Geochemistry and origin of high-pH thermal springs in the Pacific coast of Guerrero, Mexico

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RESUMEN

Las aguas de manantiales termales (40-43 °C) que descargan de rocas cristalinas del complejo Xolapa, cerca de Acapulco, México, dentro de un área de aproximadamente 100 km x 50 km, se caracterizan por una baja salinidad (SDT<0.5g/kg) y muy alto pH (9.5-10). Estos manantiales representan un acuífero regional o un grupo de acuíferos con condiciones similares de circulación y de interacciones agua-roca. Los gases de los manantiales son ricos en nitrógeno y helio, con una alta proporción de He radiogénico (R/R_a = 0.12-0.3). Uno de los manantiales presenta una elevada concentración de CH_4 (10-12%) enriquecido en ^{13}C ($\delta^{13}C$ =-26‰, PDB). Todos los gases contienen muy poco CO_2 (< 0.5%) y relativamente poco Rn (8 a 25 Bq/l). La simulación numérica de las interacciones agua-roca en un reactor multipaso, usando la aproximación de "1ª onda", sugiere que este tipo de agua con elevado pH podría producirse por la disolución paso a paso del granito y la redeposición de minerales de equilibrio secundarios a lo largo del flujo. El modelo incluye la infiltración y calentamiento del agua meteórica hasta alcanzar una temperatura de 100°C, y su ascenso posterior a la superficie con enfriamiento conductivo, hasta llegar a los 40 °C. Para alcanzar los elevados valores de pH de las aguas termales a partir del agua de lluvia inicial neutra o ligeramente ácida, se requieren condiciones de sistema cerrado respecto a CO_2 y bajas concentraciones de carbono de carbonato. La presencia del material carbonoso en las rocas del acuífero puede explicar las concentraciones de metano observadas en el manantial rico en CH_4, así como su composición isotópica respecto al carbono.

PALABRAS CLAVE: Aguas termales de alto pH, interacción agua-roca, simulación numérica.

ABSTRACT

Thermal waters (40-43°C) discharging from crystalline rocks of the Xolapa complex, near Acapulco, Mexico, within an area of approximately 100 km x 50 km are characterized by a low salinity (TDS<0.5 g/kg) and very high pH (9.5-10). They represent a regional aquifer or a group of aquifers with similar conditions of water circulation and water-rock interaction. Spring gases are nitrogen- and He-rich, with a high proportion of radiogenic He (R/R_a=0.12 to 0.3). Methane from a spring with a high concentration of CH_4 (10-12%) is relatively enriched in ^{13}C ($\delta^{13}C$=-26‰, PDB). All gases are very low in CO_2 (<0.5%) and relatively low in Rn (8 to 25 Bq/l). Numerical simulation of water-rock interaction in a multistep flow-through reactor, using a "1st wave" approximation, suggests that this type of high-pH diluted water can be produced by step-by-step dissolution of granite and redeposition of secondary equilibrium minerals along a flow-path. This models the infiltrating meteoric water to the depth of 100°C and its ascending to the surface with conductive cooling to 40°C. Closed system conditions in respect to CO_2 and a low concentration of the carbonate carbon in the aquifer rock are needed to attain the high pH in thermal water from initially neutral or slightly acidic rain water. The presence of the carbonaceous material in the aquifer rocks can explain the observed concentrations of methane in the CH_4-rich spring, as well as its carbon isotopic composition.

KEY WORDS: High-pH thermal waters, water-rock interaction, computer simulation

1. INTRODUCTION

Several groups of warm (39-43°C) springs are located within the southern state of Guerrero, Mexico, close to Acapulco, within an area of approximately 100 km x 50 km along the Pacific coast. They discharge low-salinity (TDS<0.5 g/kg) and highly alkaline (pH>9.5) waters from fractures in granites and gneisses. All springs are located within the epicentral zone of the majority of earthquakes in this area. Because of the high seismicity of this continental margin re-lated to the subduction of the oceanic Cocos plate beneath the continental North America plate, these springs were chosen for the study of co- post- and pre-seismic variations in chemical and gas composition (Ramírez-Guzmán *et al.*, 2002). A preliminary geochemical study was carried out in order to understand the origin and sources of the fluid constituents, as well as the cause of high pH. We report here our data on chemical composition of waters and bubbling gases, D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$ and $^{3}He/^{4}He$ isotopic ratios and results of the multi-component chemical equilibrium calculations

of rock-water system. We find that the high pH of waters may be caused by water-granite interaction at 25-100°C at very high (>50) water/rock ratio.

2. GENERAL SETTING

The coast of Guerrero, Mexico is a continental margin related to the modern subduction of the Cocos oceanic plate beneath the North America continental plate. This is one of the most seismically active regions in the Americas. Earthquakes with magnitude around 4 occur sometimes more than 10 times per month. The last strong event with M>7 occurred in 1978 (Singh and Mortera, 1991). The seismicity is generally related to the subduction. The majority of hypocenters are recorded within the seismogenic zone at the slab-crust interface, which is here relatively close to the surface (22-25 km). However, the last shallow (6-8 km) earthquake at Coyuca (October 2001, M=5.9) was a crustal normal-faulting event (Pacheco *et al.*, 2002). The area belongs to the Xolapa complex or terrane (De Cserna, 1965). According to

Herrmann *et al.*(1994) it originated by high-grade metamorphic to migmatitic orthogenesis and paragenesis with metamorphism and migmatization that occurred from 66 to 46 My. Oligocene (35-27 My) granitic plutons crop out along the coast (Ortega Gutiérrez, 1981). Several analyses of plutonic rocks have been presented by Schaaf (1990) and Morán-Zenteno (1992). A simplified geologic map of the area with the location of thermal springs is shown in Figure 1 (Morán-Zenteno, 1992). Unfortunately, we could not find any details about the local tectonics of the area in the literature.

