Bohrson & Reid (1995), silicic peralkaline rocks comprise up to 80% of the surface of the island, rendering Socorro unique in the Pacific. Bohrson & Reid (1995) divide the eruptive history of the island into pre-, syn-, and postcaldera phases. They suggest that the whole volcanic edifice of approx.  $2400\text{ km}^3$  is composed mainly of basalts, but the subaerially exposed deposits are silicic peralkaline rocks including ignimbrites that erupted between approx. 540 and 370 ka. Postcaldera silicic rocks have been erupted between approx. 180 and 15 ka and cover the northern, western, and southern quadrants of the island. Postcaldera alkaline basalts (approx. 20 vents with lava flows, Lomas Coloradas) are largely restricted to the southeastern part of the island (Fig. 1B).

The presence of the caldera may indicate that the associated silicic magma chamber is shallow and probably resides within the upper oceanic crust or the edifice (Bohrson *et al.* 1996). Fumarolic activity at the Cerro Everman dome indicates that a hydrothermal system is developed above this shallow magma chamber.

## Hydrothermal activity

More than 100 individual steam vents and several bubbling and boiling water and mud pools can be seen around the hydrothermally active dome and on its slopes almost up to the summit (Fig. 1C). The most intensive, ‘noisy’ fumaroles are situated on the SE slope of the dome in a short and shallow canyon. All fumaroles are characterized by the boiling point temperature near  $97^{\circ}\text{C}$  at this elevation (950–1050 m asl). The water contained in a series of hot pools is chloride-free, steam condensate. The island is located in the tropical zone with marked dry and wet seasons and with annual precipitations of about 700 mm (Atlas de Agua). There are no cold springs on the island, and the only freshwater sources are small rainwater-filled pools or temporary lakes within the cinder cones. Taran

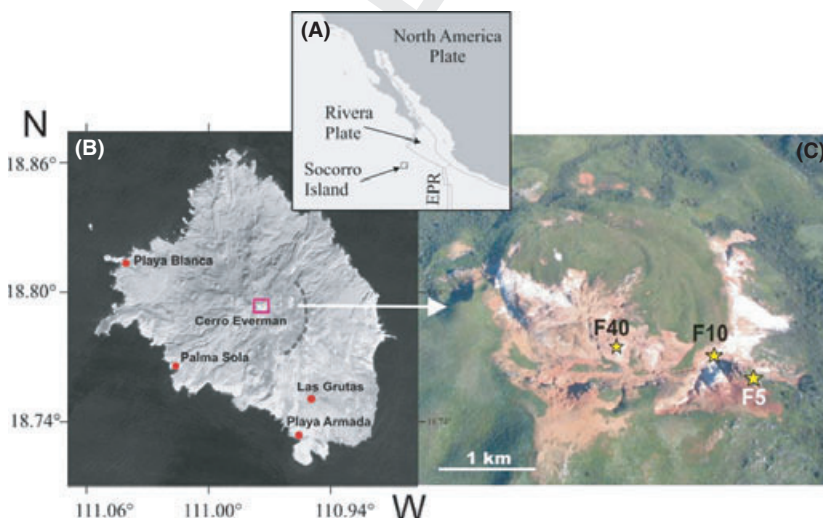


Fig. 1. (A) Location of Socorro Island relative to the Mexican Pacific coast. (B) Location of thermal springs and the summit fumarolic field; caldera rim is shown by a dashed curve. (C) Alteration and fumarolic field of the Cerro Everman dome. Stars are sampled fumaroles F5, F10, and F40.

*et al.* (2002) suggested the presence of a steam-dominated aquifer beneath the caldera based on the chemical and isotopic analyses of fluids collected from two fumaroles and a steam-heated pool. The surface of the dome and surrounding slopes are intensively altered within an area of approx. 1.5 km<sup>2</sup> (Fig. 1C). Besides, there are several hydrothermal manifestations on the island. Playa Armada and Playa Blanca warm springs discharge diluted seawater from fractures in the lava flows on the tide lines of the south, southwest, and west shoreline. Palma Sola springs discharges diluted water (approx. 300 ppm of Cl) and thus is the best representative for the isotopic composition of meteoric water. In a lava tunnel named La Gruta, 1.5 km from the southern coast, within the Lomas Coloradas area, there is a small area of steaming ground.

## SAMPLING AND ANALYSIS

Gas samples from fumaroles and pools were taken into Giggenbach's bottles filled with 40–50 ml of 4–5 N NaOH or KOH solution (Giggenbach 1975) using a Ti-tube or a plastic funnel and a short Tygon silicon hose. Because of the high fraction of noncondensable gases ( $H_2 > CH_4 > N_2$ ), the flasks were filled rapidly, and the headspace pressure was never lower than 0.5 atm. Several gas ampoules were filled with dry gas simultaneously at each sampling location by pumping condensate through two consecutive bubblers cooled with ice. These samples were used for the carbon and hydrogen isotope analyses in CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, as well as hydrogen and oxygen isotopes in the vapor condensate. Splits of the headspace gases were used for the chemical analysis of hydrocarbons, carbon and hydrogen isotope analysis in hydrocarbons and He isotopes.

Gas analysis was performed by using a Perkin-Elmer 8500 and a Gow-Mac 350 gas chromatographs with Ar and He as carrier gases, packed columns with 5A Molecular Sieves and TCD detector. Argon was separated from O<sub>2</sub> using a composite CT-III Altech column with He as the carrier gas at room temperature. Carbon monoxide was determined using FID detector, a Carbosieve S-II column, and a methanizer only in the 2008 dry gas samples. Dry gases were analyzed for the CO to avoid effects of the formate formation in the alkaline solution during the storage of samples (Giggenbach & Matsuo 1991). The detection limits were about 5 ppmV for He, 3 ppmV for H<sub>2</sub>, and 0.5 ppmV for CO. Concentrations of hydrocarbons C<sub>2</sub>–C<sub>4</sub> were analyzed simultaneously with carbon isotopes in Instituto de Geología, UNAM.

Helium and nitrogen isotopes were analyzed in the National Institute of Geophysics and Volcanology (INGV), Palermo. The <sup>3</sup>He/<sup>4</sup>He ratios were measured by a static vacuum mass spectrometer (VG-5400TFT, VG Isotopes) modified to detect <sup>3</sup>He/<sup>4</sup>He ion beams simultaneously, reducing the error of the <sup>3</sup>He/<sup>4</sup>He measurements in

<sup>3</sup>He-rich gases down to values lower than 0.1%. <sup>3</sup>He/<sup>4</sup>He ratios were corrected for atmospheric contamination on the basis of the difference between the <sup>4</sup>He/<sup>20</sup>Ne of the sample and in the air (Sano & Wakita 1985).

Carbon isotope analysis of CO<sub>2</sub> and hydrocarbons was conducted on a GC-isotope ratio mass spectrometer system composed of an Agilent 6890A capillary gas chromatograph connected to a Thermo Finnigan MAT 253 mass spectrometer. A PoraBond Q column (50 m × 0.32 mm) was used. The temperature program started at 40°C for 10 min before increasing to 220°C at 5°C min<sup>-1</sup> with a final hold 8 min. An Oztech tank with CO<sub>2</sub> (δ<sup>13</sup>C = -10.99‰ V-PDB) was used as a working standard. Matheson Tri Gas micro MAT 14 mixture with 1000 ppmV of linear alkanes C<sub>1</sub>–C<sub>6</sub> in He was used for the calibration of C<sub>2</sub>–C<sub>4</sub> concentrations and determination of the precision of the isotopic analyses of hydrocarbons. Concentrations of ethane in the headspace of Giggenbach's bottles usually were approx. 200 ppmV. At these concentrations and the aliquot volume of 2 ml, the precision was approx. 1 permil as determined on 10 analyses of the standard mixture. For CO<sub>2</sub> and CH<sub>4</sub>, the precision was ±0.3 permil.

