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

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RESUMEN
Las aguas de manantiales termale (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 (TDS<0.5 g/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, = 0.12-0.3). Uno de los manantiales presenta una elevada concentración de CH₄ (10-12%) enriquecido en ¹³C (δ¹³C=-26‰, PDB). Todos los gases contienen muy poco CO₂ (<0.5%) y relativamente poco Rn (8 a 25 Bq/l). La simulación numérica de las interacciones agua-roca en un reactor multistep, usando la aproximación de “1° onda”, sugiere que este tipo de agua con elevado pH podría producirse por la dilución 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 meteorica 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 termale a partir del agua de lluvia inicial neutra o ligeramente ácida, se requieren condiciones de sistema cerrado respecto a CO₂ 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 CH₄, 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,=0.12 to 0.3). Methane from a spring with a high concentration of CH₄ (10-12%) is relatively enriched in ¹³C (δ¹³C=-26‰, PDB). All gases are very low in CO₂ (<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 “1° 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 CO₂ 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 CH₄-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 related 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, δ¹⁸O/δ⁶⁸O, ¹³C/¹²C and ³He/⁴He 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 subduction 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.](image-url)
Table 1
Coordinates and short description of thermal springs near Acapulco

<table>
<thead>
<tr>
<th>Name of spring</th>
<th>Coordinates Latitude N Longitude W</th>
<th>Flow rate (approx.) kg/s</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dos Arroyos</td>
<td>16°59.41' 99°39.52'</td>
<td>&gt;5</td>
<td>~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.</td>
</tr>
<tr>
<td>Agua Caliente</td>
<td>16°53.68' 99°40.42'</td>
<td>&gt;25</td>
<td>“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.</td>
</tr>
<tr>
<td>Cocoyul</td>
<td>16°45.73' 99°29.19'</td>
<td>2.5</td>
<td>Washing place. Right bank of a dry creek bed.</td>
</tr>
<tr>
<td>Río Cortés</td>
<td>16°46.46' 99°30.60'</td>
<td>&gt;15</td>
<td>Many pools. 1 km along the left bank of Río Cortés to N from the bridge.</td>
</tr>
<tr>
<td>Paso Real</td>
<td>17°05.27' 100°04.40'</td>
<td>3-4</td>
<td>Left bank of the Coyuco river. Rancho Agua Caliente. 3 km from village of Paso Real to W.</td>
</tr>
</tbody>
</table>

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 HNO₃. 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, SO₄, F) was performed using Metrohm 750 ionic chromatograph system without dilution of samples. Alkalinity and HCO₃ 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 H₂ analyses and helium as the carrier gases for analyses of N₂, Ar, O₂, CH₄ and CO₂. 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 δ¹⁸O) and isotopic composition of carbon in CH₄ and CO₂ 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-SO₄-HCO₃ 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 SO₄-HCO₃ 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 K²/Mg diagram (Figure 3). According to Giggenbach’s (1988) classification, all waters are partially equilibrated with hydrothermally altered rock at 80-100°C.
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 HCO₃, na – not analyzed; nd – not determined. Analytical errors for the majority of species except of Mg and B are within ±5%.