There are six groups of thermal springs within an area of about 50 km x 100 km (Figure 1 and Table 1). Each group discharges thermal water with a temperature close to 40°C near contacts between plutonic (granites, diorites, monzonites) and metamorphic rocks (mostly, gneisses), therefore it is difficult to suggest the associated rock composition of the aquifers. The flow rate of the springs varies between about 3 kg/s for the Paso Real group, to more than 20 kg/s for the total discharge of all Río de Cortés springs.
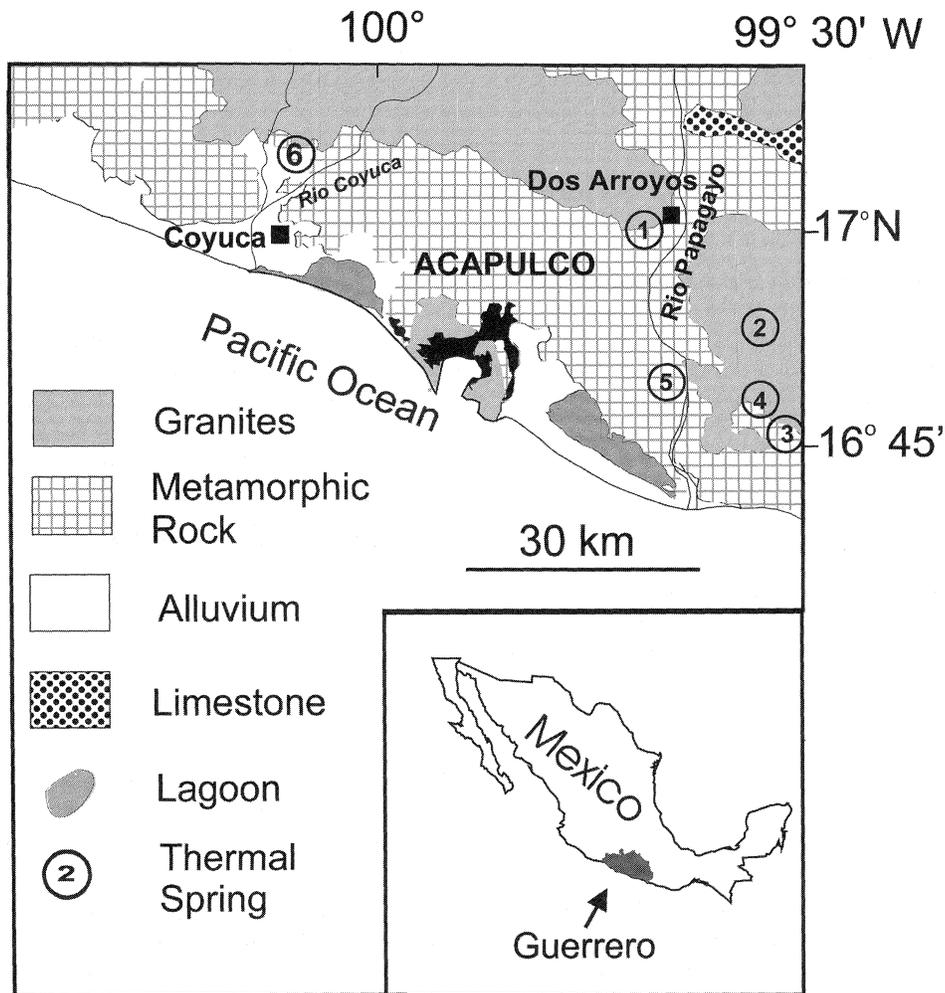

Fig. 1. Location map of thermal springs near Acapulco, Guerrero State, Mexico. Geological background is taken from Morán-Zenteno (1992). Numbers of groups of springs: 1 – Dos Arroyos; 2 – Tamarindo; 3 – Cocoyul; 4 – Río Cortés; 5 – Agua Caliente (Borbollon); 6 – Paso Real.

Table 1

Coordinates and short description of thermal springs near Acapulco

| Name of spring | Coordinates | | Flow rate (approx.) kg/s | Comments |
	Latitude N	Longitude W		
Dos Arroyos	16°59.41'	99°39.52'	>5	~1 km to W from Río Papagayo. 10 km to SE from the village of Dos Arroyos. 6-7 pools on the right bank of a small creek. Río Papagayo basin.
Agua Caliente	16°53.68'	99°40.42'	>25	"Borbollón" – a concrete well (washing place) in a swampy area. More springs on the right bank of Río Papagayo. Many are flooded in rainy season.
Tamarindo	16°51.04'	99°31.53'	2-3	Washing place. Right bank of a small creek. Río Cortés basin.
Cocoyul	16°45.73'	99°29.19'	2.5	Washing place. Right bank of a dry creek bed.
Río Cortés	16°46.46'	99°30.60'	>15	Many pools. 1 km along the left bank of Río Cortés to N from the bridge.
Paso Real	17°05.27'	100°04.40'	3-4	Left bank of the Coyuco river. Rancho Agua Caliente. 3 km from village of Paso Real to W.

3. SAMPLING AND ANALYSIS

After measuring temperature (±0.1°C), pH (±0.05 pH units), Eh (±10 mV), and conductivity (±2%) in the spring, each water sample was filtered through 0.45 μm Millipore filter into a 250 ml prewashed plastic bottle. Samples for cation analysis were acidified to pH~2 with ultrapure HNO_3. Bubbling gas was collected into 125-ml dark glass bottles with a septum, by displacement of spring water by the gas bubbles. These samples were used for the gas chromatograph analyses. Gas for the He isotope analysis was collected into a 25-ml two stopcock helium-impermeable glass ampoule. A plastic funnel was used to precollect bubbling gas. The funnel was submerged to the bottom of a spring in order to minimize exchange between air dissolved in the spring water and the gas issuing from the bottom. Gas was transferred to bottles and ampoules through a Tygon silicon tube or by a 100-ml plastic syringe. A portion of gas (100 ml) from the funnel was transferred by a plastic syringe into a preevacuated 150 ml Lucas cell for Rn analysis.

