

Chemical and isotopic characteristics and origin of high-pH thermal springs near Acapulco, State of Guerrero, México

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ABSTRACT: Several groups of warm (39-43°C) springs are located within the southern part of the state of Guerrero, Mexico, close to the city of Acapulco within an area of approximately 100x50 km² along the Pacific coast. They discharge low-salinity (TDS<0.5 g/kg) and highly alkaline (pH=9.5-10) waters from fractures in granites and gneisses. We report here our data on chemical composition of waters and bubbling gases, ³He/⁴He, D/H and ¹³C/¹²C isotopic ratios and results of the multi-component chemical equilibrium calculations of rock-water system supporting our suggestion that the high pH of waters can be caused by water-granite interaction at 25-100°C and very high (>50) water/rock ratio.

1 DESCRIPTION OF THE STUDY AREA

The coastal part of the state of Guerrero, Mexico is a classical continental margin related to the modern subduction of the Cocos oceanic plate beneath the North America continental plate. The area belongs to the so-called Xolapa complex or terrain. According to Herrmann et al. (1994) it consists of high-grade metamorphic to migmatitic orthogenesis and paragenesis with metamorphism and migmatization occurred from 66 to 46 Ma. Oligocene (35-27 Ma) granitic plutons crop out parallel to the coast. There are 6 groups of thermal springs within an area of about 50x100 km² (Fig.1). Each group issues thermal water with temperatures close to 40°C on contacts between plutonic (granites, diorites, monzonites) and metamorphic (mostly gneisses) rocks. The flow rate of the springs varies between about 2 kg/s for the Paso Real group, to more than 20 kg/s for the total discharge of all Agua Caliente springs.

2 FIELD RESULTS

Water compositions are shown in Figure 2. All waters are very dilute, with TDS ~ 500 mg/l. Waters from El Tamarindo and Rio Cortes are similar in anionic composition while water from the Dos Arroyos springs is more of the SO₄-HCO₃ type. All waters are relatively high in F with the maximum of 11 mg/kg in the Cocoyul spring.

The common feature for all waters is their extremely high pH and high negative Eh. Major cation composition of springs is plotted on the log Na/K vs

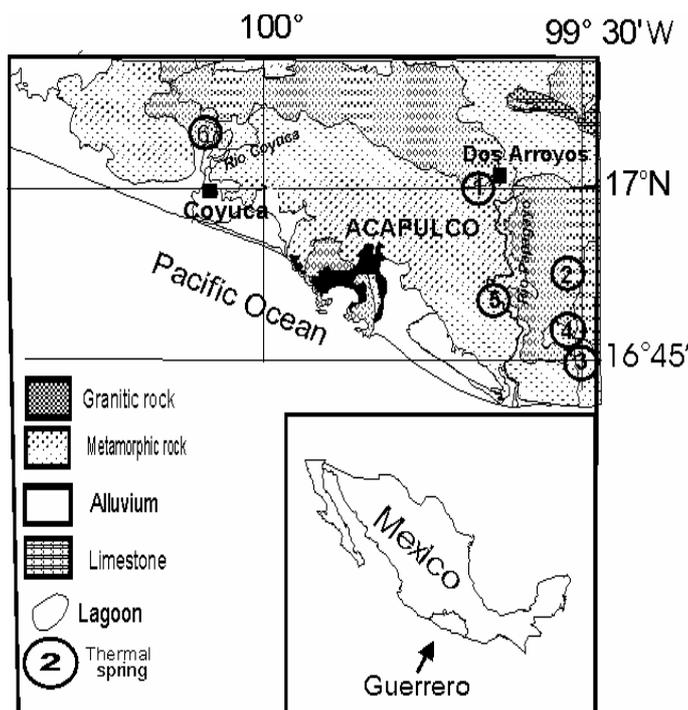


Figure 1. A simplified geological and location map of the Guerrero State near Acapulco. 1 – Dos Arroyos; 2 – Tamarindo; 3 – Cocoyul; 4 – Rio Cortes; 5 – Agua Caliente; 6 – Paso Real.

log K²/Mg diagram (Fig. 2). According to Giggenbach's (1988) classifications, all waters are partially equilibrated with hydrothermally altered rock at 80-100°C.