For the δD analysis of hydrocarbons, the same PoraBond Q column was used together with a pyrolysis oven at 1450°C. A Molecular Sieves 5A column was used for the separation of H<sub>2</sub> and CH<sub>4</sub>. An Oztech tank with H<sub>2</sub> (δD = -124.15‰ v-SMOW) was used as a working standard. Precision of measurements for the standard hydrocarbon mixture usually was better than ±5‰.

## RESULTS

### Chemical composition of gases

Chemical compositions (without hydrocarbons) of 20 gas samples collected in 2001–2008 are shown in Table 1. Samples collected from different vents are generally similar: they have about 95 mol% of water vapor (mean gas content  $X_g \approx 50 \text{ mmol mol}^{-1}$ ), and the predominant component of dry gas is carbon dioxide. The most intriguing feature is the high H<sub>2</sub> and CH<sub>4</sub> contents: up to 20% and 4% in dry gas, respectively. Giggenbach (1987) proposed the use of  $R_H = \log(X_{H_2}/X_{H_2O})$  as a redox parameter for hydrothermal systems instead of  $f_{O_2}$  ( $X$  are concentrations in mole fractions or any other units). The Socorro geothermal steam is characterized by a mean  $R_H$  value of -2.0, almost one order of magnitude higher than analyzed fluids from other steam-dominated hydrothermal fields.

### He, <sup>3</sup>He/<sup>4</sup>He, and CO<sub>2</sub>

Data on <sup>3</sup>He/<sup>4</sup>He together with gas concentrations are shown in Table 1. All measured samples are characterized by high <sup>3</sup>He/<sup>4</sup>He (7.2–7.6  $R_a$ ) along with high He/Ne

**Table 1** Chemical composition (mol % in dry gas) and helium isotope ratios ( $R/R_a$ ) of fumarolic and bubbling gases of the Socorro Island.  $X_g$  – gas content in mmol mol<sup>-1</sup> ( $H_2O = 1000 - X_g$ ).

Fum No	Date	T°C	$X_g$	CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	N <sub>2</sub>	Ar	He	CH <sub>4</sub>	CO	$R/R_a$	$^4\text{He}/^{20}\text{Ne}$	CO <sub>2</sub> / <sup>3</sup> He (×10 <sup>9</sup> )
F5	December 2001	98	53	77.5	1.12	15	3.09	0.048	0.0027	3.15	nd	7.55	185	2.8
F10	December 2001	98	50	76.6	1.35	17.3	2.1	0.025	0.0035	2.6	nd	7.56	432	2.1
F10	March 2002	98	36	83.5	1.5	13	0.86	0.012	0.0042	2.62	nd	7.41	161	2.1
P1	March 2002	48		77.2	0.61	18.9	0.54	0.01	0.0021	2.6	nd			
F5	November 2003	98	48	80.8	1.1	11.1	2.8	0.046	0.0031	4.12	nd	7.61	62	2.5
F5	November 2003	98	56	80.6	1.32	13.1	1.45	0.034	0.0038	3.52	nd	6.24	8	2.5
F10	February 2004	99	46	81.9	1.08	10.2	2.3	0.031	0.0034	3.52	nd	7.54	15	2.3
F40	February 2004	99	32	82.1	0.95	13.2	0.5	0.026	0.0023	3.03	nd	7.59	311	3.4
P1	February 2004	56		78.7	0.71	16.2	0.91	0.013	0.0026	3.46	nd	7.53	557	2.9
F5	March 2005	98	45	77.7	1.86	16.9	0.23	0.004	0.0036	2.2	nd	7.48	465	2.1
F5	March 2005	98	67	77.4	1.09	17.1	1.02	0.0095	0.0041	2.63	nd	7.66	220	1.8
F40	March 2005	98	54	74.5	1.85	20.7	0.34	0.0028	0.0029	3.11	nd	7.21	530	2.5
F40	March 2005	98	45	80.6	1.83	14.9	0.41	0.0059	0.0026	2.26	nd	7.54	230	2.9
F5	March 2008	98	34	77.5	1.35	17.8	0.20	0.005	0.0072	3.15	0.0008			
F5	March 2008	98	48	77.4	1.61	16.9	0.92	0.022	0.0034	3.19	0.0007			
F10	March 2008	98	54	80.4	1.16	13.7	0.27	0.004	0.0067	4.47	0.0012			
F40	March 2008	98	49	76.1	0.94	19.1	1.16	0.029	0.0040	2.70	0.0005			
F40	March 2008	98	51	77.4	1.13	17.7	0.92	0.026	0.0064	2.84	0.0013			
P1	March 2008	52		75.1	0.58	18.9	1.44	0.033	0.0031	3.97	0.0006			
P1	March 2008	52		74.8	0.93	19.6	0.75	0.021	0.0078	3.90	0.0012			

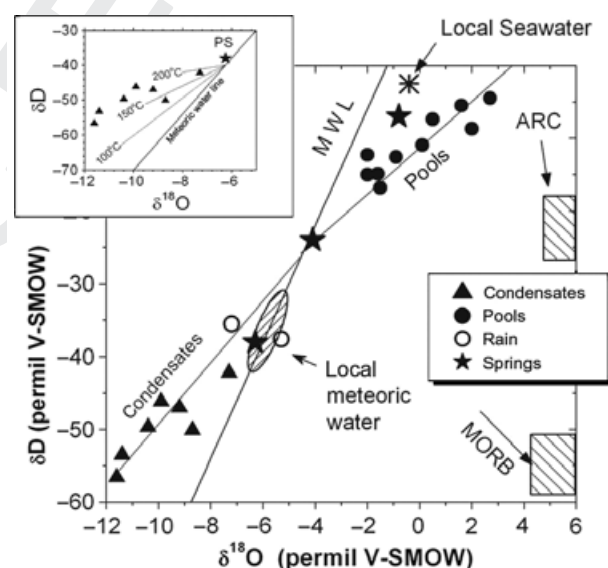
ratios indicating little direct air contamination of the samples. He concentrations are high, and CO<sub>2</sub>/<sup>3</sup>He ratios are within the range of MORB glass values of  $(1-6) \times 10^9$  (Marty & Jambon 1987).

