

Spring water and CO₂ interaction at Popocatépetl volcano, Mexico

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RESUMEN

Se presentan los resultados del monitoreo de HCO₃⁻ y pH en manantiales del volcán Popocatépetl durante seis años del actual periodo eruptivo. Los pequeños picos en HCO₃⁻ y P_{CO2} en manantiales se asocian a ascensos de pulsos pequeños de magma en el Popocatépetl. El magma proporciona fluidos ricos en CO₂ al sistema hidrológico que es controlado por recarga meteórica. La P_{CO2} en equilibrio con los manantiales es de 2 a 4 órdenes de magnitud mayor al de agua saturada con aire. La alta presión de CO₂ también sugiere una interacción directa con los fluidos magmáticos. Los isótopos de carbono apoyan un origen principalmente magmático para el CO₂ disuelto.

PALABRAS CLAVE: Manantiales, CO₂, Popocatépetl.

ABSTRACT

Six years of monitoring HCO₃⁻ and pH at selected springs at Popocatépetl during the present eruptive period are presented. Small peaks in HCO₃⁻ concentration and P_{CO2} in springs are associated with small magmatic pulses at Popocatépetl volcano. The magma provides CO₂-rich fluids into the water system controlled by meteoric recharge. The P_{CO2} in equilibrium with the springs is two to four orders of magnitude higher than air-saturated water. The high partial pressure of CO₂ also suggests a direct interaction with the magmatic fluids. The isotopic signature of carbon as well, supports a magmatic origin for dissolved CO₂.

KEY WORDS: Spring Water, CO₂ interaction, Popocatépetl volcano.

INTRODUCTION

Spring water monitoring at active volcanoes may indicate changes in water-rock interaction, the plumbing system of the volcano or fluctuating eruptive activity. Three representative springs at different distances from the volcano (14-40 km) were chosen to study the possible correlation of HCO₃⁻ and P_{CO2} with the volcanic activity. The partial pressure of CO₂ in equilibrium with spring waters was computed on the basis of equilibria of carbon species in solution utilizing the computer program PHREEQC (Parkhurst, 1995).

Results of monthly sampling at Popocatépetl from 1994 to 2000 are presented. During this time period, small ash eruptions have alternated with crater dome growth and explosive clearing.

The volcano has an explosive history on a longer time scale (Plinian eruptions on the order of 1000 to 3000 years) but every century at least 1 period of small eruptions has been recorded (Martin Del Pozzo *et al.*, 1997a). The last Plinian eruptions occurred in the first century A. D. and the

last small ash eruptions in the 1920's (Martin Del Pozzo *et al.*, 1997b).

After several years of increased fumarolic activity and seismicity, Popocatépetl started erupting again on December 21, 1994. This eruptive activity has continued through 2001. Proximity of Popocatépetl to Mexico City and Puebla with populations of over 20 and 2 million respectively has caused considerable concern over the effect of these eruptions. Multidisciplinary geophysical and geochemical monitoring is being carried out by UNAM and CENAPRED.

Popocatépetl is a very large volcano that rises to 5452 masl. Springs lie between 1320 to 3640 masl, at distances of 14 to 40 km from the crater (Figure 1). Heavy rainfall, 900-1300 mm/yr (CNA, 2001), mainly in the summer months, seeps into the pyroclastic deposits made up of widespread pumice fall, pyroclastic flows and lahars to create a large water system. The general geological framework for the Popocatépetl springs is given in Martin-Del Pozzo *et al.* (2002). Some of the springs have a very high flow all year round and one of the sub-basins alone has a volume of surface water of about 19 419 thousand m³ (Bellia *et al.*, 1992).