The gases are relatively rich in He (up to 900 ppm). The N₂/Ar ratios in all springs are close to the atmospheric air value. All gases are extremely low

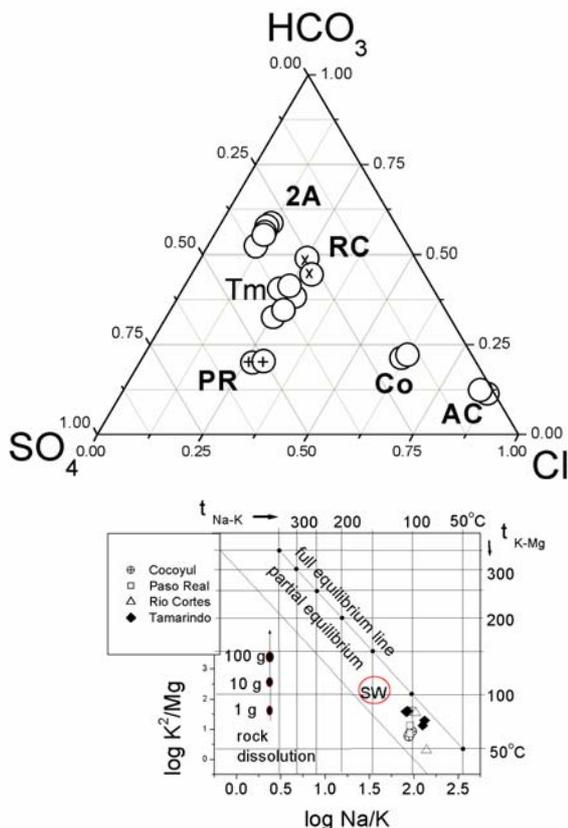


Figure 2. Major anion (triangle) and cation composition in the Guerrero thermal waters: 2A- Dos Arroyos, RC – Rio Cortes, Co – Cocoyul, Tm – Tamarindo, PR – Paso Real, SW – sea water.

in CO_2 ; usually its concentration in bubbles is lower than that in the air (0.034 vol%).

The isotopic composition of waters ($\delta\text{D} \sim -60\text{‰}$ and $\delta^{18}\text{O} \sim -8.5\text{‰}$) corresponds to meteoric waters of some higher elevations than the springs are located. Isotopic ratios $^3\text{He}/^4\text{He}$ are about 5 times lower than in the atmosphere. These are probably the lowest values of $^3\text{He}/^4\text{He}$ measured in thermal waters of Mexico (Taran et al. 2002 and references therein). Isotopic composition of carbon in CH_4 in the Cocoyul spring ($\delta^{13}\text{C} = -25\text{‰}$) corresponds to “thermogenic” CH_4 .

3 THERMOCHEMICAL MODELING AND ORIGIN OF HIGH-pH WATERS IN GRANITIC AQUIFERS

3.1 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 1. There are two main types of high-pH (~ 10) waters in nature: waters of “soda”-lakes and springs, and waters discharging from ultramafic rocks. “Soda-waters” contain up to 85 g/L

of total carbonate and are characterized by pH up to 10.1. (e.g. Cioni et al. 1992). High-pH waters associated with ultramafic rocks are, in contrast, usually diluted and carbonate-poor (Barnes et al. 1978; Bruni et al. 2002), although their pH can reach values as high as 12. Another known type of alkaline waters is high-temperature waters from so-called “weir-box” – waters from deep geothermal wells or boiling springs, which lost steam at atmospheric pressure. These waters can approach pH values up to 9.6. However, thermal waters from the granite-gneiss regional aquifer of the Guerrero state are neither associated with carbonatites nor ultrabasic rocks, nor are they of high-temperature hydrothermal systems. There are not too many examples of such waters. Hem (1985) showed one analysis of a 57°C spring in Oregon discharging a very dilute water from a quartz monzonite aquifer with $\text{pH}=9.4$. Nordstrom et al. (1989) published data on chemical composition of cold dilute waters from a Stripa well (Sweden) with pH up to 10.0.

Waters from Guerrero are similar to the dilute hot and cold waters from crystalline (igneous and metamorphic) rocks. Probably, the mechanism controlling pH during the interaction of water with granites or metamorphic crystalline rocks critically depends on the water/rock ratio and carbonate C 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 the excess of Na^+ is compensated by the formation of OH^- .

Table 1. Chemical composition of the Cocoyul thermal water and other high-pH waters of different origin.

	1	2	3	4	5	6
$t^\circ\text{C}$	41	57	27.1	15.6	8.6	12
pH	9.98	9.4	10.10	11.78	10.06	11.86
Na	88	72	39300	40	218	23.7
K	0.84	2.4	547	1.1	0.44	3.1
Ca	0.5	1.3	1.82	48	94	47.4
Mg	0.02	0.3	1.11	0.4	0.03	0.02
Cl	61.3	6.5	7460	32	460	21.2
HCO_3	37	20	85400	0.0	18	1.3
SO_4	20	32	144	1.4	57	0.14
F	10.4	16	1350	0.00	5.3	-
SiO_2	57	75	378	5.2	18	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 – Spring in Red Mountain, California. Ultrabasic rock (Hem, 1985); 5 - Stripa well, 960m, Sweden. Granite (Nordstrom et al. 1989); 6 – Cold spring, Genova province, Italy. Serpentinites (Bruni et al. 2002).