### Water isotopes

Table 2 shows data on the isotopic composition of water samples from Socorro island. Analyses of meteoric water are limited to two samples of rainwater (Table 2, Fig. 2). Permanent cold springs are absent on the island. There are three warm coastal springs: Playa Blanca (31°C), Palma Sola (35–37°C), and Playa Armada (31.5°C) shown in

**Table 2** Isotopic composition (permil, V-SMOW) of fumarolic steam, thermal and meteoric waters of Socorro Island.

Site/year	δD	δ <sup>18</sup> O	Site/year	δD	δ <sup>18</sup> O
Condensates			Thermal pools		
F10/2004	-53.2	-11.4	P1/2004	-12.3	-2.0
F5/2003	-49.7	-10.4	P2/2004	-14.9	-1.6
F5/2004	-56.6	-11.6	P3/2004	-11.0	0.1
F40/2008	-46.2	-9.9	P7/2004	-16.8	-1.5
F5/2008	-42.2	-7.3	P1/2008	-4.5	2.7
F10/2008	-50.1	-8.7	P4/2008	-12.6	-0.9
SG2/1998	-47.0	-9.2	M1/1998	-7.4	0.5
Rains			M2/1998	-5.5	1.6
02.2004	-35.5	-6.2	M4/1998	-15.0	-2.0
01.2008	-37.6	-5.3	M1/2000	-8.7	2.0
Pacific Ocean 2004			Thermal springs (2006)		
	-2.5	-0.4	Palma Sola	-35.2	-7.2
			Playa Blanca	-7.5	-0.8
			Playa Armada	-25.0	-4.1



**Fig. 2.** δD versus δ<sup>18</sup>O plot for waters of Socorro Island. Inserted is a model for δD of vapor after a single-step steam separation at different boiling temperatures from water with δD = -40‰ and δ<sup>18</sup>O = -6.25‰. PS, Palma Sola spring. Also shown areas for arc magmatic waters (Taran *et al.* 1989) and water from undegassed MORB glasses (e.g. Poreda 1985). See text for details and discussion.

Fig. 1. Water from Playa Blanca is significantly (40–70%) mixed with seawater. The Palma Sola warm spring discharges thermal water of a low salinity (Cl < 300 ppm) with isotopic composition close to rain waters and thus represents the local meteoric water composition with δD ≈ -38 ± 5‰ (Fig. 2).



**Table 3** CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> (mol % in dry gas), and light hydrocarbons (mmol mol<sup>-1</sup> CH<sub>4</sub>) in fumaroles and bubbling gas.

Site	Date	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	<i>n</i> -C <sub>4</sub>	<i>i</i> C <sub>4</sub>	C <sub>1</sub> /C <sub>2</sub>
F5	November 2003	80.8	11.1	4.12	0.91	0.57	0.06	0.17	1098
F10	February 2004	81.9	10.2	3.52	1.23	0.76	0.12	0.25	813
F40	February 2004	82.1	13.2	2.03	1.16	0.29	0.09	0.06	862
P1	February 2004	78.7	16.2	3.46	2.68	0.89	0.16	0.06	373
F5	March 2008	77.5	17.8	3.15	1.1	0.6	0.2	0.1	909
F10	March 2008	80.4	13.7	4.47	1.52	0.52	0.12	0.25	657
F40	March 2008	76.1	19.1	2.70	1.09	0.51	0.11	0.06	917
F40	March 2008	77.4	17.7	2.84	1.2	0.45	0.06	0.06	833
P1	March 2008	75.1	18.9	3.97	1.68	0.53	0.21	0.09	595

**Table 4** Carbon isotopes in CO<sub>2</sub> and hydrocarbons and hydrogen isotopes in hydrocarbons, molecular H<sub>2</sub>, and water vapor.

Site	Date	$\delta^{13}\text{C}$ ‰ V-PDB					$\delta\text{D}$ ‰ V-SMOW				
		CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub> O
F5	November 2003	-5.3	-17.9	-21.5	nd	nd	-568	-110	nd	nd	-49.7
F10	February 2004	-5.4	-17.2	-24	-24.7	-24.2	-580	-74	nd	nd	-53.2
F40	February 2004	-5.6	-19.3	-23.4	-23.1	bd	-558	-92	nd	nd	nd
P1	February 2004	-3.8	-16.7	-19.8	-17.3	-19.8	-565	-117	nd	nd	-12.3
F5	March 2008	-5.1	-19.4	-21.4	-26.5	-23.5	-565	-73.7	-107	-96	nd
F10	March 2008	-4.9	-20.2	-22.7	-26.3	bd	-562	-70	-120	bd	-50.1
F40	March 2008	-5.3	-18.9	-21.6	-25.3	-22.7	-566	-102	-107	-116	-46.2
F40	March 2008	-5.4	-19.3	-22	bd	bd	-556	-99	-121	bd	-46.2
P1	March 2008	-5.4	-21.1	nd	nd	nd	nd	nd	nd	nd	nd

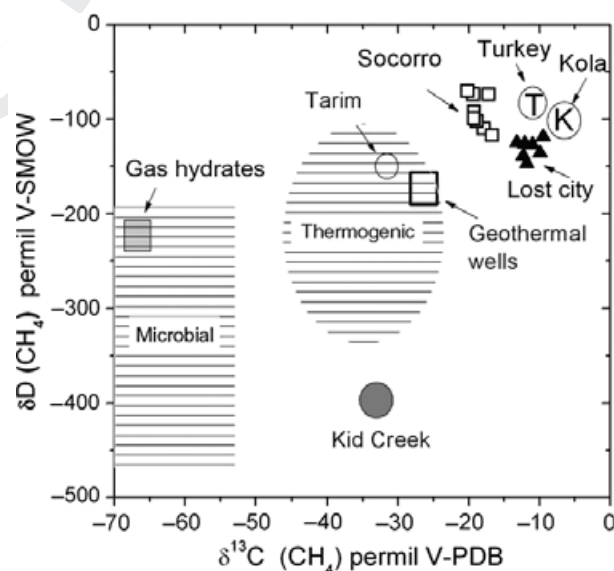
bd, below detection limit; nd, not determined.

### C<sub>1</sub>–C<sub>4</sub> hydrocarbons

Chemical abundances of C–H–O gases including H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, ethane, propane, and butanes in Socorro gases are given in Table 3. Methane concentrations vary from 2.0 to 4.5 mol% in dry gas. It can be seen also that CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratios are high (approx. 400–1100), similar to those reported for gases associated with serpentinization (Lyon and Giggenbach, 1996; Proskurowski *et al.* 2008) and hydrothermal gases from Nisyros island (Fiebig *et al.* 2009). The distribution of C<sub>2+</sub> hydrocarbons in Socorro gases is monotonic: on average C<sub>2</sub>/C<sub>3</sub> ≈ C<sub>3</sub>/C<sub>4</sub> ≈ 3 (Table 3).

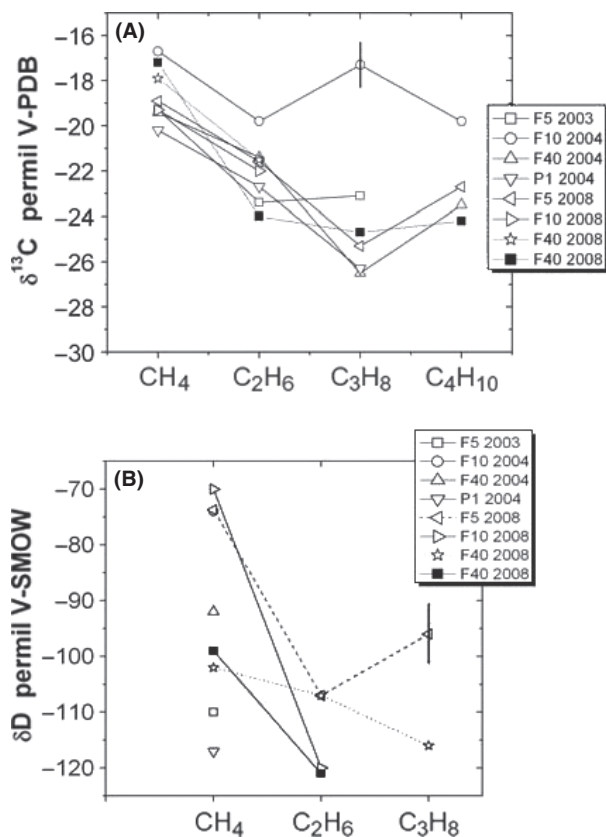
### Carbon and hydrogen isotopes in CO<sub>2</sub>, H<sub>2</sub>, and hydrocarbons