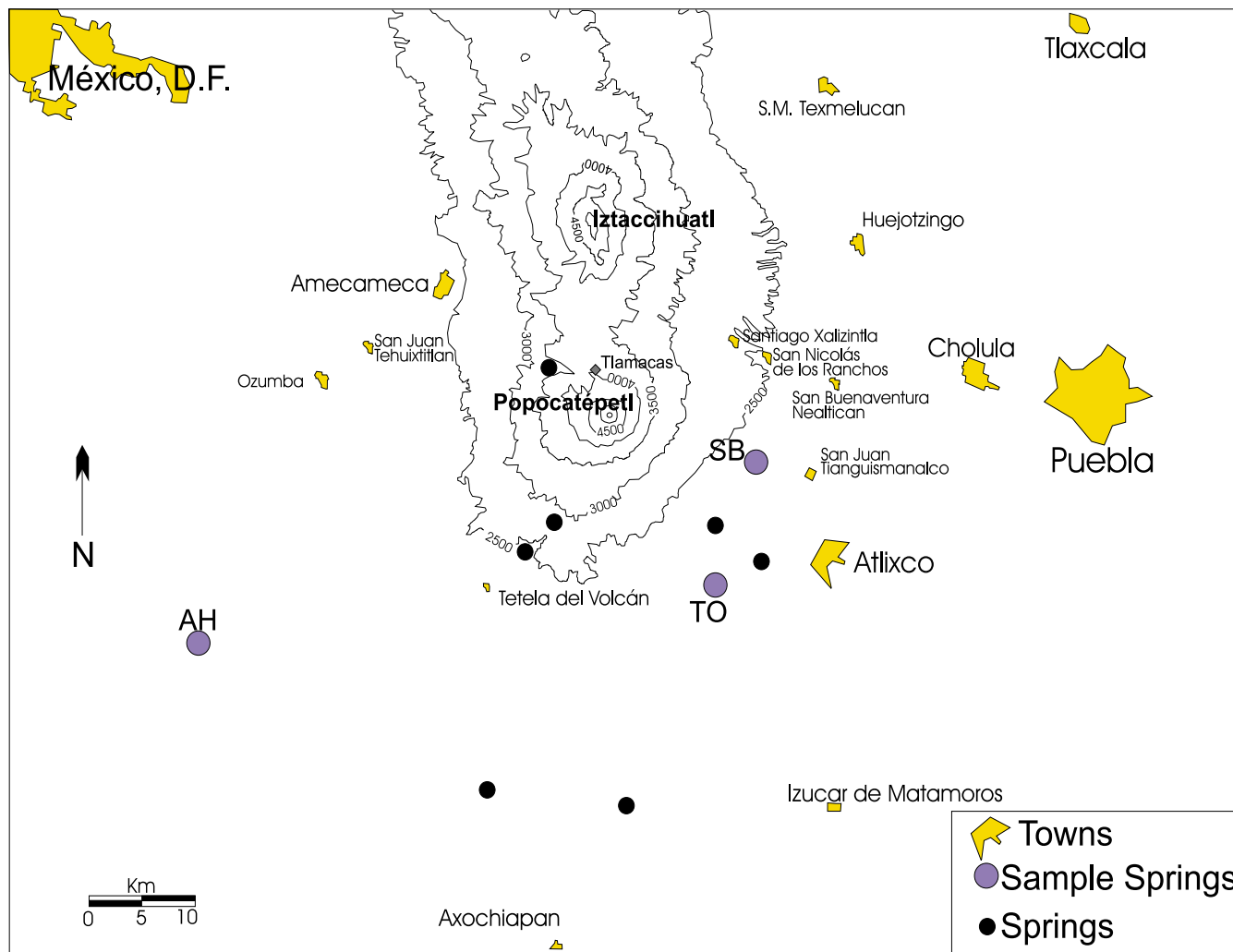


Fig. 1. Map of Popocatepetl volcano showing location of springs.

MAIN ERUPTIVE ACTIVITY

The present eruptive period of Popocatepetl began on December 21, 1994. The intensity of the ash eruptions decreased slightly afterward and then increased in mid-January. Ash emission became more sporadic after February 1995 and then stopped till March 5, 1995 when ash eruptions resumed. At the end of March growth of a new dome marked the beginning of a period of formation and explosive clearing of successive crater domes.