Analysis of major anions (Cl, SO_4, F) was performed using Metrohm 750 ionic chromatograph system without dilution of samples. Alkalinity and HCO_3 content were analyzed by titration with 0.05N HCl. Na and K were analyzed by flame photometry, Ca and Mg by atomic spectroscopy.

Gas samples were analyzed on dual-column gas chromatograph (Gow-Mac 350) using argon for He and H_2 analyses and helium as the carrier gases for analyses of N_2, Ar, O_2, CH_4 and CO_2. Argon was analyzed at room temperature using Altech combined column. He/Ne ratios were determined when the gas samples were being prepared for the He isotopic analysis, which was performed following procedures outlined in Italiano *et al.* (1999). Stable isotope values of water samples (δD and $\delta^{18}O$) and isotopic composition of carbon in CH_4 and CO_2 were obtained by mass spectrometry (Varian-MAT 250) using standard procedures.

4. FIELD RESULTS

The results of water composition are presented in Table 2 and Figure 2. All waters are very diluted. Water from Agua Caliente springs is almost of the pure Na-Cl type as can be seen from Cl-SO_4-HCO_3 ternary plot on Figure 2. Waters from El Tamarindo and Río Cortés are similar in anionic composition while water from Dos Arroyos springs is more of the SO_4-HCO_3 type. All the waters are relatively high in F, with a maximum of 11 ppm in the Cocoyul spring. A common feature for all but Agua Caliente waters is their extremely high pH, low Eh and low salinity. Major cation composition of springs (Table 2) can be plotted on the log Na/K vs log K^2/Mg diagram (Figure 3). According to Giggenbach's (1988) classification, all waters are partially equilibrated with hydrothermally altered rock at 80-100°C.

Table 2

Chemical (mg/kg) and isotopic (‰, V-SMOW) composition of thermal waters from the Guerrero state. Samples were taken in dry, rainy and intermediate seasons (except of Agua Caliente and Río Cortés). Alkalinity is expressed as mg/L of HCO_3. na – not analyzed; nd – not determined. Analytical errors for the majority of species except of Mg and B are within ±5%. Errors for Mg and B are >20% because their concentrations were close to the detection limit of corresponding methods.

Name of Spring	Date mm/yy	t°C	pH field	Cond µS	SiO_2	Eh mV	Na	K	Ca	Mg	Cl	HCO_3 (alk)	SO_4	F	B	δD	$δ^{18}O$
Paso Real	08/02	38.3	9.68	480	44	nd	90	0.9	0.4	0.22	41	83	52	4.4	0.8	-59	-8.2
Paso Real	11/02	37.0	9.67	460	50	-285	94	1.0	1.5	0.18	38	88	45	5.0	<0.5	na	na
Paso Real	03/03	38.4	9.89	434	45	-306	93	1.1	0.4	0.21	44	89	61	5.0	<0.5	-53	-7.6
Agua Caliente	06/01	38.0	9.28	540	50	nd	107	1.1	5.0	0.29	109	53	30	4.8	1.9	-65	-9.3
Cocoyul	11/01	42.0	9.90	458	57	nd	94	0.7	0.8	0.22	74	43	26	10.4	1.1	na	na
Cocoyul	08/02	40.9	9.96	430	49	-472	84	1.0	0.9	<0.15	59	35	22	11.2	1.1	-56	-8.2
Cocoyul	03/03	41.0	9.98	413	52	-443	86	1.1	0.6	0.16	82	40	19	10.4	<0.5	-58	-8.4
Tamarindo	11/01	41.0	9.66	378	45	nd	84	0.7	1.6	0.25	23	37	54	5.1	0.5	-60	-8.5
Tamarindo	08/02	42.1	9.45	350	49	nd	72	0.9	1.0	<0.15	23	40	62	5.3	<0.5	-60	-8.6
Tamarindo	03/03	43.1	9.79	341	45	-409	72	1.0	2.5	0.15	26	53	48	4.9	<0.5	-59	-8.2
Río Cortés	08/02	36.8	7.76	390	28	nd	83	0.69	0.7	<0.15	32	41	86	5.3	<0.5	-58	-8.6
Río Cortés	11/02	37.0	8.94	412	35	nd	85	1.69	0.8	<0.15	33	45	99	5.2	<0.5	-57	-8.4
Dos Arroyos	03/97	41.0	9.08	320	29	nd	64	0.51	0.7	<0.15	11	35	89	3.1	<0.5	-65	-9.0
Dos Arroyos	07/02	41.2	9.23	309	29	-346	61	0.65	0.6	<0.15	9.0	37	69	3.0	0.6	-64	-9.1
Dos Arroyos	10/02	42.0	8.78	290	36	-328	61	0.69	0.6	<0.15	9.2	33	73	3.0	0.5	-68	-9.6

There are no significant seasonal variations in water composition. Table 2 shows water analyses of samples collected in rainy, dry and intermediate seasons with variations within the analytical error range. Gas composition (Table 3) is very similar for all but Cocoyul waters, where about 10 vol% of methane is present. All gases are relatively rich in He with a systematic difference: the lowest He content is in Dos Arroyos springs (200-250 ppm) and the highest was found in Paso Real springs (700-960 ppm). The N_2/Ar ratio in all springs is close to the atmospheric air value of 83.5 All gases are extremely low in CO_2; in most cases its concentration was lower than that in air (0.034 vol%). The radon content (8, 19, 24 and 25 Bq/l for Dos Arroyos, Paso Real, Cocoyul and Tamarindo, respectively) is low for granitic and even metamorphic aquifers, where Rn content in waters can be one order of magnitude higher (Cothern and Smith, 1987). Such low values can be attributed to the high flow rates of springs through open fractures.