Carbon isotopes in CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>–C<sub>4</sub> alkanes and hydrogen isotopes in H<sub>2</sub>, H<sub>2</sub>O, and hydrocarbons are presented in Table 4. Isotopically heavy methane with  $\delta^{13}\text{C}$  from -15 to -20‰ (V-PDB) is a common characteristic for fluids from spreading ridge submarine vents (Welhan & Craig 1983; Scott 1997; Charlou *et al.* 2002; Proskurowski *et al.* 2008). The Schoell diagram (Schoell, 1988) in Fig. 3 shows  $\delta\text{D}$  and  $\delta^{13}\text{C}$  in methane from Socorro and various other sources. Methane from Socorro gases enriched with both <sup>13</sup>C and deuterium is plotted close to other ‘heavy’ methane from Lost City submarine vents,



**Fig. 3.** Plot of  $\delta\text{D}$  versus  $\delta^{13}\text{C}$  of methane for the samples from Socorro island and for fluids from other sites and different origin (Schoell diagram; Schoell, 1988). See text for more details.

mud volcanoes in Turkey, and Kola rocks. Additionally, the hydrocarbons from Socorro demonstrate an ‘inverse’ isotopic trend, where ethane is isotopically lighter than methane, which is not common for natural gases. Figure 4(A,B) shows that in Socorro fluids, such a trend is



**Fig. 4.** A: Carbon isotopic composition of hydrocarbons in Socorro fluids as a function of carbon number. B: hydrogen isotopic composition as a function of carbon number.

observed for both carbon and hydrogen isotopes in C<sub>1</sub>–C<sub>4</sub> hydrocarbons.

## DISCUSSION

### Chemical composition of gases: redox state and chemical equilibria of macro-species

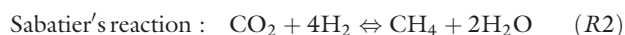
High concentrations of H<sub>2</sub> and CH<sub>4</sub> are rare but not unique among geothermal gases. Gases from The Geysers steam-dominated field in California are characterized by even higher H<sub>2</sub> and CH<sub>4</sub> on the water-free basis, up to 30% and 10%, respectively (Lowernstern & Janik 2003). In gases from the Namafiall geothermal field in Iceland, up to 25% H<sub>2</sub> was reported (Arnorsson & Gunnlaugsson 1985). The unique feature of the Socorro gases is the anomalously high H<sub>2</sub>/H<sub>2</sub>O ratio. Giggenbach (1987) showed that the upper threshold  $R_{\text{H}}$  value ( $R_{\text{H}} = \log(X_{\text{H}_2}/X_{\text{H}_2\text{O}})$ ) for hydrothermal systems is around -2.8, which corresponds to an  $R_{\text{H}}$  value in the vapor phase in equilibrium with Fe(II)- and Fe(III)-bearing wall rock (primary or altered). The proxy thermodynamic system for this ‘rock buffer’ is a mineral assemblage fayalite+hematite+quartz and water.

Taran (1988), Chiodini & Marini (1998), and Lowernstern & Janik (2003) have shown that there were no hydrothermal systems found with  $R_{\text{H}} > -2.5$ , and the only samples with  $R_{\text{H}} > -2.8$  (a few samples) were reported for the Geysers vapor-dominated field (Lowernstern & Janik 2003). Usually, very high H<sub>2</sub> concentrations in dry gas correspond to a high water vapor content with the resulting  $R_{\text{H}} \ll -2.8$ .

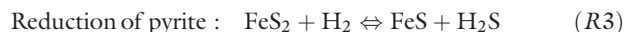
The Socorro Island  $R_{\text{H}}$  value of 2.0 may indicate that redox conditions in the Socorro aquifer are controlled by a more reduced mineral assemblage than that of continental or arc-related hydrothermal system where the aquifers are composed of altered basaltic to rhyolitic or sedimentary rocks.

Analyses of deep-sea hydrothermal fluids that have interacted with hot basalts typically produce H<sub>2</sub> concentrations in the 1–2 mmol kg<sup>-1</sup> range (Scott 1997 and references therein). H<sub>2</sub> concentrations up to 20 mmol kg<sup>-1</sup> are reported for submarine hydrothermal fluids that have interacted with ultramafic rocks (Charlou *et al.* 2002; Proskurowski *et al.*, 2005). These concentrations correspond to  $R_{\text{H}}$  in the -4.7 to -3.5 range, which is close to the ‘rock buffer’ control at 350°C in liquid phase.

To demonstrate a possible redox control for the Socorro hydrothermal gases, a set of diagrams is presented in Figs 5–7. The concentrations of following components depend upon the redox conditions: H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>S. Three reactions are chosen with the corresponding equilibrium constants computed using the HSC-6 thermochemical code (Roine 2006):



and



For the first two reactions, simple expressions can be derived for the ratios  $R_{\text{CO}} = \log(X_{\text{CO}}/X_{\text{CO}_2})$ ,  $R_{\text{C}} = \log(X_{\text{CH}_4}/X_{\text{CO}_2})$ ,  $R_{\text{S}} = \log(X_{\text{H}_2\text{S}}/X_{\text{H}_2\text{O}})$  and  $R_{\text{H}}$ :

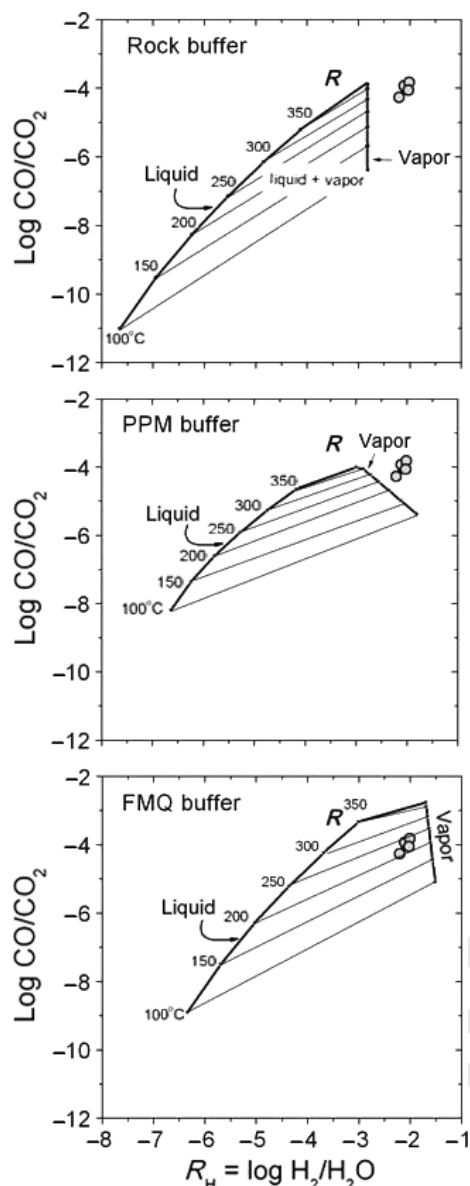
$$R_{\text{CO}} = R_{\text{H}} + 2.024 - 2082/T \quad (1)$$