Juvenile material was recorded in the larger eruptions, which occurred on April 30, 1996; October 28, December 30, 1996; June 30, 1997; December, 1997; March 21, 1998; April 27, 1998; September 22, 1998; November 23, 1998; November 25, 1998; December 17, 1998; March 12, 1999; September 26, 1999, November 20, 1999; December 18-19, 2000 and January 22, 2001. Most of these eruptions were

associated with dome formation although dome growth was also detected in January 21, 1997; December 11, 1997 and February 26, September 12, and October 2000 without major explosive activity.

METHODS

Spring water was sampled for major components and bicarbonate analysis in bottles previously washed with 10% HCl and distilled water.

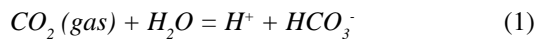
Two other bottles were collected for isotopic analysis of the water and TDIC. The isotopic composition of carbon of TDIC was performed with an analytical method based on chemical and physical stripping of CO₂ from water samples (Favara *et al.*, this volume). The isotopic analysis were carried out on a Finnigan Delta Plus mass spectrometer and the results are reported in δ per mil vs V-PDB.

The isotopic composition of deuterium and oxygen in the water was determined with a Finnigan Delta Plus mass spectrometer and the results reported in δ per mil vs the V-SMOW standard.

Temperature, pH, and conductivity determinations were made in the field using a Conductronic PC18 digital pH- μ S- $^{\circ}$ C meter and the samples were cooled during transportation to the laboratory to avoid changes in the chemical composition. In the laboratory these parameters were remeasured.

Physicochemical determinations were done by the wet methods established by APHA (Eaton *et al.*, 1995). Alkalinity is primarily a function of carbonate, bicarbonate and hydroxide content and is taken as an indication of the concentration of these constituents. Bicarbonates were quantified by titration with 0.02 N hydrochloric acid.

Determination of partial pressure of CO₂ in equilibrium with spring-water, for the TO, SB and AH springs was based on the equilibria of carbon species in solution using the PHREEQC computer program (Parkhurst, 1995). This calculation is based on the following reactions:



$$K_1 = [H^+] * [HCO_3^-] / [H_2CO_3] \quad (2)$$

$$XCO_2 = P_{CO_2} * K_H CO_2 \quad (3)$$

The partial pressure of CO₂ was calculated according to the following equation:

$$P_{CO_2} = [H^+] * [HCO_3^-] / K_1 * K_H CO_2,$$

where square parenthesis refers to molar concentration, XCO₂ is the molar fraction of CO₂, P_{CO₂} the partial pressure of CO₂ and K_HCO₂ the CO₂ Henry constant.

RESULTS AND DISCUSSION

Low outlet temperatures (13-27 degrees) characterize most springs in the area and pH ranges from 5.9 to 7.6. Water from these springs falls in the bicarbonate alkaline field (Martin Del Pozzo *et al.*, 2002). This and the low conductivity could be related to a short residence time for the water and/or low water-rock interaction.

Groundwater from the Popocatépetl springs is of meteoric origin, since sample δ D and $\delta^{18}O$ fall on the world meteoric water line (Table 1, Figure 2).

Sulphides were not detected except for low values (less than 1.5 ppm) at the AH spring. Sulphates on the other hand,

varied from 15 to 30 ppm for the TO spring, from 92 to 108 ppm for SB and 950 to 1400 ppm for the hotter AH spring. Chlorides were under 5 ppm for TO and SB but higher for AH (75 to 150 ppm). Fluoride concentrations were under 2 ppm. The TO and SB samples have low concentrations for Ca, Na, K and Mg but increase for AH. SiO₂ ranges from 45 to 75 ppm for all 3 springs.

