Seismic-related variations in the chemical and isotopic composition of thermal springs near Acapulco, Guerrero, Mexico

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[1] Chemical and isotopic analyses of waters from 4 thermal springs of the Guerrero Pacific coast, the most seismically active area in Mexico, were performed weekly during a period of 1.5 years (October 2002–March 2004). Within the same time interval more than 200 earthquakes with $3.8 \leq M \leq 5.3$ occurred in the area. The data display several anomalies in Cl^-, SO_4^{2-}, δD and $\delta^{18}O$, always immediately after an event, with a relaxation time of 3–4 weeks. The responses occurred only to earthquakes with the estimated epicenters very close to the location of a spring. These results indicate that: 1) at least for earthquakes with $M < 5.3$ within the Guerrero "seismic gap" there were no precursors in the chemical (ionic) and isotopic composition of thermal waters (on a weekly basis); 2) two groups of springs near Acapulco, Dos Arroyos and Paso Real, are sensitive to seismic activity and therefore further monitoring of these springs may help to unravel the mechanisms of the "hydro-seismo-interaction" in the area. **Citation:** Taran, Y. A., A. Ramirez-Guzman, R. Bernard, E. Cienfuegos, and P. Morales (2005), Seismic-related variations in the chemical and isotopic composition of thermal springs near Acapulco, Guerrero, Mexico, *Geophys. Res. Lett.*, *32*, L14317, doi:10.1029/2005GL022726.

1. Introduction

[2] The search for short-term precursors of earthquakes has been focused so far on the gases [*King*, 1986; *Thomas*, 1988; *Igarashi and Wakita*, 1990] (see also *Toutain and Baubron* [1999] for a review). Indeed, only two convincing examples of precursory changes in the chemistry of mineral springs have been reported to date. In both studies the authors used commercial bottled drinking and mineral waters with sampling dates starting before and finishing after the major 1995 Kobe earthquake [*Tsunogai and Wakita*, 1995] and a M = 5.2, 1996 Pyrenean earthquake, [*Toutain et al.*, 1997; *Poitrasson et al.*, 1999]. The source of waters analyzed for the Kobe earthquake study was a 100 m-deep well located about 20 km from the epicenter. *Toutain et al.* [1997] analyzed the bottled water from a mineral spring located 29 km from the epicenter. In both cases an increase in Cl concentration before the earthquake was observed. The anomalies started about 5 months before the M = 7.2 Kobe event and about 5 days before the M = 5.2 Pyrenean earthquake. In both studies the authors suggest that the chemical changes were caused by stress-strain induced mixing of waters from adjacent aquifers. These two seismic events occurred in different seismo-tectonic environments.

[3] The Pacific coast of the Guerrero state is characterized by very high seismic activity, related mainly to the subduction of the Cocos oceanic plate under the North American continent. Here, the mid American Trench is close to the shoreline and therefore most of the subduction-induced earthquakes cluster on the continent margin close to the Pacific coast. The coast of Guerrero includes the Guerrero "seismic gap" [*Singh and Mortera*, 1991], to the NW of Acapulco (Costa Grande), where the most recent large (M = 7.6) earthquake occurred in 1911. To the SE of Acapulco (Costa Chica), the last strong event occurred in 1957 (M = 7.6), and in 1962 two strong earthquakes (both with M = 7.0) had epicenters near the city of Acapulco. Hence, the probability of a large earthquake in the vicinity of Acapulco in the near future is high. It is possible that the stress build up preceding a large event may cause changes in ground-water chemistry similar to those observed before the Kobe and Pyrenean earthquakes, despite a quite different tectonic setting.

[4] Geologically, this part of the Guerrero state belongs to the so-called Xolapa block or terrain [*De Cserna*, 1965]. It is composed of Cretaceous granites and older (up to Jurassic) metamorphic rocks [*Herrman et al.*, 1994]. Several groups of thermal springs (39–43°C) are located within an area of about 100×30 km^2, close to Acapulco (Figure 1). We performed weekly sampling from 4 groups of springs for 1.5 years in order to find variations in the chemical composition of thermal waters related to the seismic activity of the region. We report here data for two groups of springs (Paso Real and Dos Arroyos), where statistically significant chemical and isotopic anomalies were observed.