$$R_{\text{C}} = 4R_{\text{H}} - 10.29 + 9067/T \quad (2)$$

$$R_{\text{S}} = R_{\text{H}} + 4.732 - 2746/T \quad (3)$$

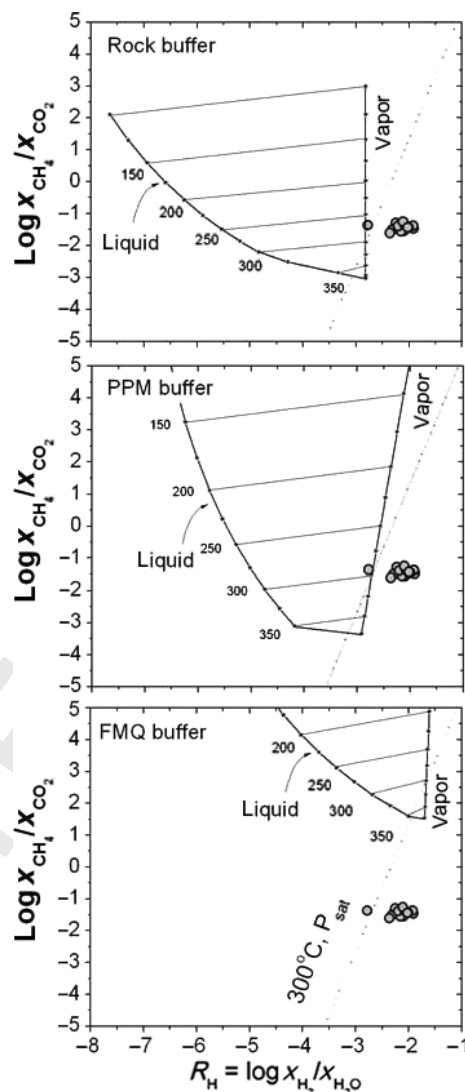
where  $X_i$  are concentrations in mole fractions in the total gas discharge and  $T$  is temperature in K.

Each of three panels in Figs 5–7 show analytical points together with lines representing phase equilibria (vapor-liquid) for three different redox buffers: FeO–FeO<sub>1.5</sub> (fayalite-hematite-quartz) or the ‘rock buffer’ of Giggenbach (1987), fayalite-magnetite-quartz (FMQ) buffer, and pyrite-pyrrhotite-magnetite (PPM) buffer under saturated water vapor pressure. Equilibria in the liquid phase were



**Fig. 5.** Plot of  $\log(X_{\text{CO}}/X_{\text{CO}_2})$  versus  $R_H$  for Socorro gases. Three 'theoretical' grids are shown with the redox control by the 'rock buffer' of Giggenbach, pyrite-pyrrhotite-magnetite (PPM), and fayalite-quartz-magnetite (FMQ) buffers.

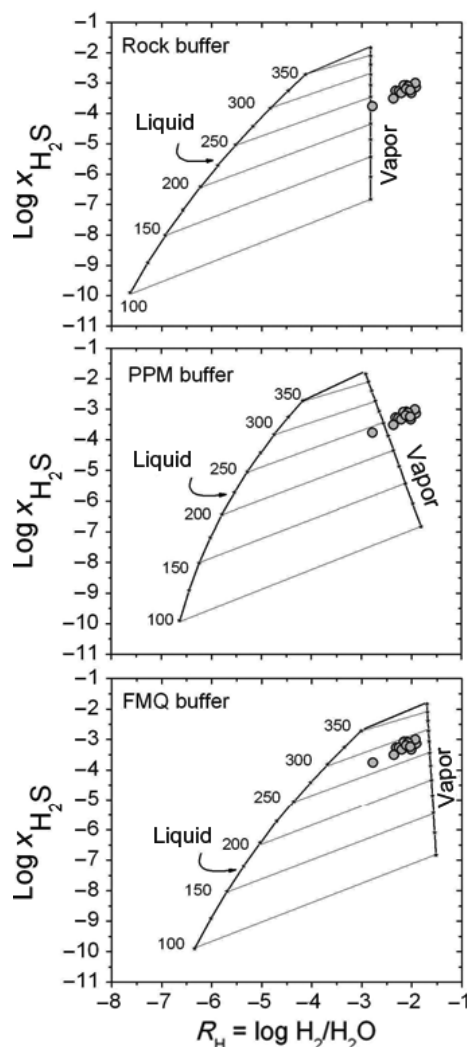
computed using the Giggenbach (1992) approximation, where liquid water is considered to be in equilibrium with water vapor, which is, in turn, in chemical equilibrium with the corresponding mineral assemblage. Additionally, an equilibrium line at 300°C and saturation pressure in the gas phase is drawn on each panel in Fig. 6 to show equilibrium relationships without redox buffering. It can be seen that the  $\text{CO}/\text{CO}_2$  pair (Fig. 5) and the  $\text{H}_2\text{S}$  mole fraction (Fig. 7) are close to equilibrium at 200–250°C, under the FMQ buffering within the two-phase region, closer to the vapor line. In contrast, the  $\text{CH}_4/\text{CO}_2$  points (Fig. 6) are



**Fig. 6.** Plot of  $\log(X_{\text{CH}_4}/X_{\text{CO}_2})$  versus  $R_H$  for Socorro gases. The 'theoretical' grids, as in Fig. 2, correspond to the 'rock buffer', pyrite-pyrrhotite-magnetite (PPM), and fayalite-quartz-magnetite (FMQ) redox buffers (see Fig. 5).

plotted far from any buffered equilibrium and the Sabatier equilibrium temperatures (reaction R2) are very high, in the range of 400–600°C.

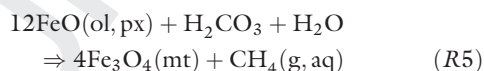
Fast equilibrating gas species ( $\text{H}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{S}$ ) most probably are indicators of equilibrium conditions in the vapor-dominated aquifer beneath the Everman dome, Socorro Island. High  $R_H$  values may indicate that the redox conditions in this aquifer are controlled by a highly reduced mineral assemblage, a hydrothermal analog of the FMQ buffer. These are uncommon hydrothermal redox conditions confirmed also by a high concentration of  $\text{CH}_4$  and the apparent absence of the sedimentary organic matter within this geologically young volcanic environment.



**Fig. 7.** Plot of  $\log P_{H_2S}$  versus  $R_H$  for Socorro gases. The 'theoretical' grids correspond to the 'rock buffer', pyrite-pyrrhotite-magnetite (PPM), and fayalite-quartz-magnetite (FMQ) redox buffers (see Fig. 5).