### Table 2

<table>
<thead>
<tr>
<th>Name of Spring</th>
<th>Date mm/yy</th>
<th>t°C</th>
<th>pH field</th>
<th>Cond μS</th>
<th>SiO₂</th>
<th>Eh mV</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl</th>
<th>HCO₃ (alk)</th>
<th>SO₄</th>
<th>F</th>
<th>B</th>
<th>δD</th>
<th>δ¹⁸O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paso Real</td>
<td>08/02</td>
<td>38.3</td>
<td>9.68</td>
<td>480</td>
<td>44</td>
<td>nd</td>
<td>90</td>
<td>0.9</td>
<td>0.4</td>
<td>0.22</td>
<td>41</td>
<td>83</td>
<td>52</td>
<td>4.4</td>
<td>0.8</td>
<td>-59</td>
<td>-8.2</td>
</tr>
<tr>
<td>Paso Real</td>
<td>11/02</td>
<td>37.0</td>
<td>9.67</td>
<td>460</td>
<td>50</td>
<td>-285</td>
<td>94</td>
<td>1.0</td>
<td>1.5</td>
<td>0.18</td>
<td>38</td>
<td>88</td>
<td>45</td>
<td>5.0</td>
<td>&lt;0.5</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Paso Real</td>
<td>03/03</td>
<td>38.4</td>
<td>9.89</td>
<td>434</td>
<td>45</td>
<td>-306</td>
<td>93</td>
<td>1.1</td>
<td>0.4</td>
<td>0.21</td>
<td>44</td>
<td>89</td>
<td>61</td>
<td>5.0</td>
<td>&lt;0.5</td>
<td>-53</td>
<td>-7.6</td>
</tr>
<tr>
<td>Agua Caliente</td>
<td>06/01</td>
<td>38.0</td>
<td>9.28</td>
<td>540</td>
<td>50</td>
<td>nd</td>
<td>107</td>
<td>1.1</td>
<td>5.0</td>
<td>0.29</td>
<td>109</td>
<td>53</td>
<td>30</td>
<td>4.8</td>
<td>1.9</td>
<td>-65</td>
<td>-9.3</td>
</tr>
<tr>
<td>Cocoyul</td>
<td>11/01</td>
<td>42.0</td>
<td>9.90</td>
<td>458</td>
<td>57</td>
<td>nd</td>
<td>94</td>
<td>0.7</td>
<td>0.8</td>
<td>0.22</td>
<td>74</td>
<td>43</td>
<td>26</td>
<td>10.4</td>
<td>1.1</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Cocoyul</td>
<td>08/02</td>
<td>40.9</td>
<td>9.96</td>
<td>430</td>
<td>49</td>
<td>-472</td>
<td>84</td>
<td>1.0</td>
<td>0.9</td>
<td>&lt;0.15</td>
<td>59</td>
<td>35</td>
<td>22</td>
<td>11.2</td>
<td>1.1</td>
<td>-56</td>
<td>-8.2</td>
</tr>
<tr>
<td>Cocoyul</td>
<td>03/03</td>
<td>41.0</td>
<td>9.98</td>
<td>413</td>
<td>52</td>
<td>-443</td>
<td>86</td>
<td>1.1</td>
<td>0.6</td>
<td>0.16</td>
<td>82</td>
<td>40</td>
<td>19</td>
<td>10.4</td>
<td>&lt;0.5</td>
<td>-58</td>