2. Geochemistry and Origin of Thermal Waters

[5] All thermal springs discharge water of low salinity (~0.5 g/kg), with high negative Eh (up to −400 mV) and high to very high pH (up to 10). The bubbling gas in all springs is N_2-rich, with very low CO_2 content (<0.05 vol.%) and relatively high in He (300–1000 ppm) with a low $^3He/^4He$ ratio (<0.2 of the atmospheric value). The main chemical features of the springs and their coordinates are shown in Table 1. The origin of the springs based on the water-rock interaction processes responsible for their composition have been discussed by *Ramirez-Guzman et al.* [2004]. The recharge area for all springs as it follows from the water isotopic composition is the southern heights (1000–1500 m) of Sierra Madre del Sur. There is no deep drilling in this region, and local tectonic maps do not exist. Therefore it is difficult to make a detailed hydrogeological description of the area. The springs are thought to be

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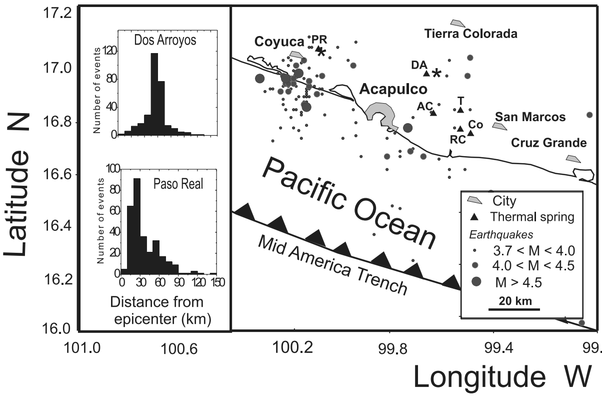

Figure 1. Location map of thermal springs near Acapulco, Guerrero, Mexico and epicenters of earthquake occurred between October 2002 and February, 2004. Names of springs: PR – Paso Real, DA – Dos Arroyos, AC – Agua Caliente, T – Tamarindo, Co – Coacoyul, RC – Rio Cortes. Two histograms show the distribution of epicentral distances of all registered events from Paso Real and Dos Arroyos springs. The two stars close to the PR and DA stations correspond to earthquakes with the resulted hydrochemical anomalies.

connected with deep-seated (3–5 km) fractured aquifers in crystalline rocks through a system of deep faults. The aquifers feeding springs to the southeast of Acapulco are characterized by different Cl and SO_4 contents. For this reason, mixing of water from adjacent reservoirs may induce changes in groundwater chemistry as observed in association with the Kobe and the Pyrenean earthquakes.

3. Methods

[6] Water samples were collected every week at the same day and hour (Wednesday, 10–11 am) in plastic bottles and were stored in a refrigerator until the date when we started the analyses, one year after October 15, 2002. Analyses of Cl and SO_4 were performed using a Metrohm-761 ionic chromatograph. Standard solutions were prepared with anionic compositions close to that of each spring and analyzed after every 5 analyses of water samples. The reproducibility (1σ) was ~1% for Cl and ~3% for SO_4. Water isotopic composition was determined on a DELTA plus XL mass-spectrometer Analytical errors are ±2‰ (1σ) for δD and ±0.2‰ (1σ) for $\delta^{18}O$.

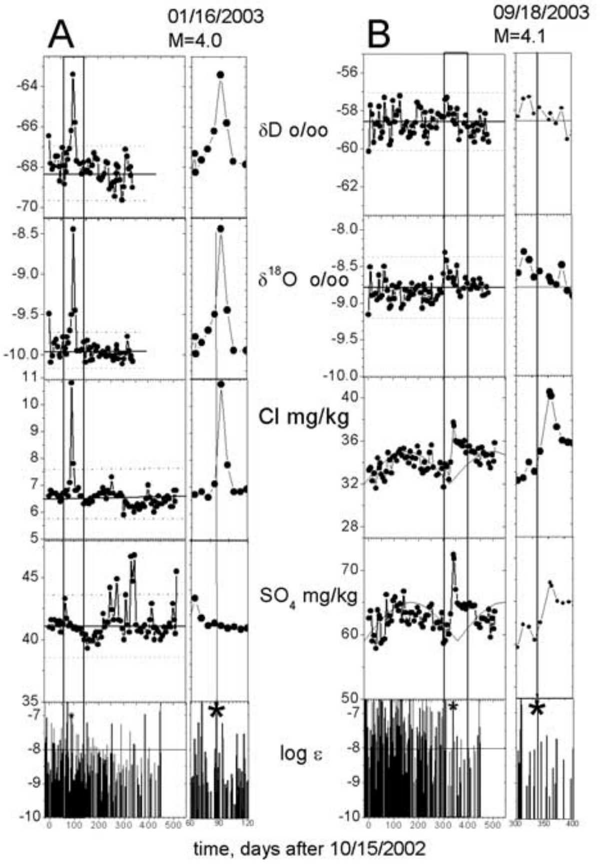

Figure 2. Time series of Cl, SO_4, δD and $\delta^{18}O$ and the strain step amplitude (ε) for the spring location associated with each earthquake within the time interval. The same plots with the expanded scale around the time interval of anomalies are also shown. A – Dos Arroyos; B – Paso Real. The mean (solid line) and 2σ interval (dotted line) are shown for geochemical parameters and the 10^{-8} level of the strain step amplitudes (solid line). Stars on the strain-step plots indicate the closest earthquakes that occurred several days before anomalies (see text).