### Serpentinization as a possible mechanism producing high $H_2$ and $CH_4$ in Socorro fluids

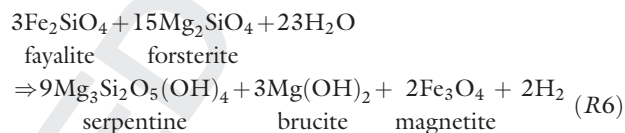
Serpentinization is a hydration reaction of water with mafic minerals such as olivine and pyroxene. Serpentinization is driven by the instability of these minerals in water at temperatures  $<300^\circ\text{C}$  (e.g. Palandri & Reed 2004; Sleep *et al.* 2004). The oxidation of Fe(II) of fayalite and/or ferrosilite reduces water, producing  $H_2$ , and reduces  $CO_2$ ,  $HCO_3^-$  or carbonates producing  $CH_4$ :



Symbols in parenthesis show that FeO is a part of olivine or pyroxenes, 'mt' denotes magnetite, and 'g' and 'aq'

denote gaseous and dissolved gases, respectively. Experimental results (Seyfried *et al.* 2007) show that the concentration of  $H_2$  produced as a result of the interaction of seawater with peridotite at  $200^\circ\text{C}$ , 500 bar and a water/rock (w/r) ratio close to 1 may reach  $70 \text{ mmol kg}^{-1}$ , which is about 20% of the theoretically predicted equilibrium  $H_2$  concentration (Palandri & Reed 2004; Sleep *et al.* 2004; McCollom & Bach 2009). According to thermodynamic modeling by Palandri & Reed (2004) and McCollom & Bach (2009), the hydrogen generation in serpentinization reaches about  $350 \text{ mmol kg}^{-1}$  at  $300^\circ\text{C}$ , under pressure when no free gas phase can be formed. The equilibrium concentration of  $H_2$  strongly increases with decreasing water/rock ratio.

The stoichiometric weight water/rock ratio for the generalized reaction of serpentinization of olivine ( $\text{Mg\#} = 0.86$ ) is about 0.15 as it follows from the reaction equation:

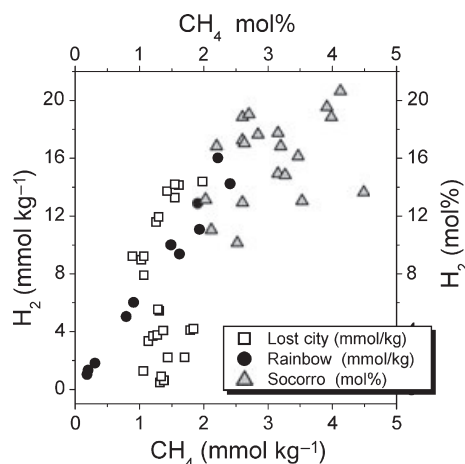


This equilibrium can be considered as a relevant redox buffer of ultramafic rocks under hydrothermal conditions (Sleep *et al.* 2004). However, the equilibrium partial pressure of  $H_2$  computed using this reaction in the  $100$ – $350^\circ\text{C}$  range is so high that, even at 500 bars of total pressure, hydrogen separates into a free gas phase with a low fraction of water vapor. Hydrogen production decreases when the modeling takes into account the substitution of Mg for Fe(II) in chrysotile (serpentine) and brucite and thus makes Fe(II) partially unavailable for  $H_2$  production (Sleep *et al.* 2004; McCollom & Bach 2009). Therefore, the modeling predicts that the observed concentrations of  $H_2$  in the ultramafic-hosted submarine vents should correspond to a water/rock ratio  $\gg 1$  and a significant substitution of Mg by Fe in serpentinites.

The methane concentration in the computer simulations of Palandri & Reed (2004) was pre-determined by the concentration of  $HCO_3^-$  in seawater or meteoric water, and therefore, 2–4 orders of magnitude lower than equilibrium concentrations of  $H_2$ . In Socorro gases, the  $H_2/CH_4$  ratio is within the range of 3–7, close to that of the ultramafic-hosted submarine vents of Lost City (Proskurowski *et al.* 2008) and Rainbow (Charlou *et al.* 2002).

Correlations of  $H_2$ – $CH_4$  for these vent gases and gases of Socorro are shown in Fig. 8. Despite significant scattering, all three thermal fields show a similar  $H_2$ – $CH_4$  relationship. The main source for  $CH_4$  in the Lost City and Rainbow vent fluids is thought to be magmatic  $CO_2$ . The same should be suggested for the Socorro gases. Therefore, serpentinization is one of the most probable reasons





**Fig. 8.** Relationship between  $H_2$  and  $CH_4$  in thermal fluids associated with ultramafic-hosted submarine hydrothermal systems (mmol kg<sup>-1</sup> scale, Charlou *et al.* 2002; Proskurowski *et al.* 2008) and gases from Socorro fumaroles (mol% in dry gas scale).

for high  $H_2$  and  $CH_4$  concentrations in Socorro gases, taking into account the tectonic setting of Socorro Island and unusually high  $R_H$  values.

#### Water isotopes, $N_2$ , Ar, and meteoric contribution

Water from Playa Armada spring water is a mixture of about 20% of seawater with groundwater and the resulting  $\delta D = -27\text{‰}$  and  $\delta^{18}O = -4.1\text{‰}$  (Table 2, Fig. 2). Plotting the isotopic compositions of water from drainless steam-heated pools within the fumarolic field produces a slope close to 3, which is a typical 'evaporation trend' for hot pools (Giggenbach & Stewart 1982). This trend intersects the meteoric water line somewhere between  $\delta D = -35$  and  $-25\text{‰}$  (Fig. 2). Points representing the results for condensates of fumarolic steam form another trend, in the opposite direction, compatible with water from the Palma Sola thermal spring (Fig. 2). A model of the single-step steam separation from water with  $\delta D = -40\text{‰}$  and  $\delta^{18}O = -6.25\text{‰}$  is inserted into Fig. 2. It can be seen from Fig. 2 that the predominant fraction of the fumarolic steam may be formed at 150–200°C as a result of boiling of ground water of meteoric origin. This groundwater, most probably, is the condensed steam 'envelope', recorded by the transient electromagnetic survey by Varley *et al.* (2004) at shallow depths of 50–100 m under the surface. It might be suggested that the initial fraction of water vapor prior to partial shallow condensation would be much lower than that measured approx. 95 mol% in the Socorro fumaroles (Table 1) and thus with much higher  $H_2/H_2O$  ratio than the measured (also very high) values approx. 0.01.

Owing to the high proportion of a meteoric component within the volcanic vapor, the 'atmogenic' components  $N_2$  and Ar show a good correlation, with the  $N_2/Ar$  ratio

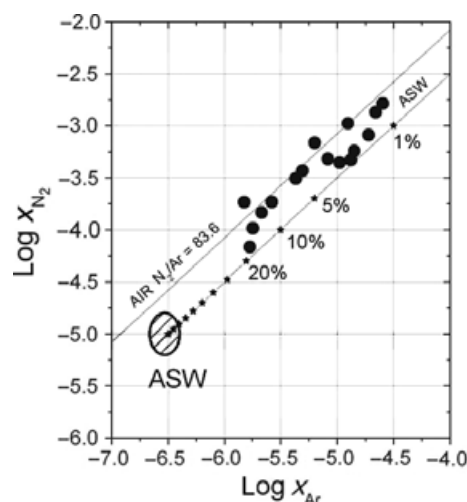
lying between the air value of 83.6 and the air-saturated water (ASW) ratio of approx. 40 (Fig. 9). This indicates that little  $H_2O$ ,  $N_2$ , or Ar originated from a deep fluid.