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

Waters from Guerrero are so-called "thermo-gradient" waters, heated at considerable depth to a given temperature corresponding to the regional thermal gradient. An estimation of this maximum temperature can be the temperature calculated from the Na/K ratio of water samples. It can be seen from Figure 2 that for all Guerrero springs Na/K temperatures are close to 100°C. Therefore, we can imagine a recharge-discharge "convective cell" with the rain water infiltrating and descending through the fractured granites up to $\geq 100^\circ\text{C}$ level (the depth depends on the local thermal gradient) and then rising up to the discharge (spring) site with temperature after conductive cooling to about 40°C. This model is similar to the Bowers and Taylor (1985) or Grichuk (2000) models of submarine hot hydrothermal systems of spreading zones (flow-through multi-step reactor). Using the CHILLER computer code (Reed and Spycher 1984) we "titrated" granitic rock on the way down and up calculating the equilibrium composition of water and equilibrium set of secondary minerals at each step at given temperature and water-to-reacted rock (w/r) ratio. Chemical composition of local granites was taken from Schaaf (1990). Descending flow is divided into 6 steps in the range of 25°C to 100°C. The ascending branch also consists of 6 steps covering the range of 90 to 40°C. The amount of reacted granite at each step was calculated using methods described by Grichuk (2000).

In our model of the "thermo-gradient" water we calculated as the first approximation relative amounts of secondary minerals and the composition of resulting water and gas phases in equilibrium after passing one kg of water with a given initial composition through 13 isothermal reactors filled with fresh granite. The water batch (1 kg) is "pressed" through a reactor at given temperature with dissolution of a portion of granite. That mass is proportional to the mass of the total dissolved rock (15 g) and to the average relative reaction rate. Water with a composition changed after the dissolution of granite and deposition of secondary minerals, reacts with another portion of fresh granite in the next reactor and so on.

3.3 Results of numerical modeling and comparison with the Guerrero thermal waters

Chemical composition of water, its pH and relative amounts of secondary minerals deposited on the way down and up are shown in Figures 3 & 4 as a function of the amount of rock reacted with 1 kg of meteoric oxygen-free water along the "convective cell". The resulting water (modeled "spring water") is es-

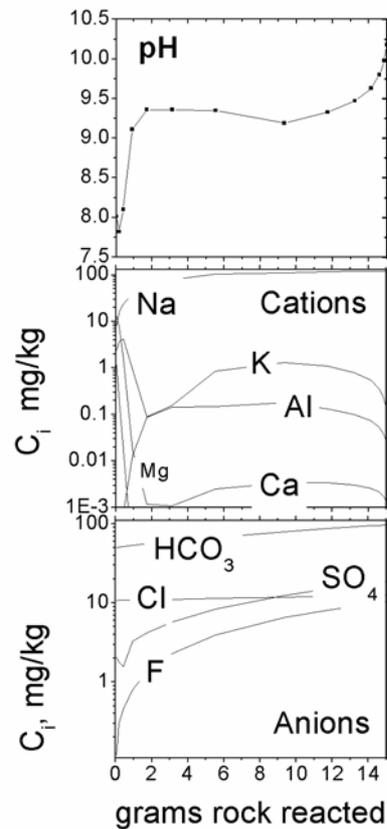


Figure 3. pH and chemical composition of the modeled water as a function of the amount of granitic rock reacted.

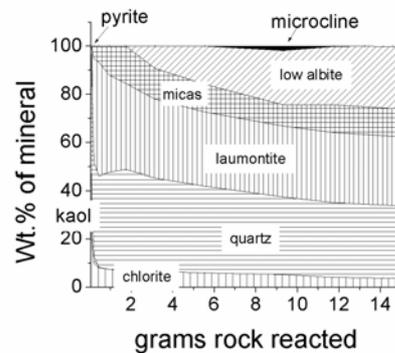


Figure 4. Mineral deposition along a "convective cell."

entially a solution of Na_2CO_3 with $\text{pH} > 10$ and high F content because of a very low concentration of Ca which prevents precipitation of fluorite. Extremely low Ca and Mg concentrations in the modeled water are probably a consequence of the thermodynamic data used for low-temperature clay minerals.

4 ACKNOWLEDGEMENTS

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