The isotopic composition of waters shown in Table 2 corresponds to meteoric waters of some higher elevations than where the springs are located. Water from a small creek near El Tamarindo springs had δD=-49‰, almost 15‰ heavier than the spring water. The isotopic ratios $^3He/^4He$ are about 5 times lower than in the atmosphere. These may be the lowest values of $^3He/^4He$ measured in thermal waters of Mexico (Prasolov *et al.*, 1999; Taran *et al.*, 2001). They
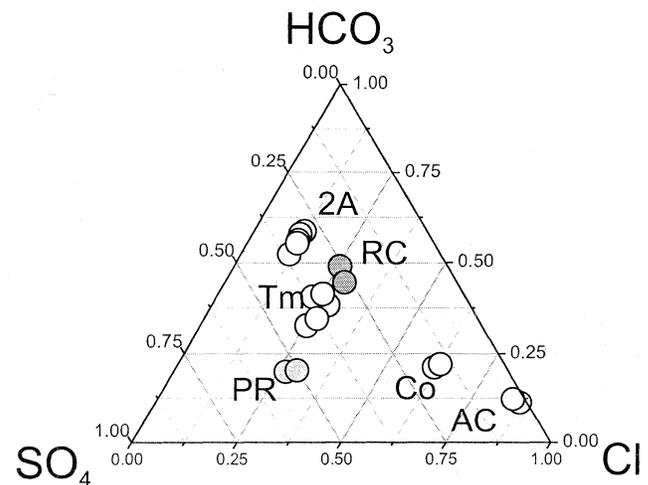

Fig. 2. Ternary (HCO_3-Cl-SO_4) plot for the Guerrero thermal waters. 2A – Dos Arroyos; Tm – Tamarindo; Co – Cocoyul; RC – Río Cortés; AC – Agua Caliente; PR – Paso Real.

correspond to a significant proportion of radiogenic He but the gases with such a low $^3He/^4He$ still contain some 1-2 % of upper mantle He with $^3He/^4He$ about of 8 of the atmospheric value (Taran *et al.*, 2001). The carbon isotopic composition of methane from the Cocoyul spring (-26‰, PDB) corresponds to "thermogenic" methane produced by a kero-

gen like material of a high grade of maturity. This is unusual taking into account the high proportion of methane in the bubbling gas (10-12%) and low aquifer temperature (~<100°C) as derived from the major cation composition (Figure 3). Such relatively "heavy" methane is characteristic of high-temperature hydrothermal fluids (Welhan, 1988; Giggenbach, 1997).

5. DISCUSSION

5.1 Processes responsible for the formation of high-pH waters

Several analyses of high-pH waters together with water from the Cocoyul spring are shown for comparison in Table 4. There are two main types of high-pH (~>10) waters in nature: waters from "soda"- lakes and springs, and waters discharging from ultramafic rocks. One of the most spectacular examples of African "soda" waters was presented by Cioni *et al.* (1992). Boiling hot springs at Lake Bogoria from the Kenya Rift System with total carbonate content higher than15 g/L and water from Lake Bogoria itself, with 85 g/L of total carbonate, are characterized by pH up to 9.8 (springs) and 10.10 (lake). These waters are associated with carbonatites, alkali basalts and phonolytic rocks (Jones *et al.*, 1977; Cioni *et al.*, 1992) and their pH is controlled by hydrolysis of CO_3^{2-}. High-pH waters associated with ultramafic rocks are, in contrast, usually diluted and carbonate-poor (Barnes *et al.*, 1978), although their pH can reach values as high as 12. They are actually diluted solutions of $NaOH+Ca(OH)_2$ depleted in Mg due to precipitation of brucite and serpentine (Barnes *et al.*, 1978; Drever, 1982).
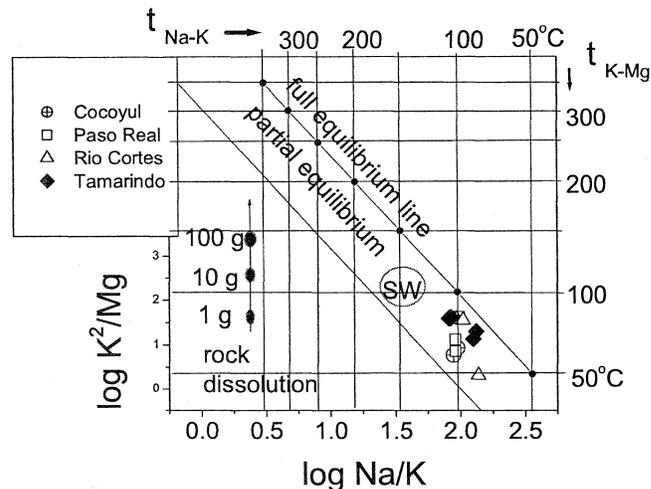

Fig. 3. Na-K-Mg plot for the Guerrero thermal waters (modified after Giggenbach, 1988). Composition of waters after incongruent (direct) dissolution of 1g, 10 g, and 100 g of Guerrero granite (Schaaf, 1990) in 1 kg of pure water is also shown. SW – seawater.

Recently, Bruni *et al.* (2002) reported an example of cold, diluted Ca-OH waters with pH up to 11.86 from the Genova province, Italy, discharging from serpentinized ultrabasic rocks.