#### He, $^3He/^4He$ , and $CO_2$ as in MORB fluids

In the absence of data on  $^{40}Ar/^{36}Ar$ , it can only be speculated as to the Socorro  $^4He/^{40}Ar^*$  ratios ( $^{40}Ar^*$  is  $^{40}Ar$  from the mantle). Taran *et al.* (2002) reported the maximum  $^{40}Ar/^{36}Ar$  of 311 in a sample with 0.021% of Ar in dry gas. This may indicate that only 5% (approx. 0.001% instead of 0.021%) of the discharging Ar may have a mantle origin. If this is the case for the collected gases (Table 1), the  $^4He/^{40}Ar^*$  ratio should be between approx. 2 and approx. 8, which is close to values for undegassed (approx. 2) and degassed (approx. 8) MORB glasses (Marty & Zimmermann 1999). Taking into account that the mantle  $N_2/Ar$  ratio is close to 100 (Marty & Zimmermann 1999), it could be suggested that the fraction of the mantle nitrogen in the Socorro gases is also about 5% of the total discharging  $N_2$ , and thus, the mantle component of the Socorro gases can be presented (in mole %) as  $CO_2 = 99.93\%$ ,  $N_2 = 0.06\%$ ,  $Ar = 0.001\%$ , and  $He = 0.004\%$ . Because we assume that all  $CO_2$  has mantle origin, this estimate leads to very high  $CO_2/N_2$  ratio (approx. 1700), significantly higher than the expected 100–200 (Marty & Zimmermann 1999).

#### $C_1$ – $C_4$ hydrocarbons: chemical composition

The monotonic distribution of  $C_{2+}$  hydrocarbons (Table 3) is typical for  $CH_4$ -rich natural gases (e.g. Jenden *et al.* 1993; Hulston *et al.* 2001), and this type of distribution is usually called Anderson-Flory-Schulz distribution—a monotonic



**Fig. 9.** The  $N_2$ –Ar correlation for fumarolic gases of Socorro island. The upper line shows the direct air contamination with the corresponding  $N_2/Ar = 83.6$ . The lower line represents  $N_2$  and Ar concentrations (mole fractions) in steam separated from the air-saturated water (ASW) with numbers corresponding to the steam fraction (weight %).

decrease in  $C_i$  concentrations as a function of carbon number following an exponential law (e.g., Anderson 1984; Giggenbach 1997a,b). Fiebig *et al.* (2009) suggested a criterion for methane produced abiogenically: if the  $CH_4/C_{2+}$  ratio in a hydrothermal gas is higher than that common for thermogenic hydrocarbons ( $<100$ ), the excess methane would have been synthesized abiogenically by the reduction of  $CO_2$  or carbonates under appropriate redox conditions; but  $C_{2+}$  hydrocarbons in such a mixture may be of thermogenic origin. If so, the reduction of  $CO_2$ , or any other oxidized form of carbon, should be very specific allowing the production of  $CH_4$  but not higher alkanes. In industry, this is possible only using so-called Sabatier process, which is a catalytic reduction of  $CO_2$  by  $H_2$  on Ni or other transition metals (but not Fe) with an excess of  $H_2$  (e.g. Lunde & Kester 1973). In nature, the only option for this type of the  $CH_4$  production is microbial  $CO_2$  reduction. Examples for such methane are gas hydrates. 'Regular' Fischer-Tropsch synthesis on Fe and Co catalysts produces hydrocarbons with low  $CH_4/C_{2+}$  ratios (e.g. Anderson 1984; Taran *et al.* 2007).

### Carbon and hydrogen isotopes in $CO_2$ , $H_2$ , and hydrocarbons

The inverse carbon isotopic trend found in Socorro island (Fig. 3) has been reported for ultramafic-hosted submarine vents (Proskurowski *et al.* 2008; Konn *et al.* 2009), in gases occluded in the alkaline igneous rocks of Kola peninsula (Galimov & Petersilie 1967; Potter *et al.* 2004; Potter and Longstaffe, 2007), in free gases of Precambrian rocks of the Canadian Shield (Sherwood Lollar *et al.* 2002, 2008), in gases from some mud volcanoes in Turkey (Hosgormez *et al.* 2008), and in some gases from a gas field in China (Tarim basin, Liu *et al.* 2008). The inverse isotopic trend for hydrogen isotopes was observed in gases from rocks from the Kola peninsula (only between  $CH_4$  and  $C_2H_6$ , Potter and Longstaffe, 2007), Lost City gases (Proskurowski *et al.* 2008) and in some gas samples from the Tarim basin (Liu *et al.* 2008). Among these gases, only those from the Lost City ultramafic-hosted hydrothermal submarine field are similar in terms of the chemical and isotopic composition of the hydrocarbon components to Socorro gases (Proskurowski *et al.* 2008). Other gases have low  $CH_4/C_{2+}$  ratios (Canadian Shield, Kola Peninsula, oil-gas fields) or have isotopically light methane and hydrogen (Canadian Shield, oil-gas fields), or have a clear positive trend in the hydrogen isotopic composition of hydrocarbons (Canadian Shield). A serious discrepancy in the case of the Lost City gases is that the total organic carbon (TOC) in the carbonate chimneys (up to 0.6 wt%) has the same range of isotopic compositions ( $-15 \pm 5\%$ ) as methane and its homologues in gases (Bradley *et al.* 2008). Taking into account the moderate temperatures of the Lost City venting (40–90°C), an additional microbial

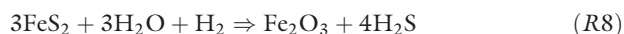
source of  $CH_4$ , undistinguishable by its isotopic composition from the deeper inorganic source cannot be excluded for the Lost City fluids.

He-isotope ratios in Socorro gases (approx. 7.6  $R_a$ ) are lower than those for the Mid Atlantic Ridge systems (7.5 to 8.8  $R_a$ ) but coincide with  $^3He/^4He$  of the northern East Pacific Rise vents (7.5–7.8  $R_a$ , Proskurowski *et al.* 2008). Therefore, it can be suggested that Socorro hydrothermal fumaroles discharge vapors of a mixed origin: (i)  $CO_2$  and He from the upper mantle (or MORB); (ii) water vapor,  $N_2$ , and Ar from the atmosphere (and/or ASW); (iii)  $H_2$  and  $CH_4$  are secondary products of reaction of water with hot ultramafic rocks.

The main difference between Socorro gases and gases from submarine vents with a high  $CH_4/C_{2+}$  ratio is the  $C_{2+}$  concentration as a function of carbon number: hydrocarbons  $C_2$ – $C_4$  from Lost City, according to Proskurowski *et al.* (2008), and is characterized by concentration ratios  $C_2/C_3$  approx.  $C_3/C_4$  approx. 10. Approximately the same ratios have been recorded from  $C_{2+}$  hydrocarbons in cold seeps from ophiolites of the Poison Bay, South Island, New Zealand (Lyon & Giggenbach 1990). In Socorro gases,  $C_2/C_3 \approx C_3/C_4 \approx 3$ . The latter are typical ratios for thermogenic hydrocarbons in  $CH_4$ -rich natural gases (Jenden *et al.* 1993; Hulston *et al.* 2001) and hydrocarbons from hydrothermal gases: for example, fumarolic gases (160°C) from La Solfatara, Italy, have  $CH_4/C_{2+} \approx 100$ ,  $C_2/C_3 \approx 7$ , and  $C_3/C_4 \approx 4$  (Capaccioni & Mangani 2001). Therefore, if the abiogenic origin for methane in the ultramafic-hosted vents, cold seeps from ophiolites, and in Socorro gases is almost unambiguous, especially, in the hot (350°C) fluids of Rainbow and Logachev vents, the origin of heavier hydrocarbons is still unclear. Following Fiebig *et al.* (2009), it can be assumed that in gases with  $CH_4/C_{2+} \gg 100$ , methane is a mixture between abiogenic, 'synthetic'  $CH_4$ , and thermogenic hydrocarbons with  $CH_4/C_{2+} \leq 100$ . If this is the case, it has to be explained why  $\delta^{13}C$  and  $\delta D$  of methane and  $C_{2+}$  in the Lost City fluids are all within the ranges  $-15\%$  to  $-10\%$  and  $-160\%$  to  $-120\%$ , respectively (Proskurowski *et al.* 2008), i.e., 'thermogenic' hydrocarbons have almost the same isotopic composition as the abiogenic methane. Socorro hydrocarbons are also characterized by similar values of  $\delta^{13}C$  and  $\delta D$  (Table 4), which could be evidence of mainly syngenetic, not mixed, origin of the hydrocarbons. Assuming that the methane is abiogenic, or 'synthetic', then the other hydrocarbons should also be produced from the same carbon source by the same abiotic process. One spectacular example of the mixing of hydrocarbons of different origins was reported by Hosgormez *et al.* (2008). In this case, methane-rich gas seepages on the Mediterranean coast of Antalya, Turkey, are characterized by  $\delta^{13}C$ – $CH_4$  within the range  $-12\%$  to  $-8\%$  (abiogenic source), but  $\delta^{13}C$  of the  $C_{2+}$  hydrocarbons varied from  $-26\%$  to  $-23\%$ , within the 'thermogenic' range.