Six years (1994-2000) of HCO₃⁻ and pH monitoring for 2 springs (and 2 years of a third) are presented in Table 2. Figure 3 shows that the concentration peaks appear to be associated with increases in the eruptive activity as indicated by the eruption triangles. After 3 years of increased fumarolic and seismic activity, especially in 1993, the volcano began erupting. The high value prior to the onset of the eruptions is also correlated with increased fumarolic activity and seismicity as well as with small changes in the leveling line which probably reflect the ascent of a batch of magma that did not reach the surface. Increases in HCO₃⁻ in December 1994 are clearly correlated with the begin-

Table 1

Isotopic water composition (δD_{H_2O} ; $\delta^{18}O_{H_2O}$) ‰ vs V-SMOW and $\delta^{13}C_{TDC}$ ‰ vs V-PDB

Sample	Data	δD_{H_2O}	$\delta^{18}O_{H_2O}$	$\delta^{13}C_{TDC}$
AH	June 2001	-73	-10.4	-5.8
SB	June 2001	-78	-11.6	-4.0
TO	June 2001	-82	-11.4	-15.3

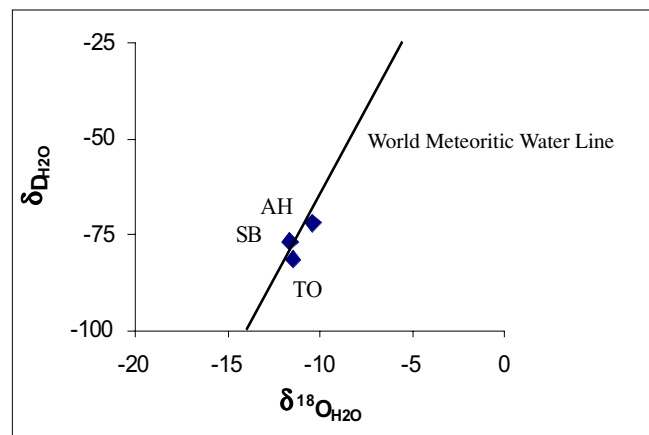


Fig. 2. World meteoric water line showing spring water samples from Popocatépetl.

Table 2
pH and HCO₃⁻ concentrations (mg/l) for TO, SB and AT springs from 1994 to 2000.