Another known type of alkaline waters are high-temperature waters from so-called "weir box" – waters after loss of steam at atmospheric pressure from deep geothermal wells. The loss of steam is accompanied by an increase in the concentration of H_4SiO_4 up to 1.5 g/L, a loss of almost all CO_2 and a corresponding shift in the carbonate equilibrium (Ellis

Table 3

Chemical and isotopic composition of bubbling gases from thermal springs of Guerrero. R=^{3}He/^{4}He and R_a is atmospheric ratio 1.39x10^{-6}. Carbon isotopic composition of methane in ‰ v-PDB (±0.2 ‰). Analytical errors of the GC determinations are within 5%.

Name of spring	Date mm/yy	t°C	He ppm	H₂ ppm	N₂ vol%	O₂ vol%	Ar vol%	CH₄ vol%	CO₂ vol%	³He/⁴He R/Rₐ	He/Ne	δ¹³C CH₄
Paso Real	10/02	39	920	-	98.1	0.66	1.09	0.05	0.001	na	na	
Paso Real	12/02	39	685	-	98.4	0.20	1.20	0.11	0.002	na	na	
Paso Real	06/03	39	890	-	96.5	2.40	0.96	0.10	0.014	0.96	66	
Cocoyul	08/01	41	396	38	88.8	0.0	1.26	9.7	0.16	0.16	21	-26.0
Cocoyul	06/03	42	510	33	87.3	0.0	1.00	11.6	0.004	0.16	41	-25.9
Tamarindo	08/01	40	250	-	96.8	1.75	1.12	0.12	0.21	0.21	22	
Tamarindo	06/03	40	340	-	97.3	1.50	1.06	0.10	0.009	0.21	14	
Dos Arroyos	11/02	41	228	10	98.6	0.10	1.14	0.03	0.14	0.34	12	
Dos Arroyos	06/03	40	298	-	98.4	0.52	0.96	0.12	0.009	na	na	
Río Cortés	10/02	37	378	-	98.0	0.68	1.20	0.05	0.01	na	na	

Table 4

Chemical composition (mg/kg) of high-pH waters from different water-bearing formations

	1	2	3	4	5	6	7	8	9	10
t°C	41	57	27.1	96	15.6	20	20.7	8.6	93.5	12
pH	9.98	9.4	10.10	9.78	11.78	11.54	9.67	10.06	9.48	11.86
Na	88	72	39300	5980	40	19	9.9	218	382	23.7
K	0.84	2.4	547	113	1.1	1.1	0.2	0.44	21	3.1
Ca	0.5	1.3	1.82	0.34	48	40	8.4	94	0.9	47.4
Mg	0.02	0.3	1.11	0.21	0.4	0.3	0.00	0.03	0.01	0.02
Cl	61.3	6.5	7460	1350	32	63	0.00	460	365	21.2
HCO$_3$	37	20	85400	12800	0.0	0.0	31	18	306	1.3
SO$_4$	20	32	144	67	1.4	0.4	14.9	57	100	0.14
F	10.4	16	1350	209	0.00	0.0	-	5.3	36	-
SiO$_2$	57	75	378	182	5.2	4.0	8.9	18	366	1.5

1 - Cocoyul spring, State of Guerrero, Mexico. Water-bearing formation – granite (?) (this work); 2 – Spring in Idaho, USA, quartz monzonite (Hem, 1985); 3 – Lake Bogoria, Kenya. Alkaline volcanic rocks (Cioni et al., 1992); 4 – Hot spring near Lake Bogoria (Cioni et al., 1992); 5 – Spring in Red Mountain, California. Ultrabasic rock (Hem, 1985); 6 – Spring in Cazadero, California, USA. Ultrabasic rock (Barnes et al., 1978); 7 – Gotthard Tunnels, Switzerland. Orthogneiss (Venturelli et al., 2003); 8 - Stripa well, 960m, Sweden. Granite (Nordstrom et al., 1989); 9 – Hot spring in Yellowstone Caldera. Volcanic rocks (Fournier, 1989); 10 – Cold spring, Genova province, Italy. Serpentinites (Bruni et al., 2002).

and Mahon, 1977). These waters can have pH up to 9.6. Natural boiling or near-boiling springs at high-temperature geothermal fields sometimes have pH up to 9.5 for the same reason (e.g. Fournier, 1989).

However, thermal waters from the granite-gneiss regional aquifer of Guerrero (Table 2) are not associated with carbonatites or ultrabasic rocks, or with high-temperature hydrothermal systems. There are not many examples of such waters. Hem (1985) showed one analysis of a 57°C spring in Oregon discharging a very diluted (328 μS) water from the quartz monzonitic aquifer with pH=9.4. Nordstrom et al. (1989) published data on chemical composition of cold waters from deep wells drilled into the Stripa granitic rocks, Sweden, with TDS around 1.2 g/kg and pH up to 10.03. Finally, Venturelli et al. (2003) defined "Na carbonate" waters – cold shallow waters with pH up to 9.7 from sedimentary-pelitic carbonate bearing rocks with Na + alkalinity ~ 12-18 meq/L, and Na > (K+Ca+Mg) and HCO$_3$+CO$_3$ > (Cl+SO$_4$). They included in this type also cold diluted and almost Cl-free waters from Gotthard Tunnels, Switzerland, discharging from crystalline rocks (gneiss) and with average pH of 9.4.