<td>-8.4</td>
</tr>
<tr>
<td>Tamarindo</td>
<td>11/01</td>
<td>41.0</td>
<td>9.66</td>
<td>378</td>
<td>45</td>
<td>nd</td>
<td>84</td>
<td>0.7</td>
<td>1.6</td>
<td>0.25</td>
<td>23</td>
<td>37</td>
<td>54</td>
<td>5.1</td>
<td>0.5</td>
<td>-60</td>
<td>-8.5</td>
</tr>
<tr>
<td>Tamarindo</td>
<td>08/02</td>
<td>42.1</td>
<td>9.45</td>
<td>350</td>
<td>49</td>
<td>nd</td>
<td>72</td>
<td>0.9</td>
<td>1.0</td>
<td>&lt;0.15</td>
<td>23</td>
<td>40</td>
<td>62</td>
<td>5.3</td>
<td>&lt;0.5</td>
<td>-60</td>
<td>-8.6</td>
</tr>
<tr>
<td>Tamarindo</td>
<td>03/03</td>
<td>43.1</td>
<td>9.79</td>
<td>341</td>
<td>45</td>
<td>-409</td>
<td>72</td>
<td>1.0</td>
<td>2.5</td>
<td>0.15</td>
<td>26</td>
<td>53</td>
<td>48</td>
<td>4.9</td>
<td>&lt;0.5</td>
<td>-59</td>
<td>-8.2</td>
</tr>
<tr>
<td>Río Cortés</td>
<td>08/02</td>
<td>36.8</td>
<td>7.76</td>
<td>390</td>
<td>28</td>
<td>nd</td>
<td>83</td>
<td>0.69</td>
<td>0.7</td>
<td>&lt;0.15</td>
<td>32</td>
<td>41</td>
<td>86</td>
<td>5.3</td>
<td>&lt;0.5</td>
<td>-58</td>
<td>-8.6</td>
</tr>
<tr>
<td>Río Cortés</td>
<td>11/02</td>
<td>37.0</td>
<td>8.94</td>
<td>412</td>
<td>35</td>
<td>nd</td>
<td>85</td>
<td>1.69</td>
<td>0.8</td>
<td>&lt;0.15</td>
<td>33</td>
<td>45</td>
<td>99</td>
<td>5.2</td>
<td>&lt;0.5</td>
<td>-57</td>
<td>-8.4</td>
</tr>
<tr>
<td>Dos Arroyos</td>
<td>03/97</td>
<td>41.0</td>
<td>9.08</td>
<td>320</td>
<td>29</td>
<td>nd</td>
<td>64</td>
<td>0.51</td>
<td>0.7</td>
<td>&lt;0.15</td>
<td>11</td>
<td>35</td>
<td>89</td>
<td>3.1</td>
<td>&lt;0.5</td>
<td>-65</td>
<td>-9.0</td>
</tr>
<tr>
<td>Dos Arroyos</td>
<td>07/02</td>
<td>41.2</td>
<td>9.23</td>
<td>309</td>
<td>29</td>
<td>-346</td>
<td>61</td>
<td>0.65</td>
<td>0.6</td>
<td>&lt;0.15</td>
<td>9.0</td>
<td>37</td>
<td>69</td>
<td>3.0</td>
<td>0.6</td>
<td>-64</td>
<td>-9.1</td>
</tr>
<tr>
<td>Dos Arroyos</td>
<td>10/02</td>
<td>42.0</td>
<td>8.78</td>
<td>290</td>
<td>36</td>
<td>-328</td>
<td>61</td>
<td>0.69</td>
<td>0.6</td>
<td>&lt;0.15</td>
<td>9.2</td>
<td>33</td>
<td>73</td>
<td>3.0</td>
<td>0.5</td>
<td>-68</td>
<td>-9.6</td>
</tr>
</tbody>
</table>