SPRING SAMPLE		S B		T O		SPRING SAMPLE		S B		T O		A H	
DATE		pH	HCO ₃ ⁻	pH	HCO ₃ ⁻	DATE		pH	HCO ₃ ⁻	pH	HCO ₃ ⁻	pH	HCO ₃ ⁻
10/03/1994		6.77	105.75	6.98	71.35	14/04/1998		6.91	101.66	6.75	67.77		
2/07/1994		7.28	98.82			16/05/1998		7.54	104.57	6.94	69.71		
11/11/1994		6.90	96.96	6.96	69.08	16/06/1998		6.64	106.78	6.85	68.44		
3/12/1994		7.60	98.86	7.18	70.35	3/07/1998		6.58	102.11	6.75	62.34		
24/12/1994		6.66	99.05			15/08/1998		6.68	100.69	6.85	68.42		
25/12/1994		6.75	99.48	6.95	72.17	26/09/1998		6.70	99.81	6.81	66.54		
26/12/1994		6.80	100.25	6.92	71.27	23/10/1998		6.60	104.41	6.74	70.34		
8/01/1995				6.93	71.26	14/11/1998		6.64	102.13	6.89	66.24		
30/01/1995		7.19	99.86	7.02	72.70	8/12/1998		6.64	99.49	6.80	67.51		
13/02/1995		7.05	100.54	7.22	68.66	16/01/1999		6.61	102.86				
1/04/1995		6.91	100.70	7.02	71.60	12/02/1999		6.70	104.57	6.92	69.71		
25/05/1995		6.85	100.57	7.21	68.60	10/03/1999		6.76	102.86	6.86	70.57	6.22	886.29
4/07/1995		6.75	101.44	7.03	60.91	16/04/1999		6.70	99.21	6.86	68.37		
28/10/1995		6.80	92.42	7.01	57.77	15/05/1999		6.63	101.33	6.89	69.33	6.24	886.66
8/03/1996		6.59	101.40	6.92	70.98	15/06/1999		6.63	103.90	6.87	68.70	6.22	911.64
10/04/1996		6.92	101.89	7.09	71.05	14/08/1999		6.68	103.66	6.93	69.11	6.28	892.46
4/05/1996		6.69	102.17	6.78	69.90	14/09/1999		6.66	103.55	6.81	69.92	6.13	898.63
3/07/1996		7.04	100.24	7.35	67.63	18/10/1999		6.98	102.36	7.12	69.04	6.40	883.76
4/11/1996		6.72	102.28	6.85	67.77	20/11/1999		6.50	104.74	6.82	67.77	6.25	884.19
9/12/1996		6.69	104.60	6.79	68.47	8/12/1999		6.80	100.57			6.34	894.04
22/02/1997		7.19	102.99	7.34	69.89	17/01/2000		6.70	103.85	5.90	70.07	6.20	900.92
12/04/1997		6.66	101.66	6.81	66.08	17/02/2000		6.79	103.37	6.95	72.11	6.25	887.05
27/05/1997		6.97	101.66	6.83	68.63	20/03/2000		6.68	102.48	6.84	69.74	6.30	893.65
17/06/1997		6.64	99.52	6.89	69.02	27/04/2000		6.65	96.15	6.62	66.10		
4/07/1997		6.62	103.23	6.16	69.21	13/05/2000		6.07	100.47	6.37	64.59	6.30	897.06
3/09/1997		6.50	102.74	6.76	71.21	12/07/2000		6.69	103.51	6.66	66.55	6.24	899.60
25/09/1997		6.63	103.76	6.88	72.32	21/08/2000				6.63	69.01	6.33	893.43
17/10/1997		6.53	103.48	6.76	71.54	21/09/2000		6.42	98.58	6.92	66.54	6.58	887.27
1/11/1997		6.57	101.14	6.14	70.02	11/10/2000						6.40	883.27
1/12/1997		6.06	101.26	5.91	69.54	20/10/2000		6.89	104.57	6.67	70.95	6.62	
11/01/1998		6.58	103.83	6.87	71.38	10/11/2000		6.46	104.57	7.48	69.71	6.61	908.77
21/02/1998		6.68	103.53	6.90	71.19	20/12/2000		6.94	101.26	7.10	69.54	6.23	902.80
14/03/1998		6.70	104.04	6.88	70.60								

ning of the present eruptive period and increased activity in January 1995 (Figure 3). The April 1996 peak is associated to the ascending juvenile magma detected at that time. In October and December 1996, the peaks were also correlated with smaller pulses of juvenile magma. In June 1997 an important pulse of magma produced mixed scoria also observed in the HCO₃⁻ increase. The January and December 1997 peaks can be correlated with dome formation. Eruptions in March-April 1998 were also associated with the HCO₃⁻ increases. From October to December, 1998, a series of important eruptions also produced observed peaks (Figure 3). Activity in 1999 decreased although the March eruption also produced a peak in HCO₃⁻. Dome formation in February and September, 2000, also accounted for other increases. A considerable amount of magma ascended in late 2000 which produced the last peaks in Figure 3.

The frequent time correlation between P_{CO₂} and the eruptions also favors the hypothesis of a CO₂ magmatic gas component mixing with shallow water which is controlled by meteoric recharge. Changes in composition are of small scale probably related to the large water system and to the small magmatic pulses at Popocatepétl.

Figure 4 shows P_{CO₂} variation with time for the TO, SB and AH springs and the values of air saturated water (ASW) for comparison. P_{CO₂} in equilibrium with the springs is from two to four orders of magnitude higher than Air-saturated-water. Eruption triangles also suggest that P_{CO₂} peaks are related to increased magmatic activity produced by CO₂-rich gas from the Popocatepétl magma rising toward the surface. Other peaks not defined by eruption triangles can also be correlated with magmatic activity, since only the major eruptions were plotted on Figures 3 and 4. Ash eruptions continued through January and sporadically in February and March, 1995 and then died down, which we believe is also linked to eruptive activity during that period which decreases afterward. At the end of January 1997 a new dome began to grow and although not shown in eruption triangles, this activity seems responsible for the increases in HCO₃⁻ and P_{CO₂}. In September and October, 1997, there were only small eruptions although they could have been linked to increased CO₂ input. During 1998 several large eruptions occurred which maintained the level high, except for mid-1998 which was relatively calm and corresponded to relatively low HCO₃⁻ and P_{CO₂} values.