## Chemical and isotopic geothermometers and a conceptual model

The application of geothermometers assumes chemical (isotopic) equilibrium between the species in the aquifer and defines a function relating the concentrations of the species to the equilibrium temperature. The Socorro geothermal system is most probably a system essentially dominated by vapor or it has a large steam 'cap', and for gas geothermometers, a purely thermodynamic (not empirical) approach can be used. The temperatures of the apparent chemical equilibrium presented in Table 5 have been calculated using thermodynamic data for species in the gas phase (thermodynamic database from the HSC-6 package, Roine 2006) and chemical reactions (R1), (R2) for the  $\text{CO}_2\text{--CO--H}_2\text{--CH}_4\text{--H}_2\text{O}$  system. The reaction of pyrite with  $\text{H}_2\text{O}$  and  $\text{H}_2$  to produce magnetite or hematite and  $\text{H}_2\text{S}$  was used as a proxy for the 'H<sub>2</sub>S-geothermometer':



Reaction (R7) represents the buffering of  $\text{H}_2\text{S}$  by a more reduced buffer than reaction (R8). Both equilibria are pressure independent (same number of moles of gas on left- and right-hand sides), and concentrations of all gaseous species can be taken from Table 1. For calculating temperatures of isotopic equilibrium, the calibration of the D/H fractionation by Horibe & Craig (1995) was used for  $\text{H}_2\text{O--H}_2$  and  $\text{CH}_4\text{--H}_2$  pairs and by Horita (1995) for the  $^{13}\text{C--}^{12}\text{C}$  exchange in the  $\text{CO}_2\text{--CH}_4$  pair.

A striking feature of data presented in Table 5 is the existence of two groups of equilibrium temperatures. The group of high super-critical temperatures in the range of 500–600°C is related to chemical and isotopic equilibrium of  $\text{CO}_2$  and  $\text{CH}_4$ . Temperatures below 300°C are related to hydrogen isotope exchange  $\text{H}_2\text{--H}_2\text{O}$  and  $\text{H}_2\text{--CH}_4$  and 'fast' redox equilibria  $\text{CO--CO}_2$  and  $\text{FeS}_2\text{--H}_2\text{S--H}_2\text{--H}_2\text{O}$  in the vapor phase. The lower equilibrium temperatures most probably reflect the conditions of the upper, vapor-dominated aquifer. High and coinciding temperatures of  $\text{CO}_2\text{--CH}_4$  chemical (at 1 kb pressure) and isotopic equilibrium may indicate a deep, highly reduced, and hot source of methane and hydrogen, similar to the source of these gases in hot, ultramafic-hosted spreading ridge systems like Rainbow and Logachev (Charlou *et al.* 2002).

## On the origin of the $\delta^{13}\text{C}_n$ inverse isotopic trend

The carbon isotopic composition of  $\text{C}_2$  to  $\text{C}_4$  hydrocarbons from Socorro gases is increasingly negative with increasing chain length (Fig. 3A). This isotopic pattern is opposite to that for hydrocarbons produced thermogenically (Galimov 1975; Chang *et al.*, 1993). The origin of

such an inverse trend in natural hydrocarbons is unclear. Light hydrocarbons produced in experiments on the catalytic reduction of CO or  $\text{CO}_2$  by molecular  $\text{H}_2$  (Fischer-Tropsch reaction) do not show the inverse trend (McCollom & Seewald 2006; Fu *et al.* 2007; Taran *et al.* 2007, 2010), rather a slightly positive one. There are only three groups of experiments that have produced the inverse carbon isotopic trend in light hydrocarbons: (i) spark-induced synthesis of hydrocarbons from methane (Des Marais *et al.* 1981); (ii) high-temperature and high-pressure dry pyrolysis of lignite (brown coal, Berner *et al.* 1995; Du *et al.* 2003); (iii) a weak inverse trend in the products of Fischer-Tropsch synthesis has been observed only in the open-system catalytic hydrogenation (reduction) of CO at low (incomplete) conversions of CO (Taran *et al.* 2007).

The inverse carbon isotopic trends in Lost City hydrocarbons and in Socorro gases may be caused by the secondary processes of the methane radicalization and the subsequent radical recombination by considering the presumably high temperature and pressure of the hydrothermal serpentinization that produce methane and higher hydrocarbons. The longer-chain hydrocarbons thus formed would be characterized by a negative isotopic trend similar to the products of the spark synthesis (Des Marais *et al.* 1981) because of the kinetic fractionation at the C–C bond formation (see Taran *et al.* 2010 for further discussion).

## SUMMARY

Hydrothermal fumaroles of Socorro Island discharge unusual fluids with an extremely high  $\text{H}_2/\text{H}_2\text{O}$  ratio and a high concentration of methane. The water vapor, nitrogen, and argon are of meteoric origin, whereas  $\text{CO}_2$  and He have an unambiguous mantle origin implied by both their isotopic composition and molecular ratios. Gases are characterized by a high  $\text{CH}_4/\text{C}_{2+}$  ratio, up to 1000, and isotopically heavy methane (–20 to –15‰). Hydrocarbons demonstrate an inverse trend in both carbon and hydrogen isotopic composition. The comparison between the analytical concentrations of Socorro gases with those expected theoretically for a range of redox equilibria potentially governing their compositions suggests that at least two main processes are responsible for the observed concentrations. High  $\text{H}_2$  and  $\text{CH}_4$  concentrations are most probably controlled by high-temperature hydrothermal serpentinization of mafic and ultramafic rocks at a considerable depth beneath the main hydrothermal aquifer.  $\text{CO}/\text{CO}_2$  and  $\text{H}_2\text{S}/\text{H}_2$  ratios correspond to conditions in a vapor-dominated reservoir at a shallow depth inside the volcano edifice. The origin of  $\text{C}_2\text{--C}_4$  hydrocarbons and the reason for the inverse isotopic trend in both  $\delta^{13}\text{C}$  and  $\delta\text{D}$  are unclear. The proximity of  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values of  $\text{CH}_4$  and  $\text{C}_2\text{--C}_4$  alkanes may indicate their syngenetic origin, i.e., the reduc-



tion of magmatic CO<sub>2</sub> as result of high-temperature hydrothermal serpentinization.

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