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 N₂/Ar ratio in all springs is close to the atmospheric air value of 83.5. All gases are extremely low in CO₂ 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/²He are about 5 times lower than in the atmosphere. These may be the lowest values of ³He/²He measured in thermal waters of Mexico (Prasolov et al., 1999; Taran et al., 2001). They correspond to a significant proportion of radiogenic He but the gases with such a low ³He/²He still contain some 1-2 % of upper mantle He with ³He/²He 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 wa-
ters 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 spec-
tacular 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
than 15 g/L and water from Lake Bogoria itself, with 85 g/L
total carbonate, are characterized by pH up to 9.8 (springs)
and 10.10 (lake). These waters are associated with
carbonatites, alkali basalts and phonolitic 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 ul-
tramafic rocks are, in contrast, usually diluted and carbon-
ate-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).

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-tem-
perature 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 con-
centration of H$_2$SiO$_4$ 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 1.39×10$^{-6}$. Carbon isotopic composition of methane in $\delta^{13}$C v-PDB (±0.2 $\delta^{13}$C). Analytical errors of the GC determinations
are within 5%.

<table>
<thead>
<tr>
<th>Name of spring</th>
<th>Date mm/yy</th>
<th>$t^\circ$C</th>
<th>He ppm</th>
<th>H$_2$ ppm</th>
<th>N$_2$ vol%</th>
<th>O$_2$ vol%</th>
<th>Ar vol%</th>
<th>CH$_4$ vol%</th>
<th>CO$_2$ vol%</th>
<th>$^{3}$He/$^{4}$He</th>
<th>He/Ne</th>
<th>$\delta^{13}$C CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paso Real</td>
<td>10/02</td>
<td>39</td>
<td>920</td>
<td>-</td>
<td>98.1</td>
<td>0.66</td>
<td>1.09</td>
<td>0.05</td>
<td>0.001</td>
<td>na</td>
<td>na</td>
<td>-26.0</td>
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<tr>
<td>Paso Real</td>
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<td>39</td>
<td>685</td>
<td>-</td>
<td>98.4</td>
<td>0.20</td>
<td>1.20</td>
<td>0.11</td>
<td>0.002</td>
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<td>890</td>
<td>-</td>
<td>96.5</td>
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<td>0.014</td>
<td>0.96</td>
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<td>38</td>
<td>88.8</td>
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<td>1.26</td>
<td>9.7</td>
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<td>510</td>
<td>33</td>
<td>87.3</td>
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<td>1.00</td>
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<td>0.004</td>
<td>0.16</td>
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</tr>
<tr>
<td>Tamarindo</td>
<td>08/01</td>
<td>40</td>
<td>250</td>
<td>-</td>
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<td>1.75</td>
<td>1.12</td>
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<tr>
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<td>06/03</td>
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<td>340</td>
<td>-</td>
<td>97.3</td>
<td>1.50</td>
<td>1.06</td>
<td>0.10</td>
<td>0.009</td>
<td>0.21</td>
<td>14</td>
<td>-25.9</td>
</tr>
<tr>
<td>Dos Arroyos</td>
<td>11/02</td>
<td>41</td>
<td>228</td>
<td>10</td>
<td>98.6</td>
<td>0.10</td>
<td>1.14</td>
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<td>0.34</td>
<td>12</td>
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<td>Dos Arroyos</td>
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<td>298</td>
<td>-</td>
<td>98.4</td>
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<td>0.96</td>
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<td>0.009</td>
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<td>98.0</td>
<td>0.68</td>
<td>1.20</td>
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</table>
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 HCO₃+CO₃ > (Cl+SO₄). 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 CO₂ content in the primary rock. High pH can be attained at high water/rock ratios and low partial pressure of CO₂ 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 CO₂ concentration (in a closed system in respect to CO₂) 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 CO₂ (with the consumption of the initial CO₂ in rock by the water phase and secondary carbonate minerals) the resulting equilibrated water is a diluted Na₂CO₃ 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 (CO₂) content is taken to be 0.05 wt% as in Japanese granitic rocks (Ishihara and Terashima, 1989). A considerable source of CO₂ is meteoric water itself with an initial content of 25-50 mg/kg of HCO₃. 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 CO₂ pressure (10⁻¹⁴ 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 aluminosilicates (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

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**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).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Wt %</th>
<th>Specie</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>73.21</td>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.67</td>
<td>Na</td>
<td>6.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.74</td>
<td>K</td>
<td>1.9</td>
</tr>
<tr>
<td>FeO</td>
<td>1.61</td>
<td>Ca</td>
<td>11.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.56</td>
<td>Mg</td>
<td>3.1</td>
</tr>
<tr>
<td>CaO</td>
<td>3.42</td>
<td>Cl</td>
<td>10.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.09</td>
<td>HCO₃</td>
<td>50</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.36</td>
<td>SO₄</td>
<td>2.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.05</td>
<td>F</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C red</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 CH₄-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 Na₂CO₃ 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 SO₄ and Cl content close to that analyzed in thermal waters of Guerrero (Table 1). Extremely low Ca and Mg concentrations in the modeled water may be due to the thermodynamic data used for low-temperature clay minerals. According to Giggenbach (1988), values of log θ_clinochlore for a wide range of analyzed hydrothermal layer silicates vary from -4.7 to -
1.3 with a mean of -2.2. The CHILLER code gives much higher activities of clinochlore in chlorites with log aclinochlore 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 CH4. 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 (δ13C = -26‰) is characteristic for a high temperature hydrothermal system; its source is thought to be a mature organic material enriched in 13C isotope (Truesdell and Hulston, 1980; Welhan, 1988). For example, δ13C = -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 CH4 with the observed isotopic composition (Deines, 1980). We can suggest that the source of CH4 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 km² 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/R0 = 0.12-0.2). One spring has a high concentration of CH4 (10-12%), which is relatively enriched in 13C (δ13C = -26‰, PDB). All gases are very low in CO2 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 CO2, 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 CH4-rich spring, as well as its carbon isotopic composition.

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BIBLIOGRAPHY


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