CO₂ is highly soluble in water and may come from underlying carbonates or from the magmatic gas. Notwithstanding, the high partial pressure of CO₂ besides the isotopic composition of TDIC (ranging from -4 to -15 ‰ vs V-PDB) exclude the hypothesis of carbonate origin (ranging from 0 to +2 ‰ vs V-PDB) and suggest a direct interaction with magmatic fluids from Popocatepétl (Table 1).

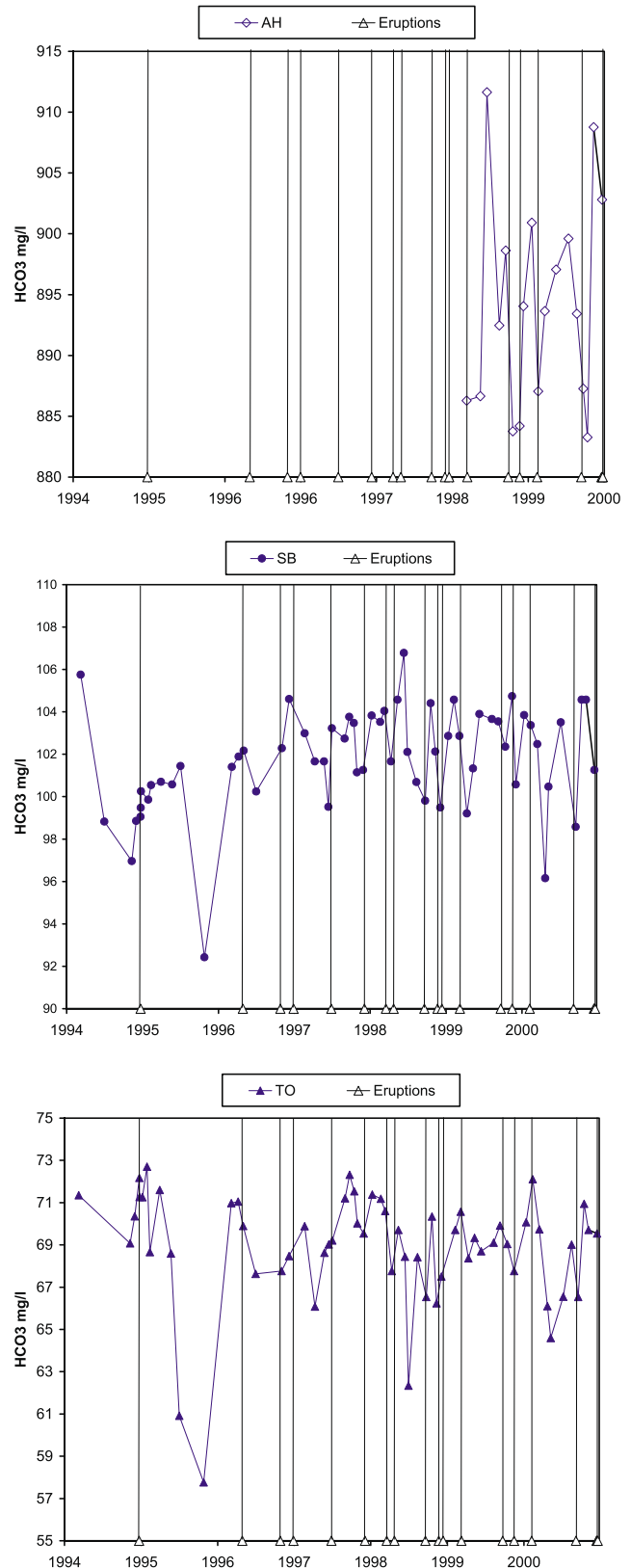


Fig. 3. HCO₃⁻ concentration in mg/l against time for TO, SB and AH springs. Main eruptions are shown in lower triangles and extended with lines.