Waters from Guerrero are more similar to diluted hot or cold waters from crystalline (igneous and metamorphic) rocks. Some of these waters (Dos Arroyos) can be also called "Na-carbonate" waters, but their origin seems to be different from Na- and (bi)carbonate-rich waters from Italy (Venturelli et al., 2003). The mechanism controlling pH during the interaction of water with granites or metamorphic crystalline rocks may depend critically on the water/rock ratio and CO$_2$ content in the primary rock. High pH can be attained at high water/rock ratios and low partial pressure of CO$_2$ at the initial stage of rock dissolution, when concentrations of mineral-forming ions (mainly Na$^+$) are still low enough for the re crystallization of secondary minerals (low albite, paragonite, Na-clays) and at low CO$_2$ concentration (in a closed system in respect to CO$_2$) the excess of Na$^+$ is compensated by the formation of OH$^-$.

5.2 Thermodynamic modeling of water-rock interaction: "thermo-gradient" waters in fractured granitic bodies

Kraynov and Ryzhenko (1997) studied pure water-granite interaction at 25°C by multi-component thermodynamic modeling using the GIBBS computer code (Shvarov, 1999). They showed that with a water/rock volume ratio >1 in a system closed to CO$_2$ (with the consumption of the initial CO$_2$ in rock by the water phase and secondary carbonate minerals) the resulting equilibrated water is a diluted Na$_2$CO$_3$ solution that can attain pH up to 10.6. Waters from Guerrero are not cold shallow waters but so-called "thermo-gradient" waters, heated at considerable depth to a temperature corresponding to the regional thermal gradient. An estimation of this maximal temperature can be the Na/K temperature calculated from the Na/K ratio of collected water samples

(Giggenbach, 1988). From Figure 3 all Guerrero springs have Na/K temperatures close to 100°C. We imagine a recharge-discharge "convective cell" with rain water infiltrating and descending through fractured granites up to ≥100°C level (the depth depending the local thermal gradient) and then rising to discharge with a temperature (after conductive cooling) of around 40°C. This model is similar to the Bowers and Taylor (1985) or Grichuk and Borisov (1983) models of submarine hot hydrothermal systems of spreading zones (flow-through multi-step reactor). Using the CHILLER computer code (Reed and Spycher, 1984) we may "titrate" granitic rock on the way down and up calculating the equilibrium composition of water and the equilibrium set of secondary minerals at each step at a given temperature and water-to-reacted rock (w/r) ratio.

Parameters of the model are shown in Table 5. The chemical composition of local granites was taken from Schaaf (1990). The fluorine and chlorine content (0.067 and 0.013 wt %, respectively) was chosen from the average for North America granites (Christiansen and Lee, 1986). Total sulfur and carbonate carbon (CO_2) content is taken to be 0.05 wt% as in Japanese granitic rocks (Ishihara and Terashima, 1989). A considerable source of CO_2 is meteoric water itself with an initial content of 25-50 mg/kg of HCO_3. Composition and pH of meteoric water is taken from Drever (1982) as in average river water which formed its chemical composition by the weathering of an average crustal rock under atmospheric CO_2 pressure ($10^{-3.4}$ bar). Descending flow is divided in six steps from 25°C to 100°C. The ascending branch also consists of six steps from 90 to 40°C. The amount of reacting granite at each step was calculated as in Grichuk (2000), based on the estimated average reaction rate of dissolution of alumosilicates (Wood and Walter, 1983). This requires a knowledge of the total w/r ratio. Fluorine leached from granite can be reprecipitated with clay minerals and fluorite. We have no thermodynamic data on the OH-F exchange for clay minerals, and our model waters were always undersaturated with respect to fluorite. Thus all F from granites in the numerical experiment is dissolved in water, and we need to dissolve 10 g to 15 g of granite with 0.067 wt% of F in 1 kg of F-free water in order to obtain an F content close to that of the Guerrero thermal springs (5-11 ppm).

There are limitations in thermochemical calculations of natural geological processes, especially at low temperatures (e.g. Helgeson, 1979, Reed and Spycher, 1984, Grichuk, 2000 and others). Kinetics of mineral dissolution and mineral precipitation at low temperature often is too slow for attaining water-rock equilibrium within a reasonable time scale. Another limitation is the lack of reliable thermodynamic data for low-temperature clay minerals. There are also serious technical difficulties in modeling an open system with multiple water-rock interactions. In order to obtain a correct "metasomatic column" we need to know how to take into account heat and mass transfer, phase transitions, reaction rates, and other factors. Grichuk (2000) discussed in detail existing methods of numerical modeling of water-rock interaction. He showed that, at least at high temperatures (150-350°C), the first batch (wave) of water passing through a multi-step, non-isothermal reactor filled with unaltered rock leaves behind a set of secondary minerals that can be considered as a proxy for the whole system until complete dissolution of the fresh primary rock. In our model of "thermo-gradient" water we calculated as a first approximation the relative amounts of equilibrium secondary minerals and the composition of water and gas phases after one kg of water with a given initial composition passes through 13 isothermal reactors filled with fresh granite.

Compositions are shown in Table 5. The water batch (1 kg) is "injected" into a reactor at a given temperature with dissolution of a portion of granite, whose mass is proportional to the mass of the total dissolved rock (15 g), and to the average reaction rate (see Figure 4). After the dissolution of granite and the deposition of secondary minerals, the water reacts with fresh granite in the next reactor and so on. This is the "1st wave" approach according to Grichuk and Borisov (1983) and Grichuk (2000). When water with the initial composition is pressed through the same set of reactors but filled with the already partially altered granite after the 1st wave, we have the "2nd wave", and so on.