Table 1. Location, Chemical (mg/kg) and Isotopic (permil, V-SMOW) Composition of Thermal Springs Near Acapulco[a]

	DA	AC	Ta	Co	PR
N	70	4	70	85	70
t°C	41	38	42	41	38
pH	9.23	9.28	9.45	9.96	9.67
Eh, mv	−346	−156	−409	−472	−306
SiO_2	29	50	45	49	44
Na	38	107	59	69	90
K	0.65	1.1	1.0	1.1	1.1
Ca	0.6	5.0	1.6	0.9	0.4
Mg	0.1	0.3	0.15	0.1	0.21
Cl	6.5	109	20	56	34
HCO_3	37	53	40	37	89
SO_4	41	30	39	18	63
F	3.0	4.8	5.1	10.5	4.9
δD	−69	−56	−60	−56	−59
$\delta^{18}O$	−9.8	−8.3	−8.5	−8.3	−8.8
Lat. N	16.99	16.88	16.85	16.76	17.08
Long.W	99.66	99.66	99.53	99.49	100.07

[a]DA – Dos Arroyos; AC – Agua Caliente; Ta – Tamarindo; Co – Coacoyul; PR – Paso Real. Averaged data without the earthquake related anomalies (N- number of analyses).

[7] All data on magnitudes, coordinates of epicenters and depths of earthquakes in the area were taken from unpublished reports of the National Seismological Survey of Mexico (http://www.ssn.unam.mx). According to the NSS catalogue, the errors in determination of epicenters vary depending on the location relative to seismo-stations. Three stations (Cayaco, Acapulco, San Marcos, see Figure 1) provide for events with M~4 the uncertainty of the epicentral locations within ±(2–5) km and may be more than 10 km for hypocenters.

4. Results

[8] Background variations of chloride and sulfate (Figure 2) in Paso Real and Dos Arroyos springs significantly

exceed the analytical error level, and the Paso Real spring has an unambiguous seasonal trend in chemical composition. The 1 STD level of the background scattering is about of 5% relative to the mean value. Several peaks can be seen; two anomalies, one in the Dos Arroyos spring (January, 2003) and the other in the Paso Real spring (September, 2003). These significantly exceed the 2σ level (Figure 2). More than 200 events with magnitudes from 3.5 to 5.3 occurred within the area (Figure 1) during the period of monitoring (~500 days starting, from October 16, 2002). Most of the events cluster close to the Paso Real springs. They are mainly replicas of the M = 5.9 Coyuca earthquake that occurred in October 2001 [*Pacheco et al.*, 2002]. Despite many shallow earthquakes within the Paso Real area with epicentral distances of less than 30 km (Figure 1) and M > 4, the Paso Real spring has responded notably by changes in the chemistry only once, immediately after a relatively deep, subduction-related earthquake with M = 4.1 (17.05N; 100.02W) that occurred on Sept. 18, 2003, 5 ± 5 km from the springs (17.08N; 100.06W) with hypocenter at ~18 km depth. Two samples collected on Sept. 22 and 24 had anomalous (~10% above the base level) Cl and SO_4 contents, and after two weeks the concentrations decreased to the base level (Figure 2b). Within this time interval (two weeks before and two weeks after the chemical anomaly) two more earthquakes with M ≥ 3.7 occurred within a 30 km radius of Paso Real: one on September 12 (M = 3.7, 28 km), and another one on October 4 (M = 3.7, 24 km).

[9] The number of earthquakes to the east and southeast of Acapulco is much less (Figure 1). Nevertheless, during the period of monitoring several events with M > 4.5 occurred there, with some epicenters located close to the spring sites. However, as can be seen from Figure 2a, the Dos Arroyos spring showed a significant (~50%) anomaly in the Cl content only in January 2003. The anomaly coincides with the period of a relatively strong seismic activity (January, 8–16, 2003) that occurred in the area. This period included one interplate earthquake with M = 5.3, and 3 shallow events with M > 4, all closer to the Paso Real spring without any hydrochemical response in that spring. Two deep events (26 and 18 km), on January 11 and 16, with M = 3.8 and 4.0, respectively, had epicenter coordinates (16.98N; 99.59W and 17.00N; 99.64W) very close to the Dos Arroyos spring location (16.99N; 99.66W). These were the only earthquakes during this month (January 1–January 31) with the epicentral distance from Dos Arroyos closer than 30 km.

[10] In order to have an independent source of geochemical data we also performed a series of water isotopic analyses (D/H and $^{18}O/^{16}O$) for the Dos Arroyos and Paso Real springs. The background variations in the water isotopic composition do not exceed the 2σ of the analytical uncertainty (Figure 2). Isotopic anomalies, both in δD and $\delta^{18}O$ coincide with the chemical ones only for Dos Arroyos: increase in the Cl concentration coincides with the enrichment of waters with heavy isotopes. The Paso Real springs also showed the same D and ^{18}O enrichment, but the effect is below the 2σ range.