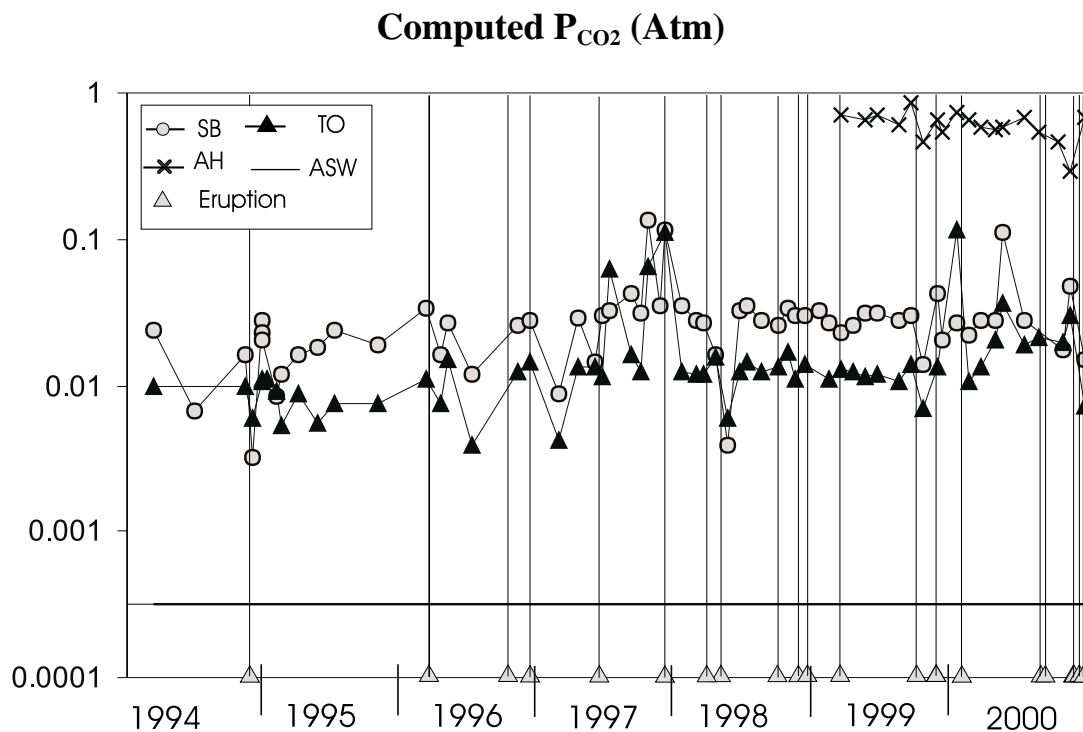


Fig. 4. P_{CO_2} against time for TO, SB and AH springs. Values of air saturated water (ASW) are indicated by the lower line. Main eruptions are shown in lower triangles with extended lines.

CONCLUSIONS

Many volcanic springs show changes in chemical composition preceding eruptions, but in most reported cases these changes are related to large eruptions, small scale changes are associated with small magmatic pulses at Popocatepetl volcano. Detailed long-term monitoring can reveal chemical precursors which in many cases go unnoticed.

Similar behavior is seen in the springs although minor differences in magnitudes could be related to different CO_2 – water ratios.

The groundwater in the Popocatepetl surroundings is of meteoric origin as seen from the coincidence with the meteoric line. Low outlet temperatures and conductivity indicate low water-rock interaction for the water. Increases in HCO_3^- are related to ascending magma pulses which supply CO_2 -rich fluids to the springs. Small changes in concentrations of magmatic components in spring water can be camouflaged by seasonal variations and different degrees of water rock interactions. Nevertheless, changes in the water chemistry at Popocatepetl during the recent eruptive period are considered to be related to the interaction of the water

with volcanic gases. Variations are short-termed and correlated with eruption dates and therefore magma ascent. P_{CO_2} calculations support this hypothesis.

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