5.3 Numerical modeling and comparison with Guerrero thermal waters

The chemical composition of water (initially oxygen-free, rain water), its pH and relative amounts of secondary
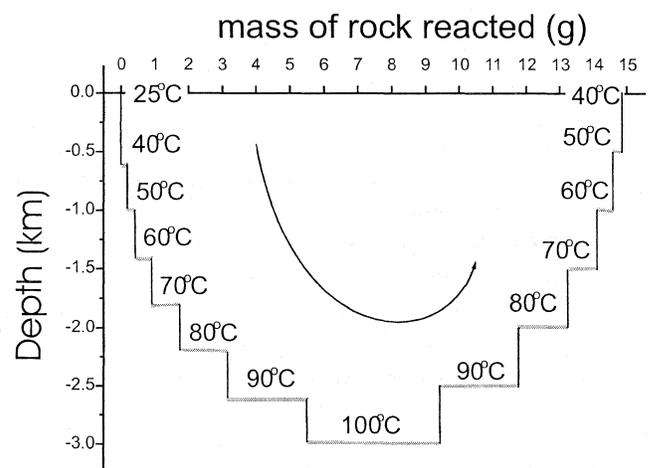
Fig. 4. A scheme showing amount of rock reacted at each temperature along the reaction path modeling "thermo-gradient" convective cell in the upper crust with average thermal gradient (25-30°C/km). Rain water infiltrates into the crust up to 100°C level and ascents through fractures in fault zones.

Table 5

Composition of rock and water taken for simulation of water-rock interaction. Composition of granite is from Schaaf (1990). Concentrations of volatiles are taken as average for granitoids (see text). Composition of rain water is taken from Drever (1982)

Granite		Rain water	
Oxide	Wt %	Specie	mg/kg
SiO_2	73.21	pH	7.0
$Al2O_3$	13.67	Na	6.8
$Fe2O_3$	0.74	K	1.9
FeO	1.61	Ca	11.0
MgO	0.56	Mg	3.1
CaO	3.42	Cl	10.8
Na_2O	4.09	HCO_3	50
K_2O	1.36	SO_4	2.1
CO_2	0.05	F	0.1
S	0.03		
F	0.07		
Cl	0.013		
C red	0.03		

minerals deposited on the way down and up are shown in Figures 5 and 6 as a function of the mass of reacted rock. We added 0.03 wt% of reduced carbon to the primary granite (Table 5) in order to fit the calculated gas composition to the measured gas composition of the CH_4-rich Cocoyul spring (10-12 vol% of CH4, Table 2). The relative amounts of solid phases produced through reaction of 1 kg of meteoric oxygen free water with granite along the "convective cell" are shown in Figure 6. The most abundant is quartz followed by laumontite, mica, and chlorite. Micas are represented mainly by muscovite with a low amount of paragonite and celadonites after 1.5 g of granite reacted. Chlorite is an almost 1:1 mixture of clinochlore-14A and daphnite-14A. Low amounts of kaolinite and pyrite appeared at the start of the descending path. Microcline appeared only in the 90-100°C reactors, and low albite is a relatively abundant phase after 2 g of granite reacted.

Water composition and partial pressure of dissolved gases for the "1st wave" run are shown in Figures 6 and 8. The resulting water is essentially a solution of Na_2CO_3 with pH>10 and high F content because of the very low concentration of Ca which prevents precipitation of fluorite. The final concentration of F was a criterion for the chosen total water-reacted rock ratio (see above). The solution has SO_4 and Cl content close to that analyzed in thermal waters of Guerrero (Table 1). Extremely low Ca and Mg concentra-
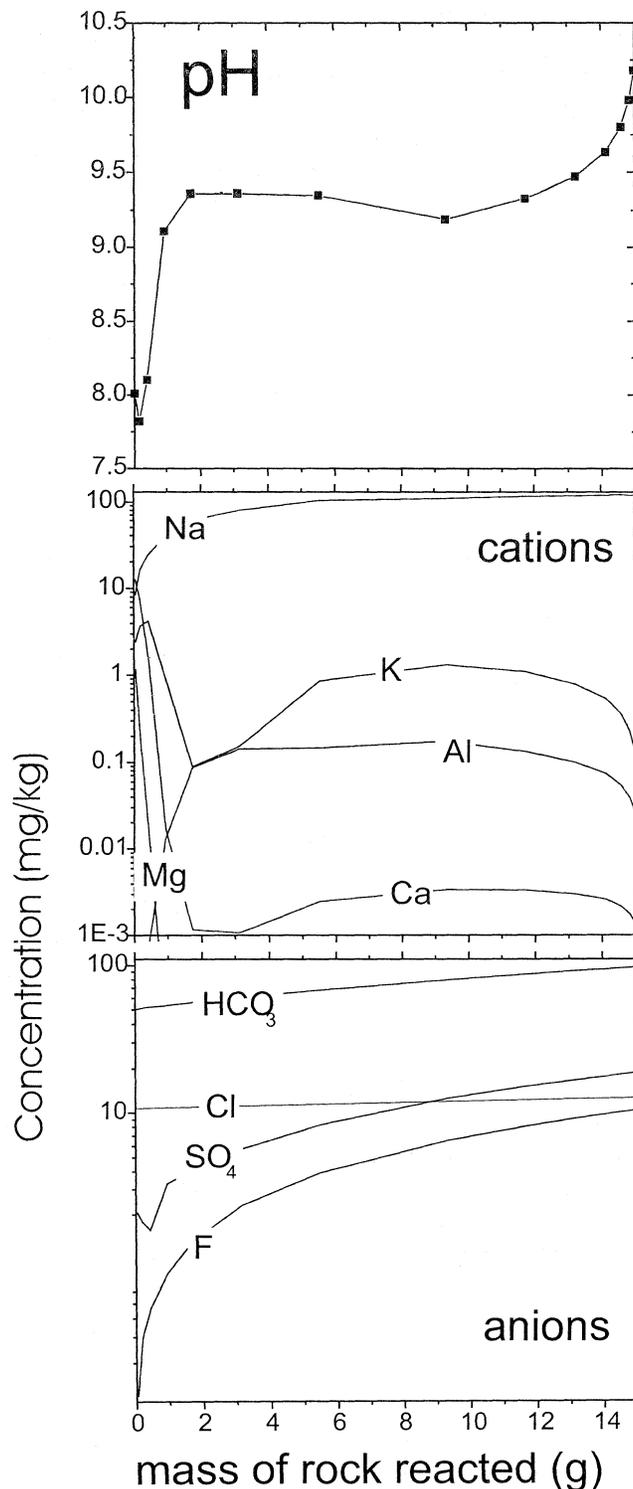