[11] In order to estimate the seismic activity at the spring site, at least semi-quantitatively, for each earthquake within the area (150 km-radius of a circle around Acapulco) we calculated the strain step amplitudes using the magnitude-distance relations of *Wideman and Major* [1967]. These amplitudes for each event also shown in Figure 2 along with a threshold line of 10^{-8} derived by *Igarashi and Wakita* [1990] for the coseismic appearance of Rn anomalies in groundwaters.

5. Discussion

[12] The main problem is to link the observed hydrochemical anomalies to specific seismic events. The strain-step amplitude is an extremely averaged parameter designed for the estimations of a local strain field of the earthquake. It can be seen from Figure 2 that for springs in Guerrero, there were many earthquakes with estimated amplitudes higher than 10^{-8}, however, they did not shift the chemical characteristics of waters beyond the background level. Therefore, Figure 2 demonstrates a uselessness of the strain-step amplitude approach to the variations in the solute content.

[13] Two statistically significant anomalies in the chemical and isotopic composition of waters (Dos Arroyos and Paso Real) have occurred immediately after relatively weak (M~4) events. The only important difference between these two events and more than 200 others in the area during that period of time was the location of their epicenters (Figure 1). These two occurred very close to and directly beneath the springs. This is the main reason why we believe that the chemical anomalies were related to these particular earthquakes, and not to other seismic events occurred before or after the sampling. Among 11 earthquakes with M ≥ 4 that occurred during the monitoring period within a 20 km-radius circle around the Paso Real spring, only one had the epicentral location coinciding with the location of the spring. Chemical anomalies were observed immediately after this event. Of the four events with M ≥ 4 that have been registered within a 30 km radius of Dos Arroyos, chemical and isotopic anomalies were only observed after the one event which occurred immediately beneath the sampling site. In both cases, significant Cl-anomalies occurred over a 3–4 week period. Heavy isotope enrichment was only significant at Dos Arroyos. This means that a mixing with a more Cl-rich and isotopically heavier water occurred, but not a dilution by surface or rain water. The chemical (Cl content) and isotopic composition of this water can be estimated by chemical and isotopic balance. Within error, such water can be characterized by $\delta D \approx -56‰$ and the Cl content ≈20 ppm if the mixing fraction is about 35%. At a lower mixing fraction the admixed end-member should have slightly higher Cl content and much higher δD values. In both cases (Dos Arroyos and Paso Real) a Cl-enriched water could be from a deeper part of the same aquifer. It can be also the earthquake induced changes in the mixing proportions of the deep and surface (phreatic) waters close to the discharge vents.

[14] Following *Wakita* [1996] we may say that we found "sensitive" sites, suitable for the hydrochemical monitoring related to the seismic activity within a particular area, close to the city of Acapulco. We understand that the tectonic setting and the hydrogeology of the Pacific coast of Mexico are quite different from the Pyrenean or Kobe area. Moreover, the thrust-type events on the interface between oceanic and continental plates in Mexico anticipate by a different

stress-strain field than the strike-slip events in Kobe and Pyrenees. Nevertheless, we believe that before a strong quake, precursory changes in the groundwater chemistry may occur at "sensitive" sites near Acapulco as it did near Kobe in 1995.

[15] The most "promising" site for the precursory hydrochemical changes is Dos Arroyos spring. It has a stable baseline and the geochemical anomalies there are well outside the background level.

6. Concluding Remarks

[16] This work can be considered as a study of the background level of hydrochemical variations in the deep-seated groundwater within a seismically very active region near Acapulco. Two chemical and isotopic anomalies were observed in two springs after earthquakes whose epicenters were close ($<5 \pm 5$ km) to the spring location. This indicates that these springs are sensitive to the mechanical changes in the crustal block containing aquifers.

[17] The Pacific coast of Mexico, from the boarder with Guatemala to the latitude of $\sim$21°N, is an area of strong, destructive, seismic activity, where most hypocenters are located at relatively shallow levels (15–20 km deep), on the interface between subducting Cocos and Rivera plates and the continental North American plate. This is also an area of low-temperature hydrothermal activity caused in most cases by meteoric waters, heated within the crust while descending, and then rising to the surface through deep faults [*Ramirez-Guzman et al.*, 2004; *Taran et al.*, 2002]. At least 9 groups of hot springs are located within the epicentral zone of $\sim$20 km parallel the Pacific coast from Acapulco to Puerto Vallarta. It might be one of the best and most convenient natural laboratories for the study of relation between the subduction-related seismicity and hydrochemistry.

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