Fig. 5. Calculated pH and ionic composition of water as a function of the amount of granite reacted.

tions in the modeled water may be due to the thermodynamic data used for low-temperature clay minerals. According to Giggenbach (1988), values of log $a_{clinochlore}$ for a wide range of analyzed hydrothermal layer silicates vary from –4.7 to –
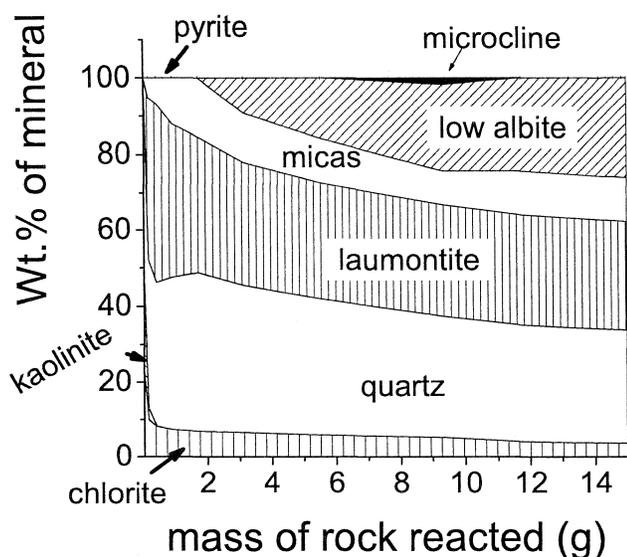
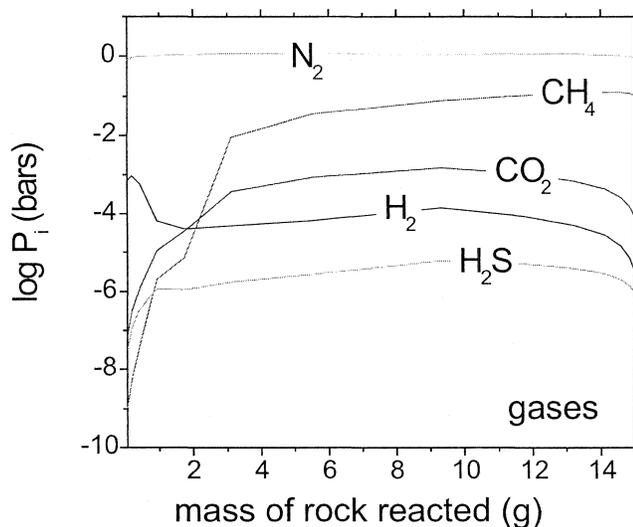Fig. 6. Calculated relative amount of secondary minerals along the flow path as a function of granite reacted.

Fig. 7. Calculated gas composition (partial pressures of dissolved gases) as a function of granite reacted.

1.3 with a mean of –2.2. The CHILLER code gives much higher activities of clinochlore in chlorites with log $a_{clinochlore}$ in the range of –0.3 to –0.5.

The computed gas composition (Figure 8) is close to the measured gas composition of the Cocoyul spring with 10-12% of CH_4. This coincidence was achieved by the incorporation of 0.03% of reduced carbon into primary granite, which is in the range of measured values in some granitoids (Ishihara and Terashima, 1987) Usually, the carbonaceous material in granites is present as dispersed bitu-

mens and flakes of graphite. Its speciation may range between mature kerogens and graphite (e.g. Zieng *et al.*, 2001). Methane with the isotopic composition as in the Cocoyul spring ($\delta^{13}C=-26‰$) is characteristic for a high temperature hydrothermal system; its source is thought to be a mature organic material enriched in ^{13}C isotope (Truesdell and Hulston, 1980; Welhan, 1988). For example, $\delta^{13}C=-15‰$ to $-17‰$ was measured in coalified wood particles in cuttings from a deep well of the Mutnovsky geothermal field, Kamchatka, Russia (Taran *et al.*, 1987). Such a source can produce CH_4 with the observed isotopic composition (Deines, 1980). We can suggest that the source of CH_4 in the Cocoyul spring is carbonaceous material of the granites or crystalline metamorphic rock, but not shallow organic-rich sediments or bacteria-produced methane.

6. CONCLUSIONS

Thermal waters (40-43°C) from crystalline rocks of the Xolapa complex near Acapulco, Mexico, within an area of approximately 100x50 km^2 are characterized by a low salinity (TDS<0.5 g/kg) and very high pH (9.5-10). They represent a regional aquifer or a group of aquifers with similar conditions of water circulation and water-rock interaction. Spring gases are nitrogen- and He-rich, with a high proportion of radiogenic He (R/R$_a$ = 0.12-0.2). One spring has a high concentration of CH4 (10-12%), which is relatively enriched in ^{13}C ($\delta^{13}C$ = -26‰, PDB). All gases are very low in CO_2 and relatively low in Rn (8-24 Bq/l).

Numerical modeling showed that this type of high-pH diluted water could be produced by pure water-granite interaction at high water/rock ratios, in a closed system with respect to CO_2, and a low concentration of carbonate carbon in the aquifer rock. The presence of carbonaceous material in the aquifer rocks may explain the observed concentrations of methane in the CH_4-rich spring, as well as its carbon isotopic